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Assessment of technogenic pollution by silver compounds on the biological properties of the soil (model experiment)

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ABSTRACT

Introduction: Silver (Ag) has increasingly become one of the priority pollutants of soils, which is accompanied by a number of consequences for humans and soil biota. To fully assess the effects of the entry of different chemical forms of Ag into soils, it is necessary to conduct experiments with different types of soils, different exposure periods, as well as a wide range of biological indicators. The purpose of the study is to assess technogenic pollution by silver compounds (silver oxide (Ag_2O) and nitrate ($AgNO_3$)) on the biological properties of the soil in model experiment of the soil in a model experiment, followed by the use of the data obtained in the normalization of the Ag content in the soil.

Materials and methods: The effect of Ag_2O and $AgNO_3$ was investigated in specific permissible concentrations of biological indicators of the state of Haplic Chernozems Calcic (HCC), Haplic Cambisols Eutric (HCE) and Haplic Arenosols Eutric (HAE). Ecotoxicity was assessed by the degree of changes in the indicators of enzymatic activity, microbiological and phytotoxic indicators of soils 10, 30 and 90 days after contamination. Activity of catalase it was determined gasometrically, dehydrogenases, peroxidase, polyphenoloxidase, ferrireductase, ascorbatoxidase, phosphatase, invertase, urease, protease was determined photocolorimetrically, the total number of bacteria by luminescent method, Azotobacter sp. abundance by the method of fouling lumps on the Ashby medium, length of shoots and roots of wheat (Triticum aestivum L.) morphometrically.

Results: It was revealed that Ag ecotoxicity was determined by the content of Ag in the soil, its form, the period from the moment of contamination and soil type. In most cases, $AgNO_3$ had a stronger ecotoxic effect on biological parameters. Phosphatase activity and number of soil bacteria are the most sensitive indicators. The activity of invertase, urease, dehydrogenases and Azotobacter sp. abundance are the most informative indicators.

Conclusion: Abundance is the most informative indicator. The results obtained to assess the ecotoxicity of soils contaminated with Ag, as well as the identified sensitive and informative indicators, can be used for diagnosis and as an indicator of the ecological state of soils.

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Introduction

Heavy metals (HMs) are widely distributed in the environment because of natural processes and anthropogenic human activity. Their migration into ecosystem components contributes to the pollution of the environment, including soil. Entering soil ecosystems, HMs can accumulate in living organisms and thereby cause disruption of their vital activity. The use of low-quality untreated coals with a high ash content in thermal power plants contributes to environmental pollution with toxic trace amounts of silver (Ag) [1, 2] and increases its content in the soil to 126 mg/kg [3]. Over the past ten years, it has been believed that silver nanoparticles (AgNPs) and ions are not fatal to animal and human cells [4]. Currently, many scientists are concerned about the effects of AgNPs on human health. There are a limited number of studies of this kind and all of them are mainly conducted in vitro. Silver nanoparticles enter the human body through direct contact with the skin, through the respiratory tract when inhaled, or through the gastrointestinal tract when eating food contaminated with silver nanoparticles [5]. The assessment of the toxicity of AgNPs is significantly influenced by their movement inside the human body [6]. Silver nanoparticles from the respiratory system can be transported to the lymphatic ducts and then into the bloodstream [7]. Penetrating through the blood-brain barrier and cell membranes, AgNPs accumulate in vital organs and biological systems [8]. The accumulation of AgNPs in the human body most often occurs in plasma, erythrocytes, liver, spleen, kidneys and brain cells [9-12]. Silver nanoparticles, after incorporation into biological systems, can undergo biochemical transformation, which can eventually lead to long-term harmful effects on human health [13]. Silver nanoparticles exhibit toxicity against brain cells [14], liver [15]. Moreover, they are more toxic to liver cells than ionic forms [16]. They disrupt the functioning of the human gastrointestinal system [17]. According to the results of the research, it was shown that the toxicity of silver nanoparticles depended on the dose, duration of exposure and size of the nanoparticles. When exposed to silver nanoparticles at a concentration of 50 μg/mL on lung cells, no toxic effect was recorded. However, seven days after the introduction of silver nanoparticles at a concentration of more than 50 μg/mL, a decrease in lung function was noted [18]. It is known that smaller AgNPs (10 nm) are more toxic to human lung cells than larger ones [19]. When exposed to 2.0 μg/mL of silver nanoparticles on brain cells, no toxic effect was detected. A concentration of more than 4.0 μg/mL significantly reduced the activity of all brain enzymes [20].

The main cause of AgNPs toxicity is oxidative stress, which causes cell damage and apoptosis [11, 18]. Silver ecotoxicity was noted for most representatives of the soil biota and is manifested in the inhibition of the number of bacteria under the influence of nitrate [21], oxide [22] and Ag nanoparticles [23-25]. The inhibition of the enzymatic activity of soil under the influence of nitrate [26, 27], oxide [27] and AgNPs [24, 28-30] was noted. Under the influence of nitrate [31-33], oxide [22] and AgNPs [34-36], a decrease in germination and length of root and plant shoots was noted. The number of surviving soil animals decreased in the presence of [AgNPs [37, 38]. It should be noted that the ecotoxicity of chemical forms of Ag has been studied differently. Most often, the effect of AgNPs on representatives of soil biota is investigated, while a small number of studies have been devoted to the ecotoxicity of Ag_2O. Forecasting the effects on soil biota under the influence of Ag is still relevant. To pollute soil in model experiments, oxide (Ag_2O) and a solution of silver nitrate ($AgNO_3$) are most often used Ag_2O often enters the environment, including soils [1, 39-41]. The use of $AgNO_3$ as a contaminant in experiments makes it possible to assess the maximum toxicity to biota. Because this compound has a high solubility in water [33, 42]. Soil biota is associated with numerous functions of the soil ecosystem and is sensitive to any changes in the soil caused by environmental or anthropogenic factors. With the help of bioindicators, it is possible to determine the degree of Ag impact on

soil fertility [36, 43-45].

The initial response to anthropogenic impact is demonstrated by biological indicators [46-49]. Changes in enzymatic activity, microbiological indicators and plant growth and development serve as an indicator of soil disturbance and the full performance of their ecological functions [50]. Soil microorganisms participate in the C, N and S cycle [23]. Soil microorganisms are very sensitive to silver contamination [23, 43]. To determine the state of decomposing substances in the soil, it is recommended to use the total number of bacteria. Azotobacter sp. abundance are widely used as an indicator of soil contamination with heavy metals, in particular silver [47, 51].

The main route of pollution the soil by Ag is after the combustion of coal for flying ash containing silver oxide (Ag_2O) and nitrate ($AgNO_3$). It is advisable to assess the impact of technogenic soil pollution by heavy metalls (as Ag) assessing changes in the biological indicators of the soil. The purpose of the study is to assess technogenic pollution by Ag_2O and $AgNO_3$ on the biological indicators of the soil in model experiment.

Materials and methods

Soils

To study the ecotoxicity of silver, soils were selected that differ significantly in their physicochemical and biological properties (Table 1). All soil samples participating in the model experiments were taken away from sources of silver contamination.

The soils differ significantly from each other not only in the sampling location, but also in texture, pH and organic matter content. Haplic Chernozems Calcic (HCC) has a slightly alkaline reaction of the environment (pH=7.8), the highest content of soil organic matter (3.7%) and a heavy loamy composition. At the same time, Haplic Arenosols Eutric (HAE) with a light granulometric composition has a strongly acidic reaction of the environment (pH=5.8) and the lowest content of soil organic matter (1.8%). These soil parameters affect the buffering capacity of the soil, including in the case of chemical pollution.

Model experiment

According to the results of the analysis for the content of 30 HMs in three types of soils, it was shown that none of the samples was contaminated above the permissible values. The silver content in three types of soils was determined by inductively coupled plasma mass spectrometry, using ELAN-DRC-e or Agilent 7700×FSUE at A.P. Karpinsky Russian Geological Research Institute (RGRI). Silver background content in HCC was 0.1 mg/kg, in HAE — 0.061 mg/kg, in HCE — 0.094 mg/kg.

The absence of developed MPCs of Ag in the soil implies the use of a specific permissible concentration (SPC) (3-4 background content) of Ag in the soil [47]. Silver oxide was introduced in the form of powder and $AgNO_3$ was introduced into each type of soil in the form of an aqueous solution: 0.5, 1, 3, 10 and 30 SPC. Due to the fact that in HCC there is a higher background content of silver, its concentration in the soil will be increased several times at 0.5, 1, 3, 10 and 30 SPC (0.025, 0.05, 0.3, 1 and 3 mg/kg), while in HCE it is slightly less (0.047, 0.094, 0.282, 0.94, 2.82 mg/kg), and in HAE it is significantly less (0.031, 0.061, 0.183, 0.61, 1.83 mg/kg).

The soil was incubated in vegetative vessels in three repetitions in the KBW Binder climatic chamber (Germany) for 10, 30 and 90 days. The mass of soil in each vessel was 200 g.

Favorable conditions for soil biota were created in the climate chamber: humidity 25–30%, temperature 24–25°C, change of lighting (day and night).

Methods

Silver ecotoxicity was assessed using biological methods of soil analysis (Table 2). Biological indicators should be sensitive and informative to Ag soil contamination. This study will help to expand the understanding of the risks to the condition and functioning of soils in case of silver contamination.

Table 1. Soil location and basic physical and chemical parameters

Type of soil	Abbreviation	Coordinates	Texture	pH	SOM
Haplic Chernozems Calcic	HCC	47°14'17.54" N, 39°38'33.22" E	clay loamy	7.8	3.7
Haplic Cambisols Eutric	HCE	47°46.015' N, 40°51.700' E	medium loamy	6.8	2.3
Haplic Arenosols Eutric	HAE	44°10.649' N, 40°9.469' E	light loamy	5.8	1.8

Table 2. Measurement of Biological indicators

No	Biological indicators	Measurement
1.	activity of catalase	Gasometric method for the decomposition of hydrogen peroxide
2.	activity of dehydrogenases	Reduction in tetrazolium chloride salts to triphenylformazans (TPF)
3.	activity of peroxidase	Colorimetric method on the oxidation of hydroquinone to quinones
4.	activity of polyphenoloxidase	Colorimetric method on the oxidation of hydroquinone to quinones
5.	activity of ferrireductase	Colorimetric method by quantity reduced ferric iron
6.	activity of ascorbateoxidase,	By the difference between the volume of residual ascorbic acid and the volume of formed dehydroascorbic acid
7.	activity of phosphatase	Colorimetric method according to the amount of released µg p-nitrophenol
8.	activity of invertase	Colorimetric method to change the content of reducing sugars
9.	activity of urease	Colorimetric method according to the amount of released ammonia
10.	activity of protease	By the volume of amino acids formed in the result of casein proteolysis
11.	the total number of bacteria,	Fluorescence microscopy in incident light according
12.	Azotobacter sp. abundance	Method of fouling lumps on Ashby medium
13.	length of shoots (*Triticum aestivum* L.)	On changes in germination rates of radish seeds
14.	length of roots (*Triticum aestivum* L.)	On changes in germination rates of radish seeds

Based on the data obtained, the Integrated Indicator of the Biological State of the Soil (IIBS) was evaluated according to the most sensitive and informative indicators. The method of calculating IIBS was presented earlier in the article by many researchers [47]. It is advisable to establish the MPC of silver in the soil based on the identified sensitive and informative bioindicators: phytotoxic and microbiological indicators, enzymatic activity of soils.

Statistical processing

Statistical data processing was carried out using ANOVA analysis. The data were analyzed using variance, followed by the determination of the least significant difference (LSD). The statistics of variations (mean values, variance) were determined, and the reliability of various samples was established using variance analysis (Student t-test).

Results and discussion

Influence of silver compounds on phytotoxic indicators of soils

The results of the influence of Ag_2O and $AgNO_3$ on the phytotoxic indicators of HCC, HCE and HAE are shown in Fig. 1. Ten days after soil contamination with 0.5 SPC of Ag_2O, a decrease in the length of wheat roots on HCE and HAE relative to the control was observed by 17 and 43%, respectively. With the content of 1, 3, 10 and 30 SPC of Ag_2O in the soil, there was a decrease in the length of wheat roots on HCC by 20, 30, 38 and 40%, HCE — by 29, 38, 36 and 44%, HAE — by 52, 56, 58 and 62% of control.

Thirty days after soil contamination with 0.5 and 1 SPC of Ag_2O, a decrease in the length of wheat roots on HCC by 23 and 32%, HCE — by 26 and 33% relative to control, respectively, was noted. At 10 and 30 SPC of Ag_2O, a decrease in the length of wheat roots on HCC by 44 and 48%, HCE — by 43 and 57% of control, respectively, as above. At 10 SPC of Ag_2O in the soil, a 21% decrease in the length of wheat roots on HAE relative to the control was noted.

On the 90 days after contamination of the soil with 0.5 SPC of Ag_2O, a decrease in the length of wheat roots on HCE relative to control by 16% and HAE — by 25% was noted.

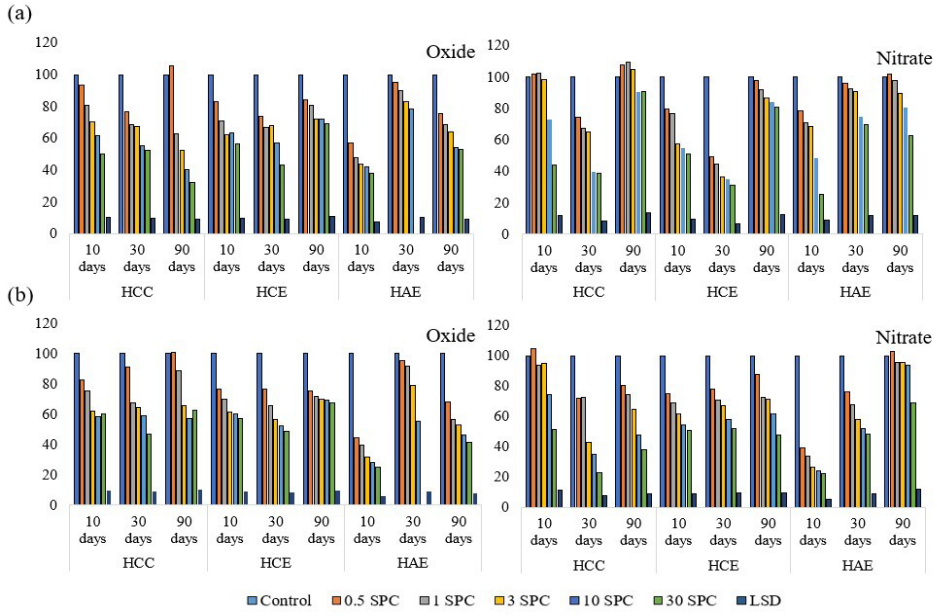

Fig. 1. Changes in soil phytotoxicity when polluted with silver oxides and nitrates, % of control: a) length of roots; b) length of shoots

With the content of 1, 3, 10 and 30 SPC of Ag_2O in the soil, the indicators of the length of roots of wheat decreased on HCC by 17, 48, 60 and 68%, HCE — by 19, 28, 28 and 31%, HAE — by 31, 36, 46 and 47% of control, respectively.

Ten days after soil contamination with 10 and 30 SPC of $AgNO_3$, the length of wheat roots on HCC decreased control by 27 and 56%, respectively. With the content of 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$ in the soil, a decrease in the length of wheat roots on HCE was noted by 20, 23, 42, 45 and 49% and HAE — by 22, 29, 31, 52 and 75% of control, respectively.

On the 30 days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$, a decrease in the length of wheat roots on HCC was recorded by 26, 33, 35, 61 and 61%, HCE — by 51, 56, 63, 65 and 69% of the control, respectively. With the content of 10 and 30 SPC of $AgNO_3$ in the soil, a decrease in the length of wheat roots on HAE of control by 25 and 30%, respectively, was noted.

On the 90 days after soil contamination with 3, 10 and 30 SPC of $AgNO_3$, a decrease in the length of wheat roots on HCE was noted by 14, 16 and 19% relative to the control,

respectively. With a content of 0.5, 1, 3, 10, and 30 SPC of $AgNO_3$ in the soil, a decrease in the length of wheat roots on HAE relative to the control by 25, 31, 36, 46 and 47%, respectively, was noted.

On the 10 days after soil contamination with 1, 3, 10 and 30 SPC of Ag_2O, a decrease in the length of wheat shoots on HCC relative to control values by 20, 30, 38 and 50%, respectively, was noted. With the content of 0.5, 1, 3, 10 and 30 SPC of Ag_2O in the soil, a decrease in the length of wheat shoots on HCE was noted by 17, 29, 38, 36 and 44%, HAE — by 43, 52, 56, 58 and 62% relative to the control, respectively.

Thirty days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of Ag_2O, a decrease in the length of wheat shoots on HCC was recorded by 23, 32, 33, 44 and 48%, HCE — by 26, 33, 32, 43 and 57% of the control, respectively. At 3 and 10 SPC of Ag_2O, there was a decrease in the length of wheat shoots on HAE of control by 17 and 21%, respectively.

On the 90 days after soil contamination with 1, 3, 10 and 30 SPC of Ag_2O, a decrease in the length of wheat shoots on HCC relative to the control was noted by 37, 48, 60 and 68%, respectively. With the content of 0.5, 1, 3, 10 and 30 SPC of Ag_2O in the soil, a decrease in the length of wheat shoots on HCE was recorded by 16, 19, 28, 28 and 31%, HAE— by 25, 31, 36, 46 and 47% of the control, respectively.

Ten days after soil contamination with 10 and 30 SPC of $AgNO_3$, inhibition of the length of wheat shoots on HCC relative to control by 27 and 56%, respectively, was noted. With the content of 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$ in the soil, a decrease in the length of wheat shoots on HCE was noted by 20, 23, 42, 45 and 49% and HAE — by 22, 29, 31, 52 and 75% of control, respectively.

On the 30 days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$, there was a decrease in the length of wheat shoots on HCC by 26, 33, 35, 61 and 61%, HCE — by 51, 56, 63, 65 and 69% relative to control, respectively. With the content of 10 and 30 SPC of $AgNO_3$ in the soil, a decrease in the length of wheat shoots on HAE relative to the control by 25 and 30%, respectively, was noted.

Ninety days after soil contamination with 3, 10 and 30 SPC of $AgNO_3$, a decrease in the length of wheat shoots on HCE relative to control values by 14, 16 and 19%, respectively, was noted. With the content of 10 and 30 SPC of silver nitrate in the soil, a decrease in the length of wheat shoots relative to the control by 20 and 37%, respectively, was noted.

Influence of silver compounds on microbiological indicators of soils

The results of the influence of Ag_2O and $AgNO_3$ on the microbiological indicators of HCC, HCE and HAE are shown in Table 1. Influence of silver compounds on microbiological indicators of soils Ag can be seen from Fig. 2, on the 10 days after soil contamination with 10 and 30 SPC of Ag_2O, there was a decrease in Azotobacter sp. abundance of control by 16 and 76%, respectively. On the 30 days after soil contamination with 30 SPC Ag_2O, there was a decrease in Azotobacter sp. abundance of control by 39%. On the 10 and 30 days after contamination with 30 SPC of $AgNO_3$, a decrease in Azotobacter sp. abundance of control was recorded by 43 and 39%, respectively.

Since the acidic environment of the soil completely inhibits the vital activity of Azotobacter sp. abundance, it is impossible to determine the effect of Ag_2O and $AgNO_3$ on this indicator in brown forest soil. On the 10 days after soil contamination with 0.5 SPC of Ag_2O, there was a decrease in the total number of HCE bacteria by 11% and HAE by 23% relative to the control. With the content of 1, 3, 10 and 30 SPC of silver oxide in the soil, a decrease in the total number of bacteria of HCC was recorded by 35, 44, 44 and 48%, HCE — by 21, 35, 49 and 59% and HAE — by 42, 50, 63 and 69% of control, respectively. On the 30 days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of Ag_2O, a decrease in the total number of bacteria of HCC was noted by 17, 29, 44, 51 and 53%, HCE — by 24, 40, 46, 55 and 57% and HAE— by 46, 58, 60, 70 and 74% of the control, respectively. On the 90 days after soil contamination with 1, 3, 10 and 30 SPC of Ag_2O, a decrease in the total number of HCC bacteria of control was noted by 20, 33, 46 and 52%, respectively. With the content of 0.5, 1, 3, 10 and 30 SPC of Ag_2O in the soil, the total number of HCE bacteria decreased relative to the control by 10, 16, 46, 49 and 63%, HAE — by 33, 37, 42, 44 and 60%, respectively.

Ten days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$, a decrease in the total number of bacteria of HCC was recorded by 24, 19, 38, 67 and 73%, HCE — by 33, 35, 50, 57 and 71% and HAE — by 35, 42, 45, 47 and 66% of control, respectively. On the 30 days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$, there was a decrease in the total number of bacteria of HCC by 37, 44, 52, 51 and 60%, HCE — by 48, 60, 66, 70 and 79% and HAE — by 42, 54, 55, 60 and 64% of the control, respectively. Ninety days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$, there was a decrease in the total number of bacteria of HCC by 22, 30, 41, 46 and 44%, HCE— by 40, 56, 62, 64 and 68% and HAE — by 46, 52, 63, 65 and 71% of the control, respectively.

Influence of silver compounds on enzyme activity of soils (class oxidoreductases)

The results of the study of the effect of $AgNO_3$ on the activity of catalases and dehydrogenases are presented in Fig. 3. On the 10 days after soil contamination with 1, 3, 10 and 30 SPC of Ag_2O, there was a decrease in the activity of catalase of HCC by 9, 25, 42 and 45% of control. With the content of 0.5, 1, 3, 10 and 30 SPC of Ag_2O in the soil, a decrease in the catalase activity of HCE relative to the control was recorded by 10, 16, 23, 24 and 29%, respectively. With the content of 10 and 30 SPC of Ag_2O in the soil, a decrease in the activity of catalase in HAE relative to the control by 16 and 35%, respectively, was noted.

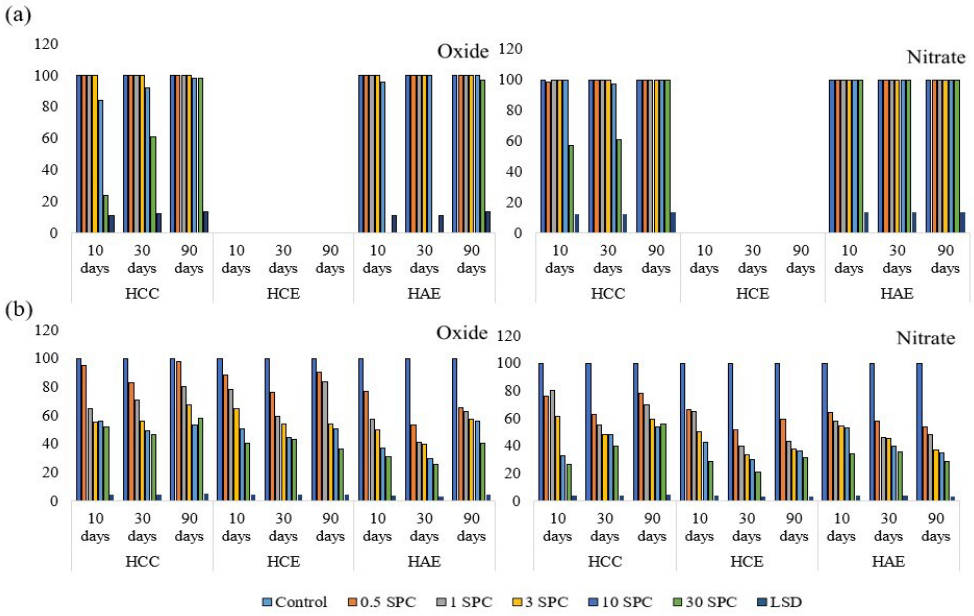

Fig. 2. Changes in the microbiological parameters of soils when contaminated with oxides and nitrates of silver, % of the control: a) Azotobacter sp. abundance; b) the total number of bacteria

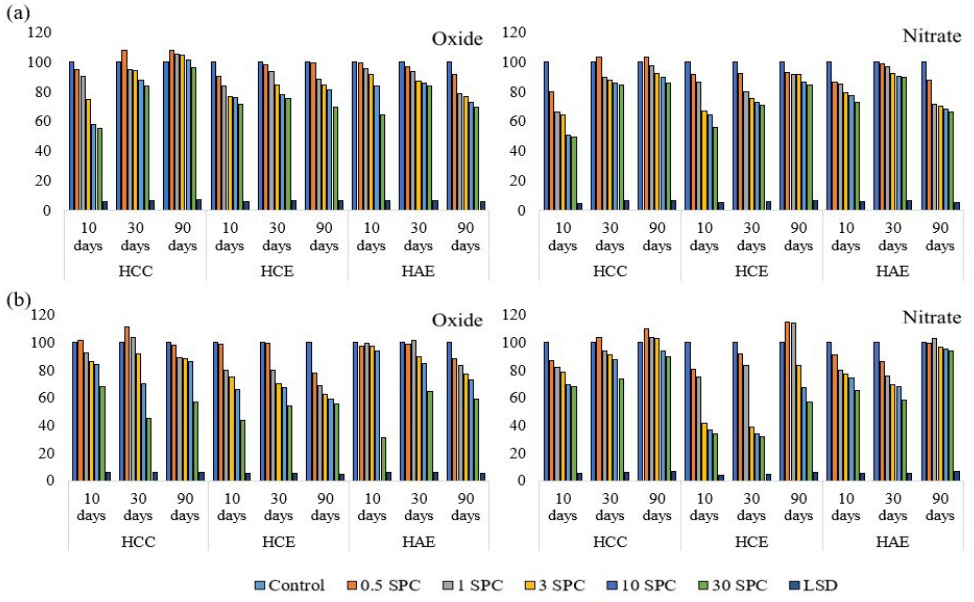

Fig. 3. Changes in the activity of catalase and dehydrogenases after 10, 30 and 90 days after contamination with silver oxide and nitrate

On the 30 and 90 days after soil contamination with 0.5 SPC of Ag_2O, catalase activity was stimulated by 8 and 8% of the control, respectively.

On the 30 days after soil contamination by 10 and 30 SPC, a decrease in the activity of catalase of HCC relative to the control was noted by 12 and 16%, respectively. With the content of 3, 10 and 30 SPC of Ag_2O in the soil, a decrease in the catalase activity of HCE was noted by 15, 22 and 24%, HAE — by 13, 14 and 16% relative to the control, respectively. On the 90 days after contamination of the soil with 0.5 SPC of Ag_2O, a decrease in the activity of catalase of HAE relative to the control was noted by 8%. With the content of 1, 3, 10 and 30 SPC of Ag_2O in the soil, there was a decrease in the catalase activity of HCE by 11, 15, 18 and 31%, HAE — by 21, 23, 27 and 30% of the control, respectively.

On the 10 days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$, there was a decrease in the activity of catalase of HCC by 20, 33, 36, 49 and 50%, HCE — by 8, 13, 33, 35 and 44% and HAE — by 13, 15, 21, 22 and 27 % of control, respectively.

Thirty days after soil contamination with 1, 3, 10 and 30 SPC of $AgNO_3$, a decrease in the activity of catalase of HCC relative to the control was noted by 10, 12, 14 and 16%, respectively. With the content of 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$ in the soil, a decrease in the catalase activity of HCE relative to the control was noted by 8, 20, 24, 27 and 29%, respectively. With the content of 3, 10 and 30 SPC of silver nitrate in the soil, a decrease in the activity of catalase of HAE relative to the control by 8, 9 and 10%, respectively, was noted.

On the 90 days after soil contamination with 3, 10 and 30 SPC of $AgNO_3$, there was a decrease in the activity of catalase of HCC relative to the control by 8, 19 and 14%, respectively. With the content of 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$ in the soil, a decrease in the catalase activity of HCE was noted by 7, 8, 8, 14 and 15%, HAE — by 12, 28, 30, 32 and 33% of control, respectively.

On the 10 days after soil contamination with 1, 3, 10 and 30 SPC of Ag_2O, inhibition of the activity of dehydrogenases of HCC by 7, 13, 16 and 32%, HCE — by 20, 25, 34 and 56% of control, respectively, was noted. With a content of 30 SPC of silver oxide in the soil, inhibition of dehydrogenases activity relative to the control by 69% was noted.

On the 30 days after contamination of Haplic Chernozems Calcic with 0.5 SPC of Ag_2O, stimulation of dehydrogenases activity relative to control by 12% was recorded. With the content of 1, 3, 10 and 30 SPC of Ag_2O in the soil, a decrease in the activity of dehydrogenases of HCE relative to the control was noted by 20, 30, 32 and 46%, respectively. With the content of 3, 10 and 30 SPC of Ag_2O in the soil, inhibition of the activity of dehydrogenases of HAE was observed by 10, 15 and 35%, respectively.

Ten days after contamination with 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$, inhibition of the activity of dehydrogenases of HCC by 13, 18, 21, 31 and 32%, HCE— by 20, 25, 59, 63 and 66% and HAE— by 9, 20, 23, 25 and 35% relative to the control, respectively. On the 30 days after contamination with 3, 10 and 30 SPC of $AgNO_3$, a decrease in the activity of HCC dehydrogenases relative to the control was recorded by 9, 12 and 26%, respectively. With the content of 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$ in the soil, inhibition of the activity of dehydrogenases of HCE was noted by 8, 16, 61, 66 and 68%, HAE by 14, 24, 30, 32 and 41% of the control, respectively. On the 90 days after contamination of HCC with 0.5 SPC of $AgNO_3$, the stimulating effect of dehydrogenases activity relative to the control by 10% was noted. At 30 SPC of $AgNO_3$, inhibition of dehydrogenase activity by 10% relative to the control was noted.

On the 90 days after soil contamination with 0.5 and 1 SPC of $AgNO_3$, stimulation of the activity of dehydrogenases of HCE of control by 15 and 14%, respectively, was noted. With the content of 3, 10 and 30 SPC of silver nitrate in the soil, inhibition of the dehydrogenase activity of HCE of control was noted by 16, 32 and 43%, respectively.

The results of the study of the effect of Ag_2O and $AgNO_3$ on the activity of enzymes of the class of oxidoreductases (peroxidase, polyphenoloxidase, ferrireductase and ascorbateoxidase) are presented in Fig. 4.

Ten days after contamination with 1, 3, 10 and 30 SPC of Ag_2O, inhibition of peroxidase activity of HCC relative to the control by 7, 18, 21 and 29%, respectively, was noted. With the content of 3, 10 and 30 SPC of Ag_2O in the soil, the activity of peroxidase in HCE decreased relative to the control by 13, 14 and 26%, respectively. With the content of 30 SPC of $AgNO_3$ in the soil, the activity of peroxidase in HCC decreased by 8% of control. When the content of 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$ in the soil, the activity of peroxidase in HCE was inhibited relative to the control by 12, 13, 14, 19 and 33%, respectively.

On the 10 days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of Ag_2O, there was a decrease in the activity of polyphenol oxidase of HCC by 16, 20, 25, 31 and 33%, HCE — by 13, 16, 19, 21 and 36% relative to the control, respectively. With the content of 1, 3, 10 and 30 SPC of $AgNO_3$ in HCC, a decrease in the activity of polyphenol oxidase relative to the control was noted by 8, 10, 13 and 21%, respectively. With the content of 3, 10 and 30 SPC of $AgNO_3$ in HCE, there was a decrease in the activity of polyphenol oxidase relative to the control by 9, 15 and 23%, respectively. With the content of 3, 10 and 30 SPC of Ag_2O in HCC, inhibition of ferrireductase activity relative to control by 11, 14 and 17%, respectively, was noted.

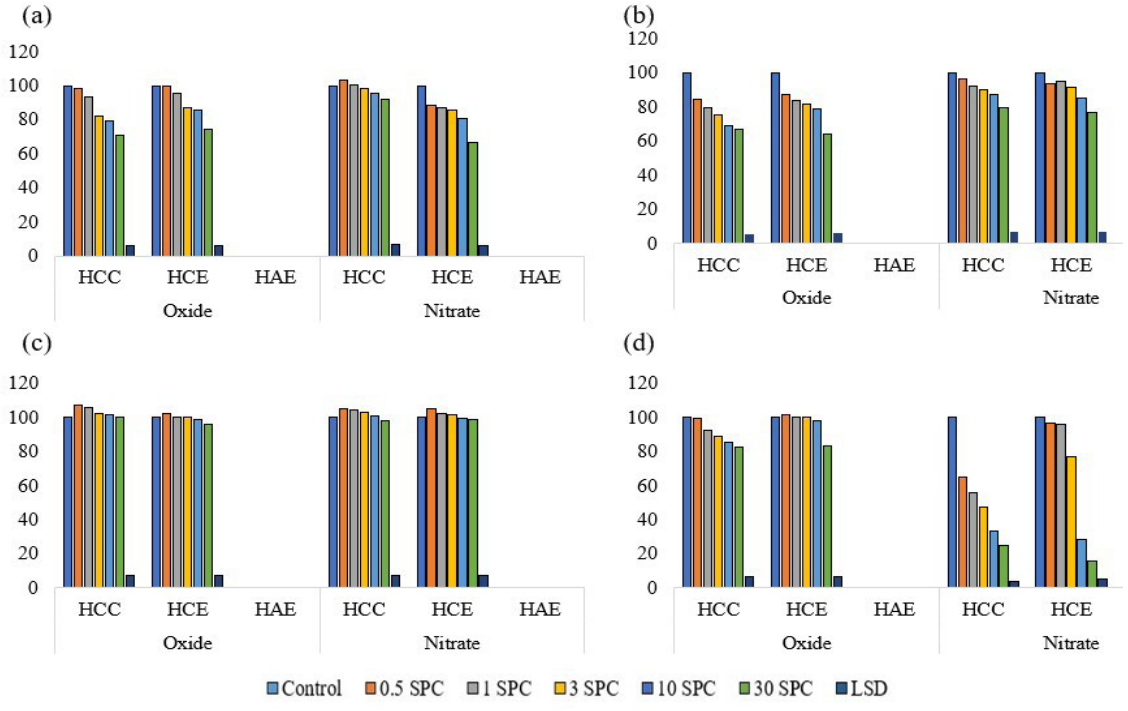

Fig. 4. Changes in the activity of enzymes of the oxidoreductase class from 10 days after contamination with silver oxide and nitrate: a) peroxidase; b) polyphenoloxidase; c) ferrieductase; d) ascorbateoxidase

When HCE was contaminated with 30 SPC of Ag_2O, the inhibition of ferrireductase activity relative to the control was noted by 17%. With the content of 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$ in HCC, inhibition of ferrireductase activity relative to control by 35, 44, 53, 67 and 75%, respectively, was noted. When HCE was contaminated with 3, 10 and 30 SPC of $AgNO_3$, a decrease in ferrireductase activity relative to the control was noted by 23, 71 and 84%, respectively.

Influence of silver compounds on enzyme activity of soils (class hydrolases)

The results of the study of the effect of Ag_2O and $AgNO_3$ on the activity of hydrolase class enzymes (phosphatases, invertases, ureases and proteases) are presented in Fig. 5. As can be seen from Table 3, 10 days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of Ag_2O, inhibition of the phosphatase activity of HCC was noted by 26, 39, 40, 41 and 41%, HCE — by 55, 65, 67, 71 and 69% and HAE — by 56, 61, 66, 71 and 72% relative to the control, respectively. With the content of 10 and 30 SPC of $AgNO_3$ in HCC, inhibition of phosphatase activity relative to the control by 12 and 20%, respectively, was noted. With the content of 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$ in the soil, inhibition of phosphatase activity in HCE was noted by 40, 50, 50, 51 and 43%, HAE — by 41, 43, 44, 55 and 69% relative to the control, respectively.

Ten days after HCC contamination with 3, 10 and 30 SPC of Ag_2O, inhibition of invertase activity relative to the control by 11, 25 and 46% was noted. With the content of 1, 3, 10 and 30 SPC of Ag_2O in the soil, a decrease in the invertase activity of HCE was noted by 11, 25, 26 and 31%, HAE — by 15, 19, 21 and 34% of the control, respectively. With the content of 1, 3, 10 and 30 SPC of $AgNO_3$ in the soil, inhibition of the invertase activity of HCC was recorded by 7, 13, 13 and 24%, HCE — by 8, 13, 33 and 51% relative to the control, respectively. With the content of $AgNO_3$ of 3, 10 and 30 SPC in HAE, inhibition of invertase activity relative to the control by 17, 30 and 35%, respectively, was noted.

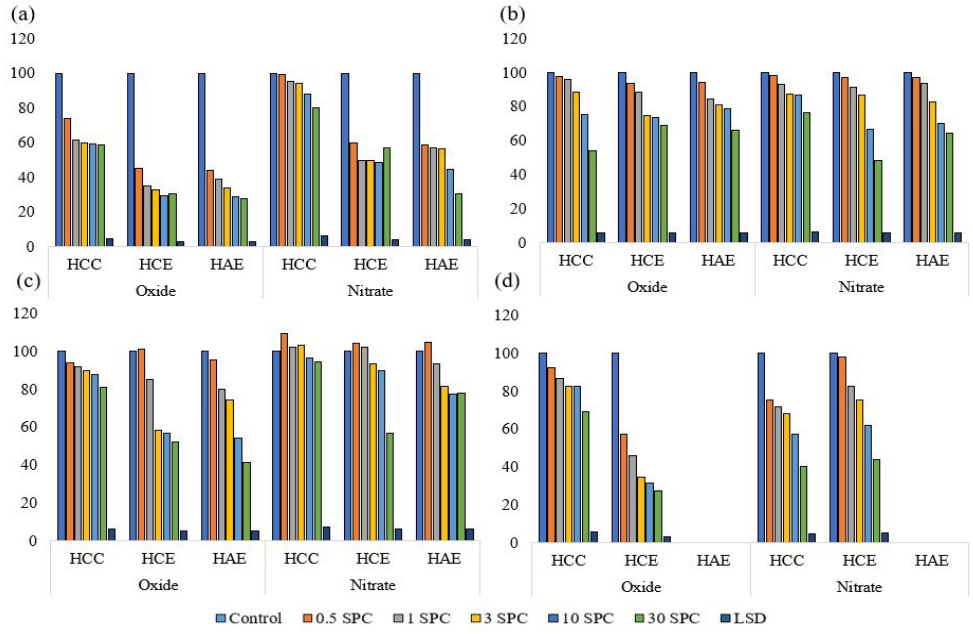

Fig. 5. Activity of hydrolase class enzymes after contamination with silver oxide and nitrate: a) phosphatase; b) invertase; c) urease; d) protease

Ten days after soil contamination with 1, 3, 10 and 30 SPC of Ag_2O, a decrease in urease activity in HCC was noted by 8, 10, 12 and 19%, HCE — by 15, 42, 43 and 48% and HAE — by 20, 26, 46 and 59% relative to the control, respectively. With a content of 0.5 SPC of $AgNO_3$ in HCC, a stimulating effect of urease activity relative to the control was noted by 9%. When HCE was contaminated with 3, 10 and 30 SPC of $AgNO_3$, inhibition of urease activity relative to control was noted by 7, 10 and 43%, respectively. With 1, 3, 10 and 30 SPC of $AgNO_3$ in HAE, inhibition of urease activity relative to the control was noted by 7, 18, 23 and 22%, respectively.

Ten days after soil contamination with 0.5, 1, 3, 10 and 30 SPC of Ag_2O, a decrease in the protease activity of HCC was noted by 8, 13, 17 and 31%, HCE — by 43, 54, 65, 68 and 73%, relative to the control, respectively. In the case of contamination of HCC with 0.5, 1, 3, 10 and 30 SPC of $AgNO_3$, inhibition of protease activity relative to the control by 25, 28, 32, 43 and 60%, respectively, was noted. With the content of 1, 3, 10 and 30 SPC of $AgNO_3$ in HCE, inhibition of protease activity relative to the control by 17, 25, 38 and 56%, respectively, was noted.

The hypothesis of the study: the higher the concentration of silver in the soil, the lower the biological indicators. This hypothesis was confirmed. As can be seen from Table 1, regardless of the form of silver chemical compound, the time of contamination and the type of soil, the higher the dose of silver in the soil, the greater the decrease in biological indicators.

Based on the obtained biological indicators of the state of soils in case of contamination with Ag_2O and $AgNO_3$, an assessment of their informativeness and sensitivity was given on Table 3.

Table 3. Ranking of biological indicators in case of contamination with silver oxide and nitrate by sensitivity ("1" is the most sensitivity, "9" is the least sensitivity)

Form of Ag	CAT	DEH	INV	UREA	PHOS	BACT	AZ	ROOT	SHOOT
Haplic Chernozems Calcic									
oxide	9	6	5	7	**1**	3	8	2	4
nitrate	4	6	5	9	7	**1**	8	3	2
Haplic Cambisols Eutric									
oxide	7	5	6	5	**1**	2	8	4	3
nitrate	7	5	6	8	2	**1**	9	3	4
Haplic Arenosols Eutric									
oxide	7	7	6	5	**1**	2	8	4	3
nitrate	5	5	5	6	2	**1**	7	4	3

Note: CAT - Activity of catalase; DEH - Activity of dehydrogenases; INV - Activity of invertase; UREA - Activity of urease; PHOS - Activity of phosphatase; BACT - Total number of bacteria; AZ - Azotobacter sp. Abundance; ROOT - Length of radish roots; SHOOT - Length of radish shoots

The most sensitive indicators of HCC, HCE and HAE by Ag_2O contamination are activity of phosphatase, the most sensitive indicators of soils by $AgNO_3$ – the total number of bacteria.

The results of the informative nature of biological indicators of soils to contamination with Ag_2O and $AgNO_3$ are presented in Table 4.

The full performance of the soil's ecosystem functions can be assessed using sensitive and informative bioindicators, which were determined during the study of the effects of soil pollution by Ag. These indicators can be used in the development of critical Ag concentrations. Earlier, it was noted that soil pollution with a wide range of heavy metals (Bi, Te, Tl, Pb, Cd, Cu, Zn, Cr, Ni, etc.) [47] causes a violation of the ecosystem functions of the soil. The dependence of the nature of the disturbance of the ecosystem functions of the soil is determined by the amount of Ag accumulated in the soil and the degree of decrease in IIBS.

Table 4. Ranking of biological indicators in case of contamination with silver oxide and nitrate by informativeness ("1" is the most informative, "9" is the least informative)

Form of Ag	CAT	DEH	INV	UREA	PHOS	BACT	AZ	ROOT	SHOOT
Haplic Chernozems Calcic									
oxide	5	2	**1**	4	9	8	3	6	7
nitrate	8	4	3	5	2	9	**1**	7	6
Haplic Cambisols Eutric									
oxide	2	**1**	4	5	8	3	9	6	7
nitrate	5	4	2	**1**	8	7	9	6	3
Haplic Arenosols Eutric									
oxide	5	2	4	3	8	7	**1**	9	6
nitrate	6	2	**1**	5	3	7	9	8	4

Note: CAT - Activity of catalase; DEH - Activity of dehydrogenases; INV - Activity of invertase; UREA - Activity of urease; PHOS - Activity of phosphatase; BACT - Total number of bacteria; AZ - Azotobacter sp. Abundance; ROOT - Length of radish roots; SHOOT - Length of radish shoots.

With an increase in the dose of Ag, the degree of influence on the germination and length of radish roots increased [36], on the germination of rice seeds and their subsequent growth and development [30], as well as on the microbiological and enzymatic activity of the soil [36, 51-53]. Increased toxicity to biota correlated with an increase in Ag in the soil. Earlier, when soils were polluted with Ag_2O and $AgNO_3$, a decrease in enzymatic activity was noted [27] as in the present study, the degree of decrease in indicators depended on the content of the element in the soil. A dose of 0.5 SPC of Ag_2O on the 30 days after contamination of HCC had a stimulating effect on the activity of dehydrogenases. At a dose of 0.5 SPC of silver nitrate, stimulation of dehydrogenases activity was noted on the 90 days after contamination of HCC. Doses of 0.5 and 1 SPC stimulated the dehydrogenases activity of HCE on the 90 days after contamination. Stimulation of urease and phosphatase activity was noted [52], the length of the roots of radish, wheat, beans and corn [54, 55] under the influence of small concentrations of Ag.

The hypothesis of the study: it is assumed that oxides are less toxic than nitrates since silver nitrates are highly soluble in water, which ensures greater mobility of Ag in the soil and, consequently, its ecotoxicity. This hypothesis was justified in most cases. As can be seen from Figs. 1 and 2 and Tables 1-3, on HCE, silver nitrates are somewhat more toxic than oxides. Earlier studies have recorded a stronger ecotoxic effect of $AgNO_3$ on the biological properties of HCC [22]. Silver nitrate had a stronger ecotoxic effect on the root length of onion (Allium cepa) [33] and oats (Avena sativa L.) [56], reduced growth and higher levels of chlorosis in (Lemna minor) [57]. It was also noted earlier that soil respiration decreased more strongly under the influence of $AgNO_3$ than under the influence of AgNPs [58]. In a comparative assessment of the effect of Ag2SNPs and $AgNO_3$ on the soil microbiome, it was found that the strongest changes in its structure were caused by $AgNO_3$. In addition, the survival rate of earthworms decreased more strongly under the influence of $AgNO_3$ [60].

The hypothesis of the study: it is expected that the highest ecotoxicity of silver will be on the 10 days after contamination. After that, the biota adapts, Ag particles are absorbed by the soil and, 90 days after contamination, the biological properties of the soil will be restored. The hypothesis was confirmed in most cases. As can be seen from Figs 1, 2 and Tables 1, 2, 3, the strongest decrease in biological indicators was noted on the 10 days after contamination. 90 days after contamination, restoration of the biological properties of soils were noted in most cases. Previously, similar results of the greatest ecotoxicity of silver were obtained on the 10 days after contamination [43, 51], when soils were contaminated with both Ag [51] and other HMs such as Hg, Cd, Pb, Cr, Cu, Zn, Bi etc. [61-65]. Nevertheless, there are studies where $AgNO_3$ was more ecotoxic to the soil microbiota on day 28 compared to the results obtained 14 days after contamination [59]. Similar trends were recorded earlier, when the toxicity of AgNPs, as well as $AgNO_3$ for soil bacteria, mainly significantly decreased with an extension of the exposure period from 90 days to a year [66].

The hypothesis of the study: HCC are more resistant to silver than HAE because they have a heavier grain-size composition which binds silver particles more strongly than the sandy loam granulometric composition of HAE. Additionally, HCC are more stable than HCE since they have a neutral pH, at which Ag particles are less mobile than in HCE with an acidic reaction of the soil environment. The hypothesis was confirmed in most cases. As can be seen from Figs 1, 2 and Tables 1, 2,

3, the biological properties of HCC decrease when contaminated with silver to a lesser extent than those of HAE and HCE. Previously, the authors noted that HCC is more resistant to Ag pollution than HCE and HAE [36, 64]. As in our study, earlier a group of scientists led by Conor Francis McGee confirmed that the activity of dehydrogenases under the influence of Ag is more strongly inhibited in acidic soils compared to neutral ones [67]. In our study, the total number of HAE bacteria reached a maximum decrease of up to 21% relative to the control. It was also noted earlier that the structures of bacterial and fungal communities under the influence of Ag in acidic soils were significantly changed, while in neutral soils they remained the same as in the control group without changes [67].

The most sensitive indicators of HCC, HCE and HAE for Ag_2O contamination are the activity of the phosphotase enzyme. The most sensitive indicators of HCC, HCE and HAE for determining $AgNO_3$ contamination are the total number of bacteria. What was typical earlier and with soil contamination AgNPs [36]. The most informative indicators of HCC, HCE and HAE for contamination by Ag_2O are the activity of invertase, activity of dehydrogenases, Azotobacter sp. Abundance. The most informative indicators of HCC, HCE and HAE for contamination by $AgNO_3$ are the Azotobacter sp. abundance, activity of urease and activity of urease too. The number of Azotobacter sp. it is also the most informative indicator for soil contamination by AgNPs [36]. The activity of catalase during the remediation of soils contaminated with oil, gasoline, fuel oil, and diesel fuel by various substances was also the most sensitive enzyme [68, 69].

The effect of silver nanoparticles (AgNPs) and ionic silver ($AgNO_3$) in two types of sandy loam and silt loam soils on the growth of northern wheatgrass (Elymus lanceolatus) and red clover (Trifolium pratense), the survival of springtails (Folsomia candida), and earthworms (Eisenia andrei) was studied [70]. It was found that organisms in the sandy loam soil responded more sensitively to Ag than organisms in the silt loam. Earthworms were sensitive to either form of Ag, but plant germination was the least sensitive to both forms of Ag. The bioavailability of Ag ions depends on the pH of the soil and the content of organic matter. In acidic soils, ecotoxicity is higher than in soils with a high content of organic matter [71]. Clay particles in the soil contribute to reducing the toxicity of Ag to biota, while sand particles, on the contrary, increase the toxicity of Ag [72].

Conclusion

Contamination of Haplic Chernozems Calcic, Haplic Cambisols Eutric and Haplic Arenosols Eutric with Ag_2O and $AgNO_3$ led to a change in the biological parameters of soils. The degree of ecotoxic effects of Ag was determined by the concentration in the soil, the form of the chemical compound, the period since contamination and the type of soil. An increase in background concentrations of Ag in the soil inhibited biological parameters. In the variants of the experiment with silver nitrate, ecotoxic effects on the studied biological parameters are more common than with silver oxide. The maximum ecotoxic effect of Ag on the studied parameters was demonstrated on day 10, followed by the tendency to achieve control by day 90. Phosphatase activity and bacterial numbers are the most sensitive indicators. The activity of invertase, urease and Azotobacter sp. Abundance are the most informative indicators.

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Competing interests

The authors declare no competing interests.

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Ethical considerations

Ethical issues (Including plagiarism, Informed consent, misconduct, data fabrication and/ or falsification, double publication and/ or submission, redundancy, etc) have been completely observed by the authors.

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