

Translocation of heavy metals and methods of their detoxification in podzolized chernozem

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Abstract. At present, the fact that all unforeseen negative consequences of anthropogenic human activity significantly affect the biochemical regime of the natural environment is obvious. Therefore, agriculture should be aimed at reducing the release of chemicals from the biological cycle. Field observations were conducted to study the effect of detoxification techniques on the accumulation of heavy metals in soil. Six experiment variants were developed, using detoxicants with various combinations of them. The results of this research indicate that the organic matter of manure binds soluble metal salts into organometallic complexes, and fertilizer phosphates convert them into sparingly soluble compounds. Thus, they improve (heal) the soil contaminated by heavy metals.

Keywords: heavy metals, detoxification methods, translocation, chernozem.

Introduction

The increase in anthropogenic pressure on the soil cover leads to degradation processes, among which chemical degradation of soil and, in particular, their contamination by heavy metals has become widespread in recent decades.

Heavy metals enter the biosphere due to technogenic dispersion from emissions of high-temperature technological processes (ferrous and non-ferrous metallurgy, thermal power plants, etc.). One of the most important components of the environment is the soil, which takes on the effects of industrial emissions and waste, residual pesticides and other toxicants, making a difference as a buffer and detoxifier. The source of soil contamination can serve as sewage sludge used as fertilizer. In addition, secondary contamination due to the removal of heavy metals from dumps of mines or metallurgical enterprises by water or air flows [3,7].

Technological emissions from stationary and mobile sources of environmental contamination enter the atmosphere, and then, falling to the earth's surface, accumulate in the upper horizons of the soil, are again included in natural and man-made migration cycles.

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The intensification of agricultural production, the dynamic development of industry, transport and energy lead to increased anthropogenic pressure on ecosystems. Contamination of the soil cover by heavy metals leads to a weakening of its resistance to technogenesis, the development of degradation processes, a decrease in fertility, and, consequently, a decrease in the productivity of both natural and agricultural landscapes, which significantly affects the volume and quality of productive resources. Agricultural products grown on contaminated soil are often toxic due to the increased content of heavy metals [1,2, 4-8].

The soil with a heavy particle-size distribution exhibits its buffering properties. The danger of plant contamination by heavy metals on such soil is much less, which is associated with a greater retention capacity of the silt fraction.

With the organic matter of the soil, metals can form organometallic complexes that are not capable of overcoming cell membranes at the soil – root contact. The most stable compounds in the soil form heavy metals with humic compounds. The stability of complexes of heavy metals with fulvic acids increases with increasing of pH.

Chernozem is a strong accumulator of heavy metals; in this regard, the urgent problem is the development of agromeliorative practices for the rehabilitation of technologically contaminated chernozems and the production of safe crop products.

The aim of our work was to study the influence of detoxification techniques for podzolized chernozem, contaminated by heavy metals, on their accumulation in soil.

Methods

Developing agrochemical methods for the decontamination of contaminated soil in a stationary lysimetric experiment (Fig. 1), a preliminary stage was carried out in which the total content of Zn, Cu, Pb, Cd in podzolized chernozem, its hydrolytic acidity (Ha) in each lysimeter were studied, and acidity was neutralized .

According to the regional gradation of soil contamination levels, compiled on the basis of the geochemical background, the content of Cu - 90 mg / kg, Zn - 110 mg / kg, Pb -40 mg / kg, and Cd - 0.6 mg / kg in the soil represents increased contamination.

Modeling of the increased complex level of soil contamination was carried out by adding to the soil. In this case, chemically pure salts were used: $Zn(CH_3COO)_2 \times 2H_2O$; $CuSO_4 \times 5H_2O$; $Pb(CH_3COO)_2$; $CdSO_4$.

For this, a soil layer of 20 cm depth was selected from the lysimeter. The calculated dose of Cu, Zn, Pb, and Cd salts was thoroughly mixed with this soil and placed in the same lysimeter.

The following fertilizer systems were studied: organic (cattle manure), organo-mineral and mineral, where double superphosphate was used periodically and annually at higher doses. For podzolized heavy loamy chernozem, the manure rate of 100 t / ha was adopted (Table 1). The annual norms of mineral fertilizers, depending on the crop, are adopted according to the recommendations for our zone.

Dates and methods of fertilizing in the rotation link were performed in the following way. In autumn, after harvesting the rotation crop, cattle manure (cattle) was introduced at the rate of 100 t / ha, with a humidity of 85%.

This organic rate was buried to a depth of 25 cm. The calculated norms of mineral fertilizers were evenly distributed manually on the surface of the lysimeter, and then the soil was dug to a depth of 12-15 cm. The surface of the soil was leveled by a rake. A mixture of herbs (fescue, timothy, clover) was sown as a leveling culture.

Urea (N - 46%), double superphosphate (P₂O₅ - 44%), potassium sulfate (K₂O - 48%) were used in the experiment.

The gross determination of Cu, Zn, Pb and Cd in manure and mineral fertilizers was carried out by the atomic absorption method.

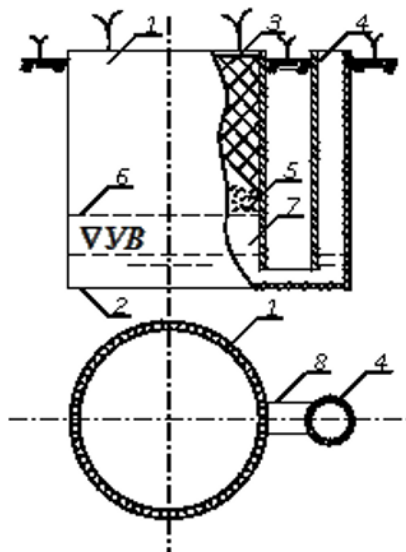


Figure 1. Diagram of a water balance lysimeter (legend: 1 - lysimeter case, 2 - lysimeter bottom, 3 - soil monolith, 4 - pocket for water extraction, 5 - gravel packing, 6 - strainer, 7 - groundwater level, 8 - communication channel).

Analytical research in determining the gross and mobile forms of heavy metals in the soil was carried out in the ACTC NIMRM. When determining the total content of elements, the soil sample was decomposed with a mixture of acids: HCl, HNO₃, HF, HClO₄ with heating. Mobile forms were recovered using an ammonium acetate buffer - pH of 4.8. The heavy metal content was determined using an inductively coupled plasma mass spectrometer Elan - 6100, and an atomic emission spectrometer Optima - 4300.

Table 1. The scheme of establishment and performance of field lysimetric experiment. Station on podzolized heavy loamy chernozem.

| Variant №№ | Names of variants, fertilizer application systems in the rotation link | Abbreviations in the tables of variant names |
|------------|--|--|
| 1 | Without fertilizers | W/f |
| 2 | Cattle manure 100 t / ha - periodic application | H100 |
| 3 | Cattle manure 100 t / ha - periodic application, N60 (N90) P60K60 (K120) - annually depending on the crop (kg / ha) | H100 N1P1K1 |
| 4 | P2 - periodic application of phosphorus, once every 2 years at a dose of 120 kg / ha, annual use of N60 (N90) K60 (K120) | P2N1K1 |
| 5 | P4 - periodic application of phosphorus, once every 4 years at a dose of 240 kg / ha, annual use of N60 (N90) K60 (K120) | P4N1K1 |
| 6 | P2 (e) - annual application of an increased dose of phosphorus (120 kg / ha) and optimal doses of N60 (N90) K60 (K120) | P2(e)N1K1 |

Statistical processing of the obtained results was carried out by generally accepted methods (assessment of significance according to Fisher's and Student's criteria) using the Microsoft Excel software package.

Results and Discussion

The total soil contamination is characterized by the gross content of heavy metals. Changes in the content of chemical elements in the soil characterize steady changes in soil properties. The negative effect of high concentrations of heavy metals on the soil depends on their mobility and solubility. While the elements are firmly connected with the constituent parts of the soil, they are inaccessible to plants, their vertical movement in soil is weakly expressed. Therefore, the content of mobile forms of heavy metals in the soil characterizes the sanitary-hygienic situation and determines the need for amelioration detoxification measures.

The problem of mobility of heavy metals in soil is very complex and multifactorial. Depending on the extractant used, a different amount of the mobile form of the heavy metal, which with a certain conditionality can be considered available for plants, is recovered.

The availability of a mobile form of heavy metal for plants depends largely on the properties of the soil and the specific characteristics of the plants. Moreover, the behavior of each element in the soil has its own specific laws inherent only to it.

For the extraction of mobile forms of heavy metals, various chemical compounds that have unequal extracting power are used. A number of authors proposed a scheme of various fractions of mobile metals in the soil:

- 1) the total stock of mobile forms (extracted by acids);
- 2) active mobile form (extracted by buffer solutions);
- 3) exchange (extracted by neutral salts);
- 4) water soluble.

According to the researchers [9–15], the majority of mobile compounds of heavy metals are confined to the humus, humus-eluvial horizons, where the roots of plants, in which biochemical processes are actively occurring and which contain a lot of organic substances, are located. Under the influence of contamination by heavy metals of the soil, organic complexes, which have high mobility, are formed in it.

Nazarova L.K. et al. [16] note that the systematic long-term use of ballast and concentrated fertilizers, including phosphorite meal on sod-podzolic heavy loamy soil did not significantly affect the gross content of heavy metals and toxic elements in the soil, but led to the almost doubled increase in their mobility in it. Alloway B.J. et al. [17-19] indicated that complete mineral fertilizer, creating optimal conditions for the growth and development of plants, significantly reduced the accumulation of mobile forms of lead and cadmium in the soil.

There is evidence of a close relation between the total content of Zn, Pb, Cd and their mobile forms, extracted by acetate-ammonium buffer (AAB) pH 4.8. Therefore, we determined the mobile forms, their mobile parts in our research of the rehabilitation measures of contaminated soil by heavy metals. AAB pH 4.8 was used (Table 2) for the extraction of mobile forms of heavy metals.

Mobile forms of metals are the most aggressive part of the gross content of HM, which can enter directly into the root system. These mobile forms are involved in migration flows, including intra-profile ones. Therefore, the liquid phase of soil is a direct source of HM for higher plants and soil biota.

The research was carried out in annual soil samples, which were selected after crop accounting. According to years of the research, variability was observed in the quantities of mobile forms of heavy metals. The average metal content in the acetate-ammonium buffer indicated that they were extracted significantly more in the variant without fertilizers. The maximum degree of mobility was observed in Cd (73.3%). All fertilizer systems used for the rehabilitation of contaminated by HM chernozem, on average, reduced the

accumulation of mobile compounds of Zn, Cu, Pb, Cd. Thus, the degree of their mobility also decreased. The organo-mineral fertilizer system reduced the mobility of zinc from 42.8% to 21.2%, copper from 15.7% to 8.3%, lead from 53.5% to 25.5% and cadmium from 73.3% to 51.6%.

Table 2. The influence of fertilizer systems on the study of the rehabilitation of contaminated by heavy metals podzolized chernozem.

| Experiment variant | Element | The amount of element extracted from the soil AAB _{pH=4,8} , mg / kg | | | | |
|--------------------|---------|---|---------|---------|------------------|------|
| | | 1 year | 2 years | 3 years | Average, mg / kg | %* |
| W/f | Zn | 26,3 | 45,3 | 69,7 | 47,1 | 42,8 |
| | Cu | 32,3 | 10,1 | 19,5 | 14,1 | 15,7 |
| | Pb | 31,2 | 10,7 | 22,2 | 21,4 | 53,5 |
| | Cd | 0,47 | 0,29 | 0,57 | 0,44 | 73,3 |
| H100 | Zn | 17,3 | 36,2 | 26,1 | 26,5 | 24,1 |
| | Cu | 11,1 | 11,4 | 4,1 | 8,9 | 9,9 |
| | Pb | 20,4 | 12,9 | 9,8 | 14,4 | 36,0 |
| | Cd | 0,49 | 0,25 | 0,30 | 0,35 | 58,3 |
| H100N1P1K1 | Zn | 4,2 | 26,2 | 39,4 | 23,3 | 21,2 |
| | Cu | 13,2 | 3,6 | 5,7 | 7,5 | 8,3 |
| | Pb | 10,0 | 11,0 | 9,7 | 10,2 | 25,5 |
| | Cd | 0,50 | 0,17 | 0,27 | 0,31 | 51,6 |
| P2N1K1 | Zn | 60,0 | 37,9 | 36,8 | 44,9 | 40,8 |
| | Cu | 31,1 | 6,7 | 7,8 | 15,2 | 16,9 |
| | Pb | 12,5 | 7,1 | 11,2 | 10,3 | 25,8 |
| | Cd | 0,41 | 0,26 | 0,32 | 0,33 | 55,0 |
| P4N1K1 | Zn | 67,0 | 63,5 | 47,4 | 59,3 | 53,9 |
| | Cu | 14,0 | 7,5 | 3,8 | 8,4 | 9,3 |
| | Pb | 7,2 | 10,2 | 8,5 | 8,6 | 21,5 |
| | Cd | 0,39 | 0,32 | 0,30 | 0,34 | 56,7 |
| P2(e)N1K1 | Zn | 7,8 | 64,0 | 44,1 | 38,6 | 35,1 |
| | Cu | 0,7 | 13,0 | 6,4 | 6,7 | 7,4 |
| | Pb | 2,5 | 20,7 | 12,2 | 11,8 | 29,5 |
| | Cd | 0,13 | 0,25 | 0,25 | 0,21 | 35,0 |

The note: * data are given on the degree of mobility of HM (the ratio of mg / kg in AAB to the gross content in the soil, expressed in %)

Almost close changes in this indicator were in the variant of the annual introduction of P2 (e) N1K1. Especially in this variant, the accumulation of mobile Cd decreased. Another ecotoxicant Pb minimized the degree of mobility from the periodic use of phosphorus fertilizers (P4) against the background of N1K1. It decreased from 53.5% (W/f variant) to 21.5% in the P4N1K1 variant.

Conclusions

So, the studied application of different fertilizer systems on podzolized chernozem significantly remove and reduce the aggressiveness of pollutants. The results of this research indicate that the organic matter of manure binds soluble metal salts into organometallic complexes, and fertilizer phosphates convert them into sparingly soluble compounds. Thus, they improve (heal) the soil contaminated by heavy metals.

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