Effect of biochar on the lead mobility in Haplic Chernozem

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Abstract. The determination of mobile Pb compounds in soil is the most important environmental task, due to their sorption by plants and migration to other adjacent mediums. The biochar is widely known as an effective for contaminated soil remediation. The aim of the research was to study the effect of biochar remediation on the Pb mobility in soil under model contamination conditions. Haplic Chernozem was artificially contaminated with Pb nitrates at rates of 5 and 10 maximum permissible concentrations (32 mg/kg). Biochar was added in doses of 2.5% and 5% of the soil mass. Loosely bound compounds include exchangeable, complex, and specifically sorbed metal. The largest increase of metal exchangeable forms was observed at a pollution dose of 320 mg/kg (up to 16%). When carbon sorbent was introduced noticeable changes in the content of loosely bound forms occurred. Pb exchangeable forms decreased by 3-10%, complex forms - by 4-13%, specifically sorbed forms - by 4-12%. The highest efficiency of sorbents has been demonstrated by biochar at a dose of 2.5% in the soil contaminated with 160 mg/kg of Pb and at a dose of 5% under contamination of 320 mg/kg of metal.

1 Introduction

There has been a growing concern in the last few years with the problem of soil contamination with chemical compounds of various classes. Among pollutants heavy metals are of special environmental and biological significance. Lead (Pb) is priority soil contaminants in Rostov Region [1].

The most common in situ remediation methods for contaminated soils are based on heavy metals immobilization. Soil cultivation by adding sorbents and / or ameliorating additives to it allows metals stabilization, which leads to a decrease in their mobility and bioavailability, and has found a wide spread use in modern remediation technologies [2]. Carbon sorbents can be obtained by heat treatment (pyrolysis) of plant materials and some industrial wastes. Pyrolysis - the process of thermal decomposition of organic-matter

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containing waste, under conditions of absence of oxidizing agent, as the result of which a solid charcoal-like residue is formed as well as a pyrolysis gas, is containing highly boiling resin-like compounds [3]. The possibility of using carbon sorbents to firmly bind pollutants in the soil is largely facilitated by their extremely high stability in the soil. Thus, the half-period of biochar mineralization (T50) reaches 100 years or more [4]. Carbon sorbents (activated carbon, biochar, soot, etc.) can firmly bind various pollutants in the soil due to their great sorption capacity [5]. The specific pore surface area of carbon sorbents is large and varies in the range of 200-2000 m²/g, sorption capacity is 200-980 g/kg [6]. Sorption of some pollutants by sorbent particle surface is thermodynamically more advantageous than their transition into solution (Mott and Weber 1992). Adsorption, on the other hand, is a more accepted and widely used remediation technique for dye and heavy metal removal due to its economic feasibility and simplicity of operation in addition to its relative environmental friendliness [7].

The biochar is chemically inert and stable, demonstrates a high absorption capacity and huge porosity [8]. Due to these characteristics it is widely known as an effective sorbent for contaminated soil remediation. A considerable attention of researchers is given to the change in the biochar properties depending on the pyrolysis temperature regime [9]. A wide variety of materials is used to produce biochar, which also leads to differences in the properties and qualities of the resulting sorbents [10, 3, 11, 12, 13]. It was shown that the application of rice straw and bamboo wood biochar to soils (sandy loam paddy soil) also significantly reduced the concentration of Cd, Cu, Pb, Zn mobile forms in the soil [14]. Despite many studies conducted in recent years in both laboratory and field conditions [15, 16], the influence of high ash sorbents on the soil is still poorly understood due to the lack of sufficient data on their long-term effect on soil properties. Due to differences in carbon sorbent properties the outcomes of their introduction into the soil are not always unambiguously positive [17,18]. In general, studies on the effect of carbon sorbents were carried out on poor sandy and acidic soils. However, the study of carbon sorbents properties and the effectiveness of their application to chernozems are still of current interest.

The purpose of the work is to study the effect of biochar on the mobility of Pb in Haplic Chernozem and the availability of metal to plants.

2 Methods

2.1 Model experiment

The present study was carried out under conditions of model experiment. The samples of the upper layer (0–20 cm) of a Haplic Chernozem were collected on the virgin area located far from possible sources of pollution. The composition of the exchangeable bases along with a significant content of organic matter, the presence of highly dispersed micellar forms of carbonates and loess-like nature of parent rocks led to the favorable physical properties of Haplic Chernozem: water and air permeability, loose composition and high moisture capacity. The physicochemical properties of the soil sample under study were pH - 7.3; 48.1% of physical clay (particles with a diameter of <0.01 mm), 28.6% of sludge (particles with a diameter of <0.001 mm), the content of organic carbon is 3.7%; carbonates - 0.1%; CEC soil - 36 cm (+) ∙ kg⁻¹. Two kilograms of soil were sifted through a sieve with a mesh diameter of 2 mm and placed into vessels with a closed drainage system. Then aqueous solutions of Pb nitrates at rates of 5 and 10 maximum permissible concentrations (32 mg/kg) were separately added into vessels with soil. The doses of metal (160 mg/kg and 320 mg/kg) corresponded to the level of soil
pollution in the impact zones of Rostov region by these metal [19]. Two month later biochar was added to the contaminated soil. Incubation took place at a temperature of + 20-22°C under natural light. The model experiment followed the scheme - 1) control (soil without pollution); 2) Pb 160 (metal at a dose of 160 mg/kg was added to the soil); 3) Pb 320; 4) Pb 160 + 2.5% biochar; 5) Pb 160 + 5% biochar; 6) Pb 320 + 2.5% biochar; 9) Pb 320+ 5% biochar. Each treatment was prepared in triplicate.

The features of topography (surface) and morphology (microgeometry) of the sorbents under study were analyzed using scanning electron microscopy (Carl Zeiss EVO-40 XVP SEM microscope). The biochar had a distinct layered structure in the form of flakes of various shapes, layered on top of each other (Fig. 1).

![Fig. 1. Microstructure of biochar](image)

### 2.2 Determination of lead loosely bound forms

To determining of loosely bound compounds of Pb parallel extraction was used [20]. The metal compounds extracted with the 1 N CH₃COONH₄ are classified as exchangeable. The 1% EDTA in 1 N CH₃COONH₄ presumably extracts exchangeable heavy metal and those bound in the organometallic complexes; hence, the difference between the metal contents in the 1% EDTA in 1 N CH₃COONH₄ and 1 N CH₃COONH₄ extracts should characterize the content of metal in complexes with the soil organic matter. The 1N HCl extracts specifically adsorbed metal together with exchangeable metal. A considerable part of the specifically adsorbed heavy metal is relatively loosely fixed by iron, aluminum, and manganese oxides and hydroxides and by carbonates. The contents of specifically adsorbed heavy metal compounds are calculated as the differences between their amounts extracted with 1N HCl and 1 N CH₃COONH₄.

The metal content in the extracts was determined using AAS. The total content of Pb and Zn in the soil was determined by the X-ray fluorescence method using X-ray spectrometer "SPECTROSCAN MAX-GV".

### 2.3 Statistical analysis

All laboratory tests were performed in triplicate. The experimental data (means and standard deviations) were statistically processed using statistical functions of STATISTICA 10.0 software. Results were considered statistically significant at p≤0.05.

### 3 Results and Discussion

The total content of Pb is in the studied uncontaminated Haplic Chernozem, which corresponds to the background levels [19] (Table 1).
The content of exchangeable compounds Pb in Haplic Chernozem does not exceed 5% of the total content (Table 1, Fig. 2). When Pb compounds are introduced into the soil the total content of metal increases, as well as the content of exchangeable, complex and specifically sorbed forms. With an increase in pollution, the content of loosely bound compounds increases.

Table 1 - Total content and concentration of exchangeable, complex and specifically sorbed forms of Pb in the soil of the model experiment, mg/kg

| Treatment, mg/kg | Loosely bound compounds | Total content |
|-----------------|-------------------------|---------------|
|                 | exchangeable | complex | specifically sorbed |               |
| Control         | 0.3±0.1*     | 0.8±0.1  | 1.4±0.2             | 28.0±1.1      |
| Pb160           | 9.0±0.7      | 10.8±1.1 | 18.0±1.8            | 180.0±17.0    |
| Pb 160+2.5% biochar | 1.8±0.2     | 5.5±0.4  | 10.9±1.0            | 182.0±19.0    |
| Pb 160+5% biochar | 0.5±0.1      | 3.6±0.5  | 8.9±0.8             | 178.0±16.0    |
| Pb 320          | 26.6±2.1     | 33.2±3.0 | 53.1±4.4            | 332.0±30.0    |
| Pb 320+2.5% biochar | 13.2±1.3    | 19.8±1.8 | 29.7±2.1            | 330.0±35.0    |
| Pb 320+5% biochar | 1.7±0.2      | 3.4±0.5  | 16.9±1.8            | 338.0±32.0    |
|                 | MPC 6.0 [21] |         |                      | MPC 32.0 [21] |

*±standard deviation

In both an uncontaminated sample and contaminated ones loosely bound metal compounds are mainly represented by their specifically sorbed forms (Fig. 2). With pollution the relative content of the most mobile forms increases - exchangeable forms (by 8–13%) and complex forms (by 7–14%).

The noticeable changes in the content and composition of loosely bound forms occurred when carbon sorbents were introduced into metal-contaminated soil. When a biochar was introduced, there was a slight decrease in the mobility of Pb: 4–11% for exchangeable forms, 4–13% for complex forms, 5–12% specifically sorbed forms (Fig. 2).

The decrease in the metal mobility increased with an increase in the dose of biochar (Table 1, Fig. 2). In the variants contaminated with 320 mg/kg of metal the content of the metal-exchangeable forms did not exceed the MPC for the soil at a sorbent dose of 2.5%. This
indicates the ability of applied sorbents to firmly bind metal on their surface and reduce their mobility in contaminated soils. The greatest decrease in the mobility of metal was observed at a 320 mg/kg dose of metal nitrate with 5% biochar. Sorbent showed high efficiency in contaminated soils.

In assessing the mobility of metal in soil an informative indicator is the relative content of exchangeable, complex, and specifically sorbed forms of the metal in the group of loosely bound compounds. In uncontaminated soil the distribution of Pb forms in the group of loosely bound compounds has been established as specifically sorbed> complex> exchangeable (Table 2).

Table 2 - The relative content of Pb in the group of loosely bound compounds, % of the total content

| Treatment, mg/kg | % from loosely bound compounds | exchangeable | complex | specifically sorbed |
|-----------------|-------------------------------|-------------|--------|-------------------|
| Control         |                               | 11          | 33     | 56                |
| Pb160           |                               | 24          | 29     | 48                |
| Pb 160+2.5% biochar |                             | 10          | 30     | 60                |
| Pb 160+5% biochar |                             | 4           | 27     | 68                |
| Pb320           |                               | 24          | 29     | 47                |
| Pb 320+2.5% biochar |                             | 21          | 32     | 47                |
| Pb 320+5% biochar |                             | 8           | 15     | 77                |

Loosely bound Pb compounds have been mainly represented by their specifically sorbed forms both in an uncontaminated and in contaminated samples (Table 2). It should be noted that when soil is contaminated, the content of specifically sorbed metal forms decreases (up to 47-48% of the group of loosely bound compounds), but the content of more mobile forms — exchangeable and complex — increase. Moreover, the distribution within the group reveals the nature of the metal itself, complex forms bound with organic matter of the soil (up to 33%) are characteristic of Pb (Table 2). A number of researchers noted that Pb was more prone to interact with soil organic matter [22,23].

The use of sorbents on contaminated soil restores the ratio of metal compounds in the group of loosely bound compounds to the level characteristic of uncontaminated soil. The most effective was the use of a dose of 5%, for both biochar applications (Table, 2).

4 Conclusions

The content of Pb in uncontaminated soil does not exceed permissible MPC values and the background level for Haplic Chernozems. The content of exchangeable Pb compounds is not more than 5% of the total content. In the group of loosely bound compounds, the distribution of Pb is as follows: specifically sorbed> complex> exchangeable forms.

Under soil contamination, an increase in the content of exchangeable, complex, and specifically sorbed forms of the metal compounds has been observed. Pb has been active in forming organic complexes and specifically sorbed forms.

Due to the highly porous structure of carbon sorbents, their application to contaminated soil resulted in the immobilization of mobile metal compounds. In a year of vegetation experiment, a dose of 2.5% biochar when soil being contaminated with 160 mg/kg of metal has demonstrated a high efficiency, as well as a dose of 5% biochar in the variant with 320 mg/kg of metal.

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References

1. T. M. Minkina, G. V. Motusova, S. S. Mandzhieva, and O. G. Nazarenko, J. Geochem. Explor., 123, 33–40 (2012)
2. O. S. Bezuglova, S. N. Gorbov, S. A. Tischenko, A. E. Shimko, J. Geochem. Explor. 184, 232–238 (2018)
3. D. Mohan, C. U. Pittman Jr., and P. H. Steele, Energy Fuels, 20 (3), 848-889, (2006)
4. A. R. Zimmerman, and L. Ouyang, Soil Biol. Biochem., 130, 105-112 (2019)
5. F. R. Oliveira, A. K. Patel, D. P. Jaisi, S. Adhikari, H. Lu, S. K. and Khanal, Biosour. Technol., 246, 110–122 (2017)
6. G. K. Vasilyeva, E. R. Strijakova, and P. J. Shea, in Viable methods of soil and water pollution monitoring, protection and remediation edited by I. Twardowska, H.E. Allen and M. H. Haggbloem (Springer, Netherlands, Neth., 2006), pp. 309-322.
7. M. Grassi, G. Kaykioglu, V. Belgirno, and G. Lofrano, in Emerging compounds removal from wastewater edited by G. Lofrano (Springer, Netherlands, Neth., 2012). pp. 15–37
8. S. Kishimoto, and G. Sugiura, Int. Achiev. Future. 5, 12-23 (1985)
9. M. I. Al-Wabel, A. Al-Omran, A. H. El-Naggar, M. Nadeem, and A. R. A. Usman, Biosour. Technol., 131, 374-379 (2013)
10. M. Ahmad, A. U. Rajapaksha, J. E., Lim, M. Zhang, N. Bolan, D., Mohan, M. Vithanage, S. S. Lee, and Y. S. Ok, Chemosphere. 125, 70–85 (2015)
11. X. Xu, Y. Zhao, J. Sima, L. Zhao, O. Mašek, and X. Cao, Biosour. Technol. 241, 887–899 (2017)
12. J. Kumpiene, J. Antelo, E. Brännvall, I. Carabante, K. Ek, M. Komárek, C. Söderberg, L. Wärell, Appl. Geochem. 100, 335–351 (2019)
13. K. Lu, X. Yang, G. Gielen, N. Bolan, Y. S. Ok, N.K. Niazi, S. Xu, G. Yuan, X. Chen, X. Zhang, D. Liu, Z. Song, X. Liu, and H. Wang, J. Environ. Manage. 186 (2), 285-292 (2017)
14. A.P. Puga, C.A. Abreu, L.C.A. Melo, and L. Beesley, J. Environ. Manage., 159, 86-93 (2015)
15. D. O’Connor, T. Peng, G. Li, S. Wang, L. Duan, J. Mulder, G. Cornelissen, Z. Cheng, S. Yang, and D. Hou, Sci. Total Environ., 621, 819-826 (2018)
16. J. E. Amonette, and S. Jospeh, in Biochar for environmental management science and technology edited by J. Lehmann, S. Joseph (Earthscan, London, 2009), pp. 241-250
17. Rizhiya, E.Y., Buchkina, N.P., Mukhina, I.M., Belinets, A.S., Balashov, E.V. Eurasian Soil Sci. 48 (2), 192-200 (2015)
18. T.M. Minkina, D.G. Nevidomskaya, T.N. Pol’shina, Y.A. Fedorov, S.S. Mandzhieva, V.A. Chaplygin, T.V. Bauer, and M.V. Burachevskaya, J. Soils Sediments. 17 (5), 1474-1491 (2017)
19. T.M. Minkina, S.S. Mandzhieva, M.V. Burachevskaya, T.V. Bauer, and S.N. Sushkova, MethodsX, 5, 217-226. (2018)
20. T.M. Minkina, S.S. Mandzhieva, M.V. Burachevskaya, T.V. Bauer, and S.N. Sushkova, MethodsX, 5, 217-226. (2018)
21. GN 2.1.7.2042-06. Maximum permissible concentrations (MPC) of chemicals in the soil: Hygienic standards (Rospotrebnadzor, Moscow, 2006).
22. A. Piccolo, and F.J. Stevenson, Geoderma, 27, 195-208 (1982)
23. A. Kabata-Pendias, Trace elements in soils and plants. 4th ed. (CRC Press, Taylor and Francis Group, NW, 2011)