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Sorption capacity of organic matter to heavy metals and its use for polluted soils recover soils recover

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Abstract

The article considers the results of leached chernozems and yellow soil research in Central Russia and in the South of Central China. The research has demonstrated that organic matter has an increased sorption capacity for heavy metals (HM), including lead (Pb) and cadmium (Cd), which are hazardous environmental pollutants. Studies conducted on chernozems demonstrate features of HM migration along a soil profile.

Thus, the total content of elements accumulates in the upper humus horizon, further down the profile it gradually decreases, following a decrease in an amount of organic matter. In a soil-forming rock an accumulation of metals is again noted due to the alkaline reaction of soil solution and silt fraction, which is enriched in soil-forming rocks. A significant increase in elements content in soils of arable land (farmland soils) was revealed in comparison with a fallow territory and a forest belt. This phenomenon explains by an additional supply of HMs as an admixture of mineral fertilizers applied on plowed chernozems. In addition, HMs are also appear as a result of agricultural machinery operations during flammable fuel combustion.

The ability of organic matter to increased sorption of HMs can be used to restore heavily polluted areas. Farmland soils of Sichuan province were studied as a model experiment.

Keywords: CHERNOZEMS, YELLOW SOIL, HEAVY METALS, LEAD, CADMIUM, TOTAL CONTENT, EXCHANGE COMPOUNDS, VORONEZH OBLAST, SICHUAN PROVINCE

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Introduction

The reactions that take place on the surface of solid particles proceed due to the presence of functional groups that determine their chemical activity. Such functional groups in the soil are primarily specific and nonspecific organic substances. All organic compounds in soils can be combined into two large groups: 1) non-specific organic compounds and 2) specific humic substances. The first group is represented by substances entering the soil, which are decomposition products of plant and living organisms, as well as products of the vital activity of soil microorganisms and plant root systems. In the molecules of nonspecific organic substances, the following groups are functional: methoxy, carboxyl, phenolic, amino groups. The second group - specific humic substances - are nitrogen-containing macromolecular compounds represented by humic acids, fulvic acids and humin. The functional groups are dominated by carboxyl and phenolic hydroxyls, and to a lesser extent by carbonyl, methoxy, amino groups, imidazole, alcohol OH-groups, and sulfhydryl SH-groups. The affinity of functional groups for HM cations, including Pb and Cd, determines the sorption properties of soil organic matter [1].

The unique property of organic matter and humus to absorb HM cations is used to restore and remediate polluted soils [2]. For example, in Chengdu plain (Sichuan province, China) an experiment was adopted, within the application of an organic liquid humic acid fertilizer combined soil control the soil was improved, productivity increased, and the Cd in product decreased accordingly.

Objects and methods

The studies were carried out on a territory of Ramonsky district (Voronezh region), and Chengdu plain, Sichuan. Objects of the research were leached low- and medium-humus medium-thick heavy loamy chernozems. Soil sections were laid on arable land, fallows (background plot) and in the forest belt, 90 years old. Sampling was carried out in layers to the depth of the parent rock. In the selected soil samples, the carbon of organic compounds of the soil was determined and converted to humus, since this chemical indicator determines the ability of the soil to bind HMs into organomineral complex compounds and firmly retain them in the form of chelate forms. The issues of restoration HM and improvement of the soil were carried out on the experiment of a grain production area in Chengdu plain. Based on this experiment the patent "A

Humic acid-Compound Microbial agent liquid fertilizer Conditioner and its Preparation Method" was taken out and accepted.

The content of HMs Pb and Cd was determined by the atomic absorption method on a KVANT.Z-ETA spectrophotometer, after preparing soil extracts to extract the total content and exchange compounds of elements. To determine the total content of Pb and Cd, the soil was first ashed, after which the samples were treated with nitric acid (1:1) and concentrated hydrogen peroxide, then the solutions were boiled for 10 minutes. According to some authors [3-5] the gross content of heavy metals does not provide comprehensive knowledge about the ecological situation, as well as their effect on plants. To solve this problem, it is necessary to know the amount of HM exchange compounds, for which an extract of ammonium acetate buffer was used, in the ratio of soil to solution 1:10. About the restoration of soil and reduction of HM in products, a humic acid organic fertilizer control and heavy metal comprehensive treatment technology was used, Kishniu green high potassium type 10 kg/mu+quicklime 75 kg/mu+twice spraying New turquoise 150 g/mu/time, Kishniu green is a root organic fertilizer applied to the soil, and New turquoise is a leaf fertilizer applied to the surface of plant, the organic liquid humic acid fertilizer is extracted from minerals.

The obtained data were statistically processed using the STATISTICA 10 software package and Microsoft Excel.

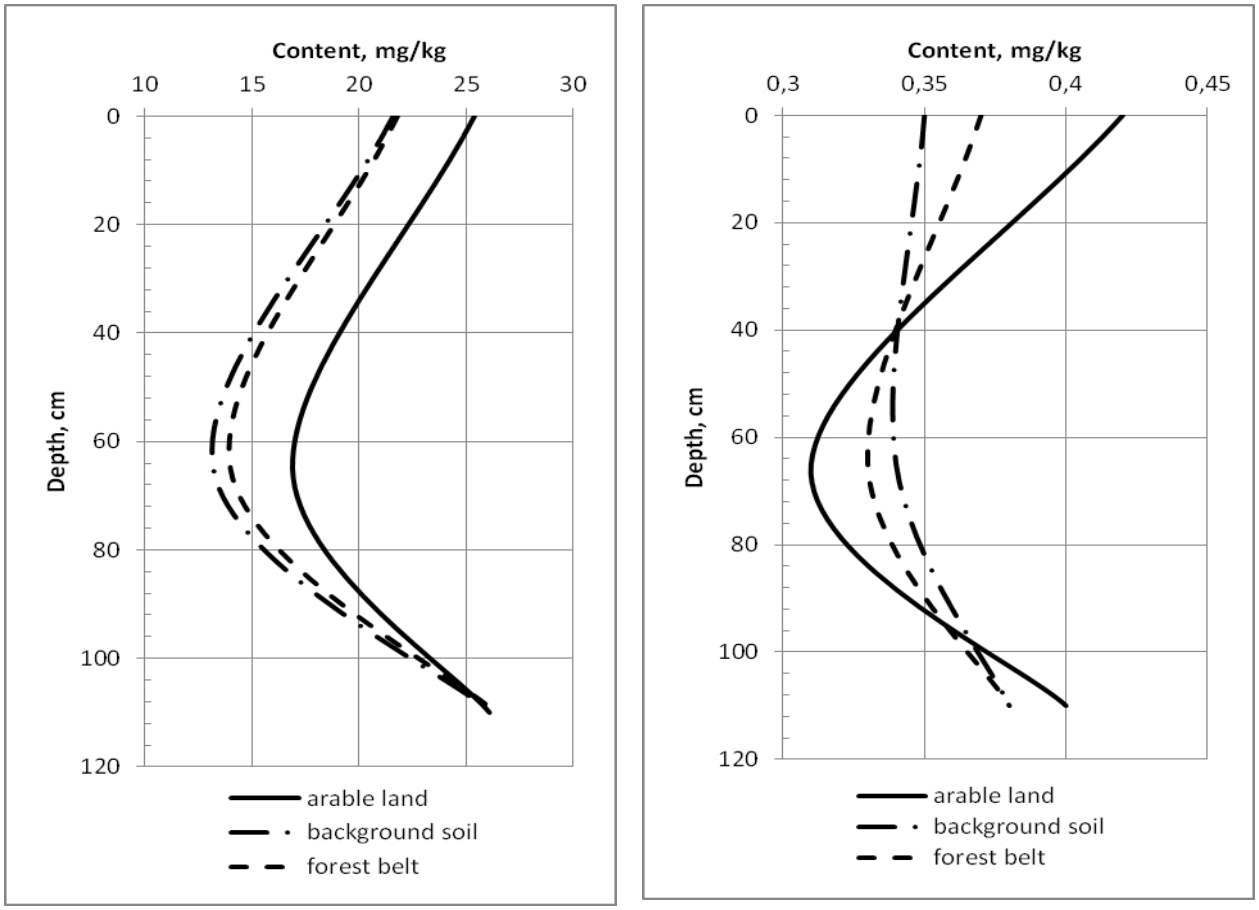
Research results

The content of organic matter and humus greatly influences the behavioral features, accumulation, and distribution of HMs. With the help of the regulation of this indicator, it is possible to influence the mobility, migration ability of metals, and, consequently, their availability to plant and living organisms. The investigated chernozems leached as a result of plowing are subjected to enhanced mineralization of organic matter. In this case, there is a removal with a crop of nutrients that are not fully replenished by the application of organic and mineral fertilizers. As a result, the humus content in the upper horizon of arable soils is 5.7 ± 0.10%. Chernozems, leached arable lands degrade to low humus.

The leached chernozems of the background plot (fallow) and under the forest belt have a significantly higher humus content, which is 7.2 ± 0.09% for the fallow, 7.8 ± 0.13% for the forest belt, the soils are diagnosed as medium humus. The preservation of organic matter at a

sufficiently high level, and to some extent its increase, is explained by the stable accumulation of plant residues on the soil surface in the form of humus of plant material and litter of woody vegetation. Then there is an intensive enrichment of chernozems with minerals, proteins and carbohydrates.

Previous studies indicate that the total content of HMs and their mobile compounds are closely related to organic matter, the reaction of soil solution, and the sorption capacity of silt particles [6, 7]. According to the data obtained, the accumulation of the total content of Pb (Fig. 1 a) and Cd (Fig. 1 b) is noted in the upper layer of the studied leached chernozems. Metals form strong organomineral chelate compounds with organic matter. Such strong chelate complexes firmly retain most of the HMs, including Pb and Cd, making them immobile and therefore incapable of migrating into adjacent media. This property of soils is actively used in the process of remediation of contaminated areas.



a) b)

Fig. 1. Profile distribution of total content of Pb and Cd in leached chernozems

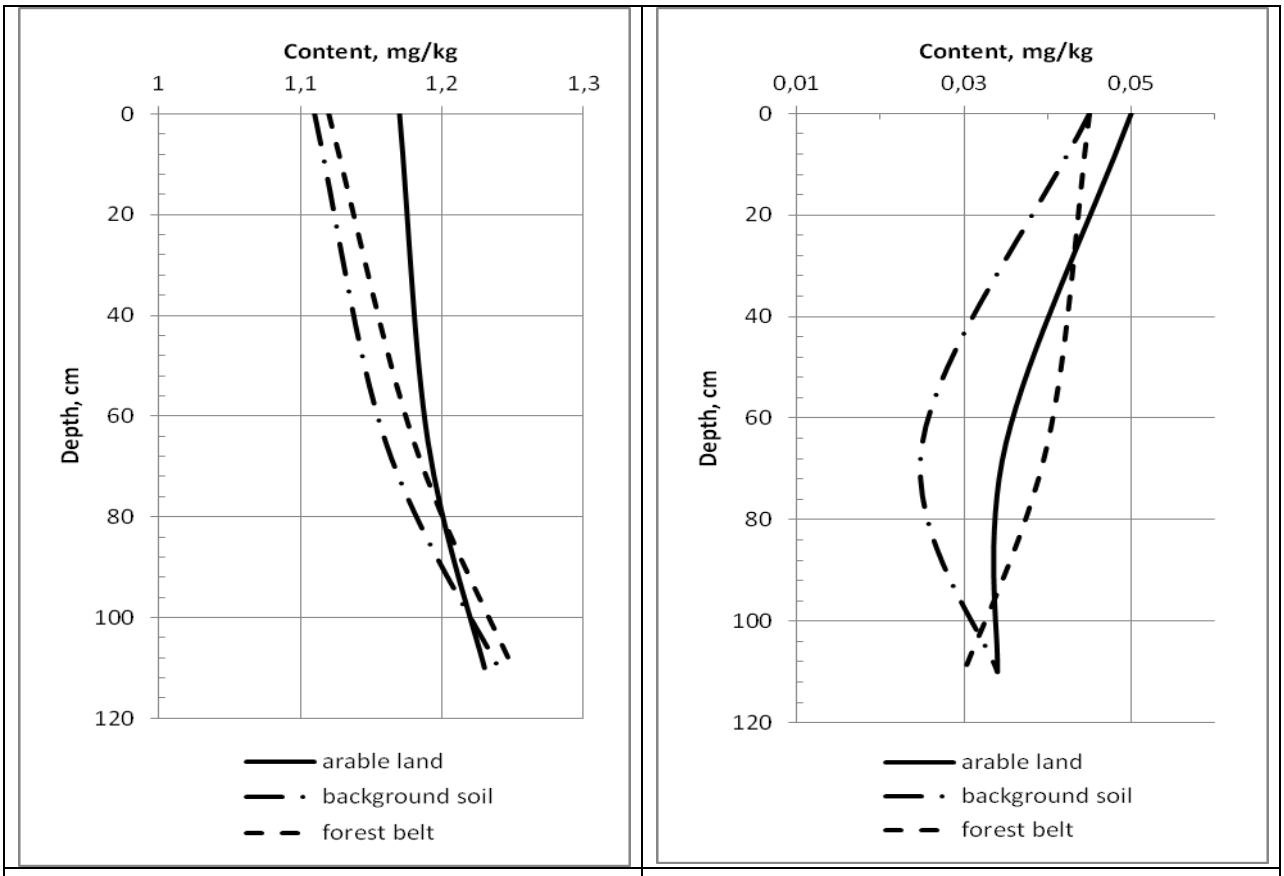
It should be noted that in the soils of arable land there is a significant accumulation of the total content of Pb and Cd relative to the chernozems of the fallow and forest belt. So the amount of Pb is 24.5 ± 1.05 mg/kg, Cd - 0.42 ± 0.13 mg/kg, while in the same 0-20 cm layer the gross content under the deposit does not exceed 21.6 and 0.35 mg/kg, under the forest belt - 21.8 and 0.37 mg/kg, respectively. The excess content of Pb and Cd in arable chernozems is explained by the fact that the studied metals are able to enter the soil surface as a result of the combustion of fuel from agricultural machines. In addition, applied mineral fertilizers, especially phosphorus ones, contain the studied elements as impurities.

Down the soil profile of all the studied soils, a fairly uniform decrease in the total content of HMs is noted (Fig. 1 a, b), following a decrease in the amount of organic matter. The described phenomenon is confirmed by the results of correlation analysis (Tab. 1), which indicate a close relationship in the profile distribution of humus and the studied HMs. In the lower part of the soil profile, the second peak of Pb and Cd accumulation is observed, which is caused by the alkaline reaction of the soil solution and the abundance of the clay fraction, which has a high sorption capacity for HMs [6, 7].

Table 1. Correlation coefficients between the total content, exchangeable forms of Pb and Cd compounds, humus in the profile of leached chernozems under various lands

land	Gross content		Exchange connections	
	Pb – humus	Cd – humus	Pb – humus	Cd –humus
arable land	0.79	0.80	-0.81	0.82
background soil (fallow)	0.85	0.89	-0.86	0.75
forest belt	0.89	0.92	-0.91	0.76

HM exchange compounds are mobile; they are able to migrate radially and laterally and enter adjacent media. Therefore, their content makes it possible to judge the ecological situation and the influence of elements on plant and living organisms [3]. The content of Pb exchangeable compounds in the upper 0-20 cm layer is 1.17±0.04 mg/kg, down the profile there is an increase in its amount to 1.24±0.01 mg/kg. The distribution curve has a regressive-eluvial type (Fig. 2 a). There is a high negative correlation dependence between the profile distribution of Pb exchange compounds and humus (Tab. 1).



a) b)

Fig. 2. Profile distribution of Pb and Cd exchange compounds in leached chernozems

The number of Cd exchange compounds varies within narrow limits (0.03-0.05 mg/kg). The profile distribution of the element is characterized by a regressive-accumulative type in the upper part and a regressive-eluvial type in the lower part (Fig. 2 b).

Pb is characterized by a low percentage of mobility (5-9%), which indicates a low migration ability of the element and its movement into adjacent environments. The mobility coefficient Cd is higher, it ranges from 8 to 24%. This phenomenon characterizes the element as more mobile, capable of migrating to adjacent environments.

The most accessible and effective way to fix HMs in the soil profile is the additional application of organic fertilizers. Currently, solutions of chelate compounds are used, which are not only well-assimilated by plants, but also capable of converting HM cations into hard-to-reach forms.

Table 2. Cd content and percentage of change in product (sample – rice), under different methods of humic acid organic fertilizer utilization and HM comprehensive treatment technology.

Mode	Sample name	Cd (mg/kg)	average value (mg/kg)	Percentage of change compared with conventional Cd content
(Test 1) Common practice	1-1	0.208	0.179	
	1-2	0.056		
	1-3	0.273		
(Test 2) Spray new turquoise high potassium 150 g/mu/times 3 times	2-1	0.282	0.149	-16.57%
	2-2	0.039		
	2-3	0.127		
(Test 3) Kirschnew green high potassium 10 kg/mu + spray twice 150 g/mu/time	3-1	0.060	0.078	-56.61%
	3-2	0.044		
	3-3	0.129		
(Test 4) Kirschneu green high nitrogen 10 kg/mu + Spray twice Neu green high potassium 150 g/mu/time	4-1	0.055	0.094	-47.49%
	4-2	0.037		
	4-3	0.190		
(Test 5) Kishniu green high potassium type 10 kg/mu+quicklime 75 kg/mu+twice spraying 150 g/mu/time	5-1	0.039	0.069	-61.45%
	5-2	0.079		
	5-3	0.089		

The Cd content in product is decreased within the use of organic fertilizer, and the decreased percentage of Cd content in rice is different under the different methods of utilization of organic fertilizer (Tab. 2). Compared with the conventional planting method, the application of humic acid organic fertilizer treatment can significantly reduce the Cd content of rice, the reduction range is from 47.49% to 61.45%. In particular, the Cd content of treatment test 5 (Kishniu green high potassium type 10 kg/mu+quicklime 75 kg/mu+twice spraying 150 k/mu/time) decreased from 0.179 mg/kg to 0.069 mg/kg, with a decrease of 61.45%, reaching a significant level. Based on the above data and the early and late rice data of last year, the best and stable formula for reducing Cd is test 5.

Conclusion

As a result of intensive plowing, increased mineralization of organic matter is noted, leading to a decrease in the percentage of humus. Leached chernozems degrade to low humus. The fallow and forest belt, on the contrary, stabilize the processes of formation and decay of

organic matter, leading to a fairly stable content of humus, its rather uniform distribution over the soil profile, and a higher percentage in the upper horizons.

The noted features of soil transformation under arable land, fallow land, and forest belt also affect the behavior of the studied HMs. The total content of Pb and Cd in chernozems leached under various types of land is characterized by the accumulation of elements in the upper humus horizon (due to the formation of strong chelate compounds with organic matter) and at the depth of the parent rock, which is enriched in the clay fraction, which has an increased sorption capacity for heavy metals. Exchange compounds Pb have a regressive-eluvial type of profile distribution. The distribution of Cd exchange compounds is more complex, combining regressive accumulative and regressive eluvial types.

There is a significant increase in both the total content of HMs and their exchangeable compounds in the upper layer of arable soils. The phenomenon is explained by the intake of elements as impurities introduced with mineral fertilizers and additional components obtained as a result of the combustion of agricultural machinery fuel.

The noted ability of soil organic matter to absorb HMs can be used during remediation and in the process of soil restoration from HM pollution, which is confirmed by the experiment laid down in Chengdu plain, the Cd content in rice is significantly decreased within the utilization of organic fertilizer, compared with conventional planting.

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References:

1. Vodyanitskii Y., Minkina T. Determination of the affinity of heavy metals to carrier phases in soils // Environmental Geochemistry and Health. – 2022. V. 44. – №4. – P. 1277-1288.

2. Kumari A., Kumari P., Rajput V.D., Sushkova S.N., Minkina T.M. Metal(loid) nanosorbents in restoration of polluted soils: geochemical, ecotoxicological, and remediation perspectives // Environmental Geochemistry and Health. – 2022. – V. 44. – №1. – P. 235-246.

3. Minkina T.M., Mandzhieva S.S., Burachevskaya M.V., Bauer T.V., Sushkova S.N. Method of determining loosely bound compounds of heavy metals in the soil // MethodsX. – 2018. – V. 5. – P. 217-226.

4. Plekhanova I.O., Zolotareva O.A., Tarasenko I.D., Yakovlev A.S. Assessment of ecotoxicity of soils contaminated by heavy metals // Eurasian soil science. – 2019. – V. 52. – № 10. – P. 1274-1288.

5. Vodyanitskii Y., Minkina T., Bauer T. Methods to determine the affinity of heavy metals for the chemically extracted carrier phases in soils // Environmental Geochemistry and Health. – 2022. – V. 44. – №4. – P. 1387-1398.

6. Горбунова Н.С., Громовик А.И., Черепухина И.В., Терентьева Ю.Ю. Сорбционные процессы в почвах. Вопросы изучения и современное состояние проблемы // Сорбционные и хроматографические процессы. – 2021. – Т. 21. – №2. – С. 265-275.

7. Rajput V.D., Minkina T.M., Kumari A., Shende S.S., Ranjan A., Barakhov A.V., Rajput P., Sushkova S.N., Faizan M., Singh A., Khabirov I., Gromovik A., Gorbunova N., Nazarenko O., Kızılkaya R. A review on nanobioremediation approaches for restoration of contaminated soil // Eurasian Journal of Soil Science. – 2022. V. 11. – №1. – P. 12020.

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