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Screening of various chemical additives, including S-containing complexion to enhance phytoextraction of mercury by white creeping clover (*Trifolium repens L.*)

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Annotation. Mercury in the modern world is a global pollutant entering the environment as a result of human activities. Currently, there are a large number of territories in the world whose soils and reservoirs contain mercury in quantities that pose a danger to human health and the environment. However, the methods that are traditionally proposed for remediation may pose a risk of secondary mercury contamination and/or negative health effects for those involved in cleaning. Phytoextraction of heavy metals from the soil environment is currently considered as one of the most promising non-invasive methods of reclamation. However, this approach has limited effectiveness for cleaning soils and reservoirs. Chemically reduced phytoextraction can increase the efficiency of this process both by converting less bioavailable mercury compounds into bioavailable fractions in the soil, and by increasing the rate of metal transfer in plants. The paper presents the results of a screening study of various chemical additives to enhance the phytoextraction of mercury with white creeping clover (*Trifolium repens L.*). The results obtained showed a good potential for reducing phytoextraction for the first time studied S-containing complexion, in which the monoethanolamine salt of dithiobiacetic acid was used as a sulfur-containing chelant (MEDBA).

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1. Introduction

The high toxicity, complex dynamics of mercury behavior in the environment, and the tendency to bio-amplification in ecosystems serve as the basis for the world Health Organization and many governments to classify this chemical element as a global pollutant [1]. As a result of various activities of industrial enterprises: from metallurgical plants, in the production of mercury elements, chlorine/alkali, from incineration plants and other stationary sources of pollution [2] – large amounts of mercury enter the environment, primarily reservoirs and soil [3]. Restoration of the soil horizon is a complex task, which has been the subject of numerous studies [4].

Phytoextraction, as a relatively new and promising technology for in situ reclamation using plants to remove waste from contaminated soils [5], has gradually gained wide recognition abroad [6]. To increase absorption and accelerate the process, chelating agents are introduced into the contaminated environment [7]. To date, successful results of induced phytoextraction have been obtained for many heavy metals (CD, Ni, Zn, Cu, Pb, As, etc.), which have inspired scientific groups from different countries to conduct research and search for effective plants and chemical corrections for mercury phytoextraction [8]. However, the existing objective reasons related to the peculiarities of the chemical nature of mercury and its behavior in the "soil-plant" system seriously complicate the work in this direction. First, mercury belongs to metals that are not necessary for the life of living organisms and plants, in particular, in contrast to a number of biometals – microelements [9, 10]. Secondly, the group of plants capable of accumulating the element is still very small [11, 12]. Third, most plants have a weak translocation of the element to ground organs (shoots, stems, and leaves), while the main amount of the absorbed element is deposited in the roots [13, 14].

It was noted that mercury belonging to the zinc group of d-metals has a high ability to complexation, characteristic of d-metals. All elements of this group have a high affinity for sulfhydryl groups, which is significantly reduced in the Hg > Cd > Zn series, and interact energetically with Halogens. The affinity for the donor sulfur atom is especially high in mercury [15]. This property was the basis for the study by foreign scientists of thiosulfates and halides as ligands in the phytoextraction of mercury [12, 16, 17]. A number of authors also note the good effectiveness of the EDTA complex, the disadvantage of which is the increased ability to leach other heavy metal ions from the soil and, thus, simultaneously increase secondary contamination of soil and groundwater [18, 19].

In this research, it was first proposed to use as an inducer for phytoextraction of mercury from the soil medium a phosphorus - and sulfur-containing complexion containing nitrogen atoms and, along with this, sulfur atoms, which have an affinity for mercury, and provide the formation of different coordination zones in the interaction of N, S-ligands with a mercury cation.

The purpose of the research is to conduct a comparative evaluation of the effectiveness of enhancing mercury phytoextraction with clover when adding S – containing complexon in comparison with other additives (sodium thiosulfate and EDTA).

2. Methods and materials

Objects of research: sprouts of white creeping clover (*Trifolium repens* L.). Model experiments were conducted in accordance with the ISO 22030:2005 standard "Soil quality. Biological methods. Chronic toxicity in higher plants". using standard laboratory equipment, phytolamps, scales with an accuracy of ± 0.1 mg, universal soil (pH 5.8-6.2), a set of plastic growing vessels for planting seeds. An aqueous solution of $Hg(NO_3)_2 \cdot H_2O$ was used to simulate mercury contamination.

During the experiment, a 1-liter vegetative vessel was filled with universal soil with the addition of 237 mg of fertilizer containing 21% nitrogen, 11% phosphorus (P_2O_5),and 11% potassium. To simulate mercury contamination, $Hg(NO_3)_2 \cdot H_2O$ was added to vegetation vessels in the amount of 9.87 mg or 19.73, which should correspond to a 5 and 10-fold excess of the MPC of mercury in the soil [20], respectively. The ground was mixed. As a control, we used a growing vessel with universal soil and fertilizer, but without adding mercury. In each growing vessel, including the control one, seeds of creeping clover were planted in the amount of 20 pieces.

For comparative analysis, the following were added to individual vegetation vessels:

- Trilon B (disodium salt of ethylenediaminetetraacetic acid), which is used to stimulate plant growth and increase the yield of various crops. The drug was added from 22 to 26 days after seed planting in an amount of 20 ml at a concentration of 0.054 mol/l;
- sodium thiosulfate, used to increase the immunity of plants, accelerate their growth. The drug was added from 26 to 30 days after seed planting in an amount of 17 ml at a concentration of 0.054 mol/l;

- as sulfur-containing chelant used monoethanolamine salt of trifluoroacetic acid, and the phosphorus — disubstituted potassium salt of oxy-ethylidene diphosphonic acid (MEBTA). The drug was added from 26 to 30 days after planting seeds in an amount of 15 ml.

Also, for comparison, vegetation vessels with mercury-contaminated soil were prepared, in which no additives were provided.

All variants of vegetative vessels with additives, with mercury without additives, and control ones with clean soil were presented three times.

After the end of the period of application of drugs in 3 days, the plants were dug out. The excavated plants were cleared of soil, washed with water and divided into aboveground and root parts. After that, the plants were dried and the mass of the obtained samples was measured. Mercury was measured using inductively coupled plasma atomic emission spectrometry (iCAP 6500 Thermo Scientific, USA) and inductively coupled plasma mass spectrometry (X-7, Thermo Elemental, США).

To determine the mercury content in dried soil samples, samples weighing 200 mg were placed in Teflon glasses, filled with a mixture of hydrochloric and nitric acids 3:1 and boiled for 5 minutes; then 5-10 cm3 of water was added for laboratory analysis, the resulting solution was transferred to polyethylene buckets, diluted with water for laboratory analysis to 20 cm3, left for 1 hour to precipitate suspended particles of the undissolved part of the analyzed sample, and then they obtained solutions were analyzed. Mercury in the obtained solutions was determined by inductively coupled plasma mass spectrometry (X-7, Thermo Elemental, США).

3. Results and discussion

The results of the experimental data are Shown in the table. It should be noted that visually, plants in vegetation vessels with clean soil, vessels with mercury-contaminated soil, and vessels with mercury-contaminated soil with the addition of sodium thiosulfate look about the same: most plants are green, some with whitish leaves. Plants in vegetation vessels with mercury-contaminated soil with the addition of Trilon B looked a little wilted, and the leaves of some plants turned brown. Plants in vegetation vessels with the addition of a derivative of S-containing complexion (MESTA) looked the weakest. most of them had withered, some of their leaves were yellow, and there was an oily coating on the ground.

Table 1. Results of a laboratory experiment of mercury phytoextraction in the presence of various additives.

Measured parameter	Number of seedlings, pieces	The mass of plants, g		Hg concentration, mcg/g		
		stems and leaves	roots	soil	stems and leaves	roots
Clean soil	9	0.1463	0.0127	2.750	-	-
Hg (5 MPC) without additives	12	0.0603	0.0043	19.867	-	-
Hg (5 MPC) + Trilon B	11	0.0507	0.0090	38.500	62.6	691
Hg (5 MPC) + sodium Thiosulfate	12	0.0643	0.0110	83.133	105	883
Hg (5 MPC) + MEBTA	13	0.0853	0.0083	27.667	85.2	289
Hg (10 MPC) without additives	8	0.0330	0.0057	39.100	-	-
Hg (10 MPC) + Trilon B	8	0.0287	0.0050	45.433	194	453
Hg (10 MPC) + sodium Thiosulfate	11	0.0333	0.0073	73.463	133	841
Hg (10 MPC) +MEBTA	10	0.0350	0.0050	48.500	204	788

A dash in the table indicates that this parameter was not determined

The dependences of the average plant growth on the degree of soil contamination and the introduction of additives are shown in Fig. 1. From which you can see a significant decrease in growth in mercury pollution at the level of 10 MPC compared to 5 MPC. It is also possible to note the depressing effect of MEBTA in this concentration on plant development in comparison with other additives.

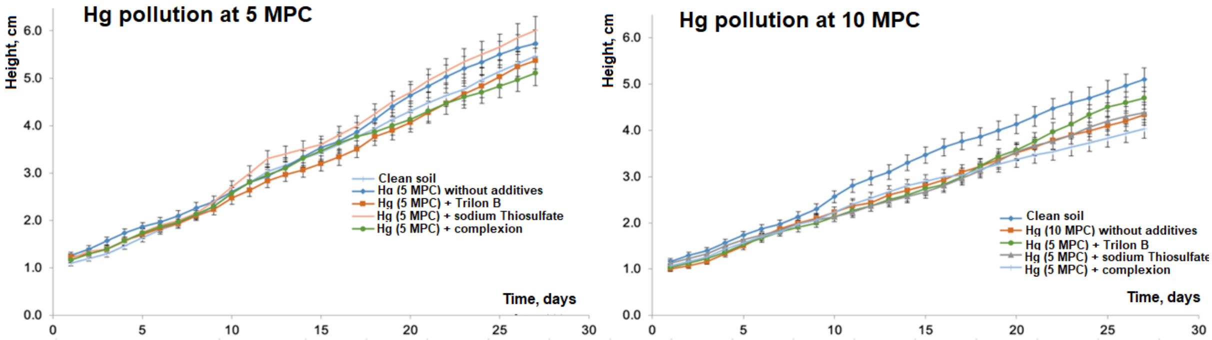

Figure 1. Based on the growth of plants from soil pollution and introduction of various additives.

Figure 2 shows the mercury concentration coefficients for terrestrial plant organs and roots, depending on the additives used.

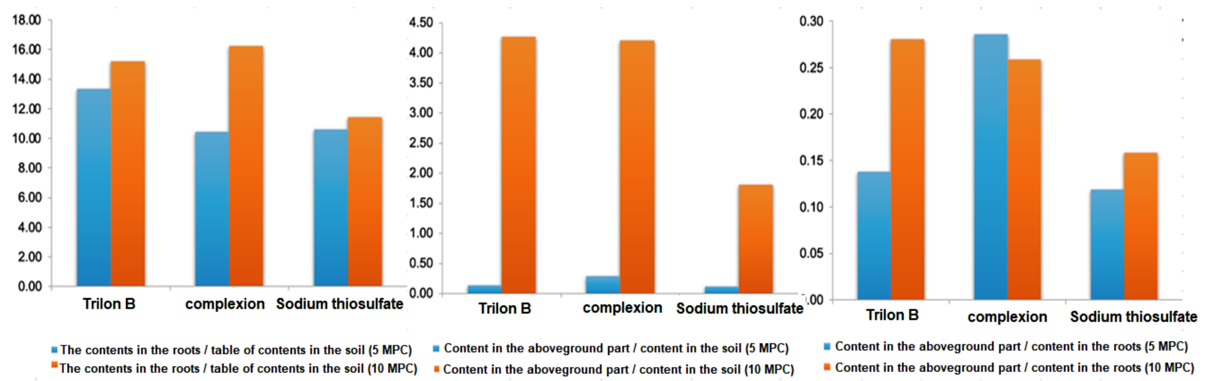

Figure 2. Dependences of bioconcentration coefficients in the ground and underground parts and translocation from roots to leaves and stems on the degree of soil contamination and application of various additives.

The results obtained allow us to note the positive effect of the S-containing complexon derivative (MEBTA) in comparison with sodium thiosulfate, and in some cases with Trilon B. Moreover, it should be noted in some cases that the translocation of mercury from roots to stems is more important for MEBTA (the ratio of mercury concentration in the ground part/mercury concentration in the roots is 0.29 at 5 MPC and 0.26 at 10 MPC) compared to Trilon B (the ratio of mercury concentration in the ground part/mercury concentration in the roots is 0.14 at 5 MPC and 0.28 at 10 MPC) and sodium thiosulfate (the ratio of mercury concentration in the ground part/mercury concentration in the roots is 0.14 at 5 MPC and 0.28 at 10 MPC).

4. Conclusion

As a result of scientific research, data on mercury uptake by the aboveground and root parts of white creeping clover (Latin Trifolium repens L.) were obtained. when soil was contaminated with mercury compounds, the highest mercury uptake was found in samples with the addition of monoethanolamine salt of dithiobiacetic acid (MEBTA) at concentrations of 10 MPC (absorbed concentration-12, 547 mcg/g). When the mercury concentration was exceeded by 5 times, the best result was shown by samples in the root parts in the presence of sodium thiosulfate (total absorbed concentration – 16.47 mcg/g). In experiments with a 5-fold and 10-fold excess of the mercury concentration, the worst absorption result was shown by samples with Trilon B Acknowledgment.

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