New methods of cleaning soil from heavy metals

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Abstract. The purpose of the work was to study new methods of cleaning soil from heavy metals. In this work, it was proposed to extract heavy metals Cd, Zn, Fe, Cu, Mn, Pb from soils using the method of biological purification. For this, we recommended to carry out preliminary treatment of soils with complexones and to carry out additional introduction of biophilic elements into complex compounds. The possibility of using electromechanical treatment for removing heavy metals from soils after a preliminary increase in the mobility of ions by acidification and the use of complexation reactions is shown. The experiments were carried out on the plants of sowing oat Avena sativa L. variety Yakov when grown in laboratory conditions on sod-podzolic soil with the introduction of soluble salts of heavy metals into the soil. It was noted that the largest amount of heavy metals is concentrated in the root system of plants. When growing oats in the field, the concentration of metals in the grain was assessed: Mn - 30-35 ppm, Fe - 55-65 ppm, Cu - 4-5 ppm, Zn - 30-35 ppm, Cd, Pb < 3 ppm.

1. Introduction
Soil pollution with heavy metals is one of the major problems of modern agriculture and the environment. Sources of pollution can be industrial emissions, fertilizers, water resources, etc. Heavy metals accumulate in soils when they are deposited in the form of poorly soluble salts, which are formed as a result of ion exchange reactions [1]. Mass transfer of heavy metals from soils to the environment occurs due to their leaching outside the soil profile [2], extraction from soils by plants and microorganisms, sorption by minerals with high cation exchange capacity, various types of other organic and inorganic sorbents [3].

It should be noted that among the heavy metals there are elements necessary for the life of plants, which belong to trace elements, as well as chemical elements, the functional role of which is currently unknown [4]. Such microelements as Co, Cr, Cu, Fe, Mn, Ni and Zn are involved in almost all processes taking place in a plant cell: energy metabolism, primary and secondary metabolism, hormonal regulation, signal transmission, etc. It should also be noted that 25-50% of all proteins work only in the presence of metal ions [5], of which the largest number (more than 1200) are functionally associated with zinc and other metals [6, 7, 8]. In addition, some trace metals are present as cofactors in the molecules of a number of enzymes. Usually, the concentrations of trace elements in plants are low (0.001% of the dry mass of the cell and below), but with an increase in their level in the...
environment, they become toxic to living organisms [9]. Some heavy metals, which are not trace elements, but belong to the most important environmental pollutants - Cd, Hg and Pb, negatively affect plants even in relatively low concentrations [10].

Depending on the source of pollution (natural or technogenic), there are noticeable differences in the profile distribution of heavy metals in the soil. With a naturally high level of these elements against the background of their small accumulation in the humus horizon, we can trace an increase in the content of metals down the soil profile. In case of technogenic pollution, heavy metals, on the contrary, are concentrated in the surface layer. The forms of finding of metals in the soil also differ. So in soils of natural anomalies, they are represented mainly in the form of sulfates, sulfides and carbonates, while in case of technogenic pollution - in the form of oxides and free ions [11]. In addition, for example, in northern territories with a naturally high level of heavy metals, special types of flora are formed, for example, gallmean flora (growing on soils with a high zinc content) and serpentine flora (with an increased content of a number of metals, including nickel and chromium), which includes metal-resistant plant species. The vegetation growing in technogenically-polluted territories, in most cases, consists of species of local flora and is characterized by a pronounced intraspecific differentiation in resistance to heavy metals [12, 13].

The level of accumulation of metals in soils depends on the chemical composition of the parent rocks, soil pH, humus content, and the reducing and absorbing capacity of soils. Due to the insignificant content of organic matter that binds heavy metals into complex compounds, the accumulation of heavy metals in the mineral soil is not as pronounced as in the organic soil [5]. In soils, copper is a weakly migratory element, although the content of the mobile form is quite high. Copper is one of the most important trace elements. The physiological activity of copper is mainly associated with its inclusion in the active centers of redox enzymes. At the same time, the high content of copper has an adverse effect on plant and animal organisms [14].

The sorption of heavy metals by sorbents and their transformation into hardly soluble precipitates lead to the creation of depositing media. Thus, delayed negative consequences are created and formed with high kinetic characteristics. The leaching of heavy metals outside the soil profile with water is ineffective, due to the low solubility of heavy metal sediments in soils, their strength, high binding energies in the soil-absorbing complex [15]. The extraction of heavy metals from soils by plants and microorganisms, as a rule, is small in comparison with their gross content, but this is a promising biological method for removing heavy metals from soils.

The aim of the work was to intensify the existing methods of cleaning soil from heavy metals and to develop new methods of soil intoxication. The aim of this work was to study the accumulation of heavy metals Cu, Zn, Fe, Mn, Pb, and Cd from model-contaminated soils into oat plants.

2. Materials and methods
Sod-podzolic medium-loamy soils were chosen as the object of research [15]. In this work, the concentration of mobile forms of heavy metals in soils was determined in the CH₃COONH₄ extract with pH = 4.8. A study was carried out of the removal of heavy metals from soils by plants after the introduction of heavy metals into them in the form of salts, soluble in water, biophilic elements and complexones, the method of electrolysis was used. The studies were carried out on seedlings and oat plants of Avena sativa L. variety Yakov. Zn, Fe, Cu, Mn, Cd in the form of sulfates were chosen as pollutants: CuSO₄ × 5H₂O, ZnSO₄ × 7H₂O, FeSO₄ × 7H₂O, MnSO₄ × 5H₂O, 3CdSO₄ × 8H₂O, and Pb in the form of water-soluble acetate Pb(CH₃COO)₂ × 3H₂O. The experiments were carried out in 4 repetitions. The atomic absorption spectrophotometer "AA-7000" was used to determine the concentration of metal ions.

3. Results and discussion

3.1. Methods for cleaning soil from heavy metals
Cleaning of soil from toxicants can be carried out by different methods:
- complete replacement of soil or part of it;
- leaching of soils from heavy metals, both under conditions of electric melioration, and using selective compositions of wash water;
- due to biological reclamation when growing crops that consume a large amount of certain toxicants when they are further removed from the territory;
- an increase in the rates of removal of certain toxicants by crops by modifying the properties of soils and increasing the absorption capacity of the root systems of cultivated crops to toxicants through the use of fertilizers, regulators of plant metabolism, etc.;
- deposition of toxicants inside the soil due to the formation of insoluble or poorly soluble precipitates or their binding into sedentary forms due to complexation and ion exchange.

3.2. Reducing the toxicity of heavy metals in soils due to their binding to poorly soluble compounds
The content of mobile forms of heavy metals in soils and their absorption by plants can be reduced by creating conditions for the deposition of pollutants in the form of sparingly soluble sediments (carbonates, phosphates, hydroxides, etc.). This is confirmed by our experimental data presented in Figure 1.

![Figure 1](image)

**Figure 1.** Content of mobile forms of cadmium in root and stem (a) and soil (b).

As can be seen from the data presented, the introduction of cadmium into the soil led to an increase in its mobile forms in the soil, root and stem. At the same time, the content of both positively and negatively charged cadmium compounds increased. However, if in the soil these changes are very large, then in the stems they are much lower. Adding lime to the soil led to a decrease in the content of mobile forms of cadmium in the soil, roots and stems. However, this clearly manifests itself for positively charged cadmium compounds, and does not appear for negatively charged cadmium complexes. The effect of K$_2$HPO$_4$ on the content of mobile cadmium compounds in the soil-plant system is less unambiguous, because in this case, the formation of cadmium phosphate complexes is possible.

We can note that soil contamination with cadmium leads to an increase in the content of Cd in roots and stems, and an increase in the proportion of positively charged cadmium compounds not bound in complexes and in the processes of metabolism in soil and plants. The introduction of K$_2$HPO$_4$ and CaCO$_3$ into the soil will not always reduce the mobility of Cd. This will happen if the resulting compounds of carbonate, phosphate, cadmium hydroxides are less soluble than the cadmium compounds present in the soil before their introduction. But in this case, the formation of cadmium complexes is possible, and the effective product of the solubility of the indicated cadmium precipitates is large. To reduce the mobility of cadmium in the system, it is more preferable to add CaCO$_3$, since this also decreases the proportion of positively charged cadmium compounds.
3.3. Electric reclamation - a method of removing heavy metals from soil

A promising method for cleaning soil from contamination with heavy metals is the method of electric reclamation. However, heavy metals, in contrast to sodium and water-soluble salts, are bound in the soil by strong bonds with the solid phase of the soil state. Therefore, in order to remove them from the soil by means of electric reclamation, it is necessary to first transfer heavy metals from a difficult-to-dissolve to a readily mobile state. This can be done by acidifying soils and by forming water-soluble complexes of heavy metals with ligands of water-soluble organic matter or with commercially available complexones such as ethylenediamine tetra acetic acid (EDTA). Until now, unresolved issues are: the necessary level of lowering soil pH, the choice of organic ligands for the formation of complexes with heavy metals with a given stability constant; parameters of electric melioration.

In our studies, it was found that the treatment of soils contaminated with heavy metals, organic ligands, salts that increase the electrical conductivity of soils, lead to an increase in the release of lead, cadmium, zinc from the soil into the solution. When soil is treated with organic reagents, the proportion of negatively charged complex compounds of heavy metals in the soil increases. We carried out an experiment on the extraction of heavy metals in the studied soils, 50 g was added to the soil sample according to the options, 15 ml of H₂O; 0.1M KNO₃; 0.001M EDTA, concentrated aqueous solution of nettle compost. After the electrolysis time elapsed, heavy metals were extracted from the sorbent layers (chromatographic paper) with a solution of 0.05M H₂SO₄ (reaction time 1 hour). The results of the influence of the reagents added to the soil on the displacement of heavy metals from the soil by the method of electric reclamation are shown in Table 1.

Table 1. The effect of additives on the displacement of metals from soil by electrolysis, mg/l.

| Additives                  | Cd  | Zn  | Pb  | Fe  |
|---------------------------|-----|-----|-----|-----|
| H₂O                       | 0.10 ± 0.01 | 1.9 ±0.3 | 1.3 ± 0.2 | 3.9 ± 0.6 |
| EDTA                      | 0.11 ± 0.01 | 2.4 ± 0.8 | 1.0 ± 0.1 | 4.7 ± 0.9 |
| KNO₃                      | 0.12 ± 0.01 | 5.2 ± 3.0 | 1.0 ± 0.1 | 6.3 ± 2.6 |
| Nettle compost organic matter | 0.13 ± 0.02 | 5.8 ± 2.9 | 1.2 ± 0.2 | 3.6 ± 0.7 |

As can be seen from the data presented, the addition of EDTA, potassium nitrate, and water-soluble organic matter to the soil to a greater extent increased the displacement of zinc from the soil. At the same time, the ratio of negatively and positively charged compounds of lead was 1.4 in soil treatment with EDTA; KNO₃ 0.6; and when treating soils with water-soluble organic matter from nettle compost - 1.6.

The addition of organic matter increased the displacement of lead and iron from soils. At the same time, for Pb and Zn, the proportion of negatively charged complex compounds increased. The displacement of Mg from soils under the action of organic ligands of water-soluble organic matter from nettle residues did not change significantly, which is associated with the lower ability of this element to form complexes.

In another experiment, we studied how the mobility in heavy metals soils changes when the soil is treated with 0.01 M HCl. We found that when treating soils with 0.01 M HCl by electrolysis, less heavy metals was displaced than when treating them with water-soluble organic matter. In this case, the proportion of negatively charged compounds was significantly lower (Figure 2).
As can be seen from the presented data, in the contaminated soils there are both positively and negatively charged heavy metals compounds, which move to the cathode and to the anode during electric reclamation. However, with an electric melioration time of 10 minutes and close to neutral pH values, the amount of migrating heavy metals is small.

According to the experiments, the rate of movement of lead from the soil into the solution is up to 1 mg/l kg in 10 minutes. Thus, the electromelioration of soils at a voltage of 14 V for 10 minutes leads to a significant displacement of heavy metals from the soils into the solution, which can be used for soil cleaning. The displacement of Pb from the soil into the solution during electrolysis is enhanced by the addition of water-soluble organic matter from the aerial part of the nettle to the soil. Soil treatment with water-soluble organic matter contained in plant residues can be used to increase the efficiency of electric reclamation of soils contaminated with heavy metals.

Removing heavy metals from soils is especially important for urban soils. At the same time, to intensify the process of removal, it is necessary to select the conditions for growing plants and the type of plants. Different plants have unequal resistance to certain types of pollution, which is determined by the characteristics of the metabolic processes occurring in them. In our experiments, we observed a positive effect on the growth and development of plants and on an increase in the rate of removal of heavy metals from the soil, if we add quartz sand, peat, zeolite to the soil. The removal of heavy metals from the soil depends on the composition, for example, on the presence and concentration of sorbents. Zeolites can be such sorbents. For example, when zeolite is introduced into the soil at a concentration of 10%, the removal of zinc can be from 150 to 460 ppm.

4. Conclusion
Various methods have been proposed for removing mobile forms of heavy metals from the topsoil. The application of each method is determined by specific soil, lithological, hydrological conditions and economic opportunities. In addition to the known methods, it is proposed to use the following methods:
- leaching of heavy metals by solutions of complexones to a certain depth and then their precipitation, followed by washing of soils with solutions that contain carbonates, phosphates with pH > 7;
- removal of heavy metals from soils through phytoremediation and absorption by fungi while creating conditions for their greater bioproducitivity;
• regulation of exchange constants in the soil-roots system; roots - the aboveground part of plants, due to the nutritional regime;
• application for phytoremediation of species and varieties of plants with a higher sorption capacity of roots to heavy metals;
• the use of long-acting sorbents for the sorption of heavy metals, taking into account the equilibrium constants in the system soil - heavy metal and sorbent - heavy metal;
• a decrease in the intake of heavy metals into plants when complexes from agricultural waste are introduced into the soil, forming stable complexes with a large molecular weight with metals;
• electromelioration of soils while creating conditions for increasing the mobility of heavy metals;
• creation of geochemical barriers in the soil profile, preventing their entry into plants, migration into groundwater and evaporation from soil.
In all cases, it is necessary to carry out a physicochemical calculation and forecast of the ongoing processes for specific soils, plants and environmental conditions.

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