Remediation of degraded soils: effect of organic additives on soil properties and heavy metals' bioavailability

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Abstract. In a three-month experiment influence of different organic amendments (coal humate, peat-gel, biochar) in comparison with mineral ameliorants (NPK and CaCO₃) on chemical and physical properties of soils at different stages of degradation has been shown. Objects of the research were abrazem and podzol soils of technogenic barrens near Monchegorsk city, Murmansk region (Russia). Festuca rubra was used as a test-culture. According to the obtained data, we can conclude that organic applicants may be suitable for remediation of soils, contaminated by heavy metals. Applicants, selected for the experiment, unequally affected the soil properties and the test-culture growth. For the most disturbed and contaminated soils – abrazem – we suggest coal humate and calcium carbonate as the most promising additives for both toxicants' immobilization and preventing bioaccumulation. Biochar and peat-gel in the tested concentration showed a more expressed positive effect on podzol soils with a lower level of contamination. In both soils, abrazem and podzol, biochar favors to the test-culture growth more, than other amendments. The potential advantage of used organic amendments, coal humate and biochar, in contrast to ameliorants is their ability to improve the physical soil properties.

1. Introduction
Pollution of the biosphere by heavy metals (HM) is one of the most crucial problems of human negative impact on the environment [1-2]. Non-ferrous metallurgy in the Murmansk region, represented by the factory complexes of the Kola Mining and Metallurgical Company – “Pechenganickel” and “Severonickel” – is one of the largest polluters in the Northern Hemisphere [3-5]. As a result of long-term exposure to gas and dust emissions of sulfur dioxide and heavy metals, mainly Ni and Cu, the territories surrounding the smelters had been degraded and transformed into technogenic barrens – vast heavily disturbed areas [5]. Negative changes in soil conditions and damage and destruction of vegetation determine the need of remediation.

The aim of this study was to evaluate in a model experiment the influence of the most perspective organic additives and ameliorants on the properties of soils of technogenic barrens at different stages of degradation in the vicinity of the “Severonickel” metallurgical complex. For this purpose, the physical and chemical properties of soils and the state of the test-culture after the experiment were estimated.
2. Objects and methods

2.1. The Object

Soil samples were collected from sites situated in 2 and 5 km from the industrial complex near Monchegorsk, Murmansk region. The first research site is 2 km from the plant (67°56.457’ N, 32°50.074’ E), soils are represented by Al-Fe-humus loamy-sand abrazem formed on moraine parent rock (eroded Entic Podzol (Phytotoxic) [6]), the profile horizons are as follows: outcropped due to erosion development BF-horizon, transitive to parent rock BC-horizon and C-horizon – parent rock. The second research site is situated 5 km from the plant (67°57.901’ N, 32°50.373’ E), soils are represented by chemically contaminated loamy-sand Al-Fe-podzol formed on moraine parent rock (eroded Podzol (Phytotoxic) [6]), the profile is as follows: remnants of litter O mixed with eroded thin intermittent eluvial horizon, mostly outcropped BF, BC-horizon transitive to parent rock and C-horizon – parent rock. Experiment was provided with samples of BF-horizon of abrazem and podzol, as most representative for surface layer (table 1).

Table 1. Properties of soils in technogenic barrens: pH$_{10}$ – pH of water extract, H – total acidity (mmol(+)/kg), TC – total carbon (%), total and water-soluble HM – Ni and Cu, mg/kg (mean and confidence interval, $n=4$, $p<0.05$).

| Soil    | Horizon | pH$_{10}$ | H mmol(+)/kg | TC % | Ni mg/kg | Cu mg/kg |
|---------|---------|-----------|--------------|------|----------|----------|
| Abrazem | BF      | 4.9±0.8   | 3.4±0.3      | 1.4±0.1 | 271±16   | 347±19   |
|         |         |           |              |       | Water soluble forms  |          |
|         |         |           |              |       | 8.1±1.5 | 28.9±4.9 |
| Podzol  | BF      | 5.6±0.4   | 3.4±0.3      | 1.0±0.1 | 86±6     | 143±10   |
|         |         |           |              |       | Water soluble forms  |          |
|         |         |           |              |       | 5.0±0.4 | 6.2±0.8  |

2.2. Additives

According to the results of our previous works [7], organic amendments – commercial products: coal humate “Extra” – CH (K-Na salts of coal alkaline extraction), peat-gel “Humic Land” – PG (product of cavitation of peat raw material in water), and biochar “BioSannie” – BC (product of wood pyrolysis) were applied equally in amount 0.5% of carbon to soil mass. For reinforcement of potential positive effect, we introduced variants with addition of mycorrhizae fungi (Glomus sp. “BioSannie” – M). We compared the effect of these applicants on soil properties and the condition of Festuca rubra as a test-culture with the effect of widely used for remediation purposes liming agent [5], [8] – calcium carbonate (L). Variants of the experiment with abrazem and podzol in which only NPK-fertilizer was added we considered as control variants (K*).

2.3. Methods

The experiment was conducted in controlled conditions in climate chamber Binder with lightning imitating the polar day, and temperature and humidity according to summer season in Monchegorsk city region, data was collected from web-recourse “Raspisanie pogody” (https://rp5.ru). For the experiment we used previously collected mixed samples of BF-horizons of abrazem and podzol, which were transported to the laboratory, then air-dried and passed through the 2 mm sieve. In each of 28 plastic vessels, 56 vessels in total, representing 7 variants of the experiment in 4 replicates, 350 g of abrazem
or podzol soil was placed. The pre-incubation period after the introduction of organic additives was 30 days, the period of experiment was 90 days. Throughout the time, soil moisture was maintained at 60% of water holding capacity. Festuca rubra was sowed as a test-culture after pre-incubation based on the seeding rate of 65 kg/ha.

Here we provide the data on phytomass of sprouts and roots, total carbon and nitrogen content in soil (by dry combustion method on CHNS-analyzer Thermo Fisher Flash-2000), content of Ni and Cu in sprouts and roots and their water-soluble forms in soils (obtained by inductively coupled plasma mass-spectrometry, ICP MS 7500a, Agilent), pH of water extract, and soil drying kinetics [9] obtained at moisture analyzer MS-70, A&D at the end of experiment. Statistical data analysis was performed in RStudio.

3. Results and discussion

3.1. Soil chemical properties

In the control variants, abrazem and podzol soils were acidic; the average pH values of water extract were 4.8 and 5.6, respectively. Treatment of soils led to significant changes: all amendments favored to the pH increase, the maximum values close to neutral were observed when coal humate and CaCO$_3$ were added (figure 1).

Initially, both abrazem and podzol soils were poor in organic matter, the total organic carbon content in the control variants was around 1.4% and 1.0% respectively. Application of all amendments, apart from CaCO$_3$, increased the total carbon content by 0.5% on average, which corresponds to the dosage had been considered in the experiment plan. Nitrogen content was not changed significantly and was around 0.07-0.08% for all variants, C/N ratio was in range from 15 to 20, which corresponds to low nitrogen saturation of organic matter in the whole diapason.

3.2. Heavy metals content in soils and plants

The control variants’ soils were characterized by high content of water-soluble Ni (8 and 5 mg/kg) and Cu (28 and 6 mg/kg) in abrazem and podzol (figure 2).
Comparing to the controls, water-soluble Ni and Cu in other variants of the experiment were immobilized significantly. The stabilization effect decreased in the rank of coal humate ≥ CaCO$_3$ > biochar > peat-gel in abrazem; in podzol stabilization effect of biochar and peat gel was expressed more.

The test-culture grew poorly in the control variants of abrazem and podzol, the root system had not been developed without additional treatment. In the series of abrazem soil test-culture grew relatively equally among the variants with coal humate, CaCO$_3$ and biochar – the total phytomass at the end of the experiment was 40-50 g/m$^2$ (both roots and sprouts), which is 10 times larger compare to control. The effectiveness of peat-gel is 2 times less comparing to other additives. For podzol, the influence of additives is distributed slightly differently: biochar and CaCO$_3$ were most effective for the test-culture growth – the total phytomass was in the range from 80 to 100 g/m$^2$, in other variants it was from 45 to 70 g/m$^2$. This noticeable difference allows us to suggest the role of sorption centers in stabilization mechanism as potentially leading.

3.3 Biological availability of heavy metals
The accumulation of significant amounts of HM by the test-culture in the control variants of abrazem and podzol may be caused by the damage to the root system in acidic contaminated soils (figure 3). According to the distribution of HM in the sprouts considering the development of the test-culture phytomass we may assume that coal-humate, CaCO$_3$ and biochar have better protection properties compare to peat-gel. Biochar demonstrates a low ability to prevent the migration of HM into the sprouts of plants particularly in case of abrazem soil, as well as the low stabilization of water-soluble Ni and Cu compounds. Nevertheless, biochar favors to maximum phytomass growth and lowest content of dissolved nitrogen after the experiment (data is not shown), which allows to make a suggestion that biochar can improve uptake of elements (nutrients as well as toxicants).

Figure 2. Test-culture phytomass (means and 95% confidence intervals) vs water-soluble Ni and Cu in soils.
3.4. Drying kinetics of soils

In the soil cover of technogenic barrens, abrazems with outcropped BF-horizon depleted in organic matter and clay-fraction are predominant. The combination of soil and climate factors along with negative impact of industrial activity determines development of erosion processes, intensified, specifically by the light sandy texture, and, consequently, by the high filtration and low water retention abilities.

For evaluation of possible influence of amendments on physical soil properties we estimated soil drying kinetics – DK (figure 4). We chose this method as one of the fastest for possible evaluation of soil water-retention properties. Here we provide the data about changes of soil sample mass, expressed in percent of moisture content (dW), through the time, expressed in minutes (dT), at constant heating at 60° along with changes of soil sample temperature (t°), expressed in Celsius degrees, to soil moisture content (W, %).

In this work we eliminate one general feature for characterization of DK curves: area of constant drying rate as a difference between moisture points, which are corresponded to the start (W1) and to the ending (W2) of the area of constant drying rate (table 2). By constant drying rate we understand the certain part of dW/dT curve at which the rate of moisture loss remains unchanging as well as the sample temperature. The moisture values W1 and W2 were determined by inflection points of dW/dT curve. Here we need to disclose, that there is also a way to interpret obtained curves by description of changes in sample temperature (t° curve), but we have chosen dW/dT curve as most informative in this very case.

DKs of soils in the control, peat-gel and CaCO₃ variants generally have the similar form with explicitly expressed peak of rising drying rate, area of constant drying rate corresponds to moisture difference W1-W2 equal to 13-16% at constant sample temperature ~ 44-45°. The control soil had higher drying rate in general comparing to the variants with additives. DKs of soil samples with added coal humate and biochar have similar tendencies to the widening of diapason of constant drying rate on diapason from W1=13% to W2=35% of moisture at constant sample temperature ~ 44-45°.
**Figure 4.** Drying kinetics of soils after the experiment: dependencies of 1) rate of sample moisture loss (dW/dT, %/min – red line) and 2) change of sample temperature (t, °C – blue line) from sample moisture (W, %).

**Table 2.** Key points of sample moisture content of drying kinetics (W1, W2 and W1-W2) at constant drying rate.

| Applicant | W1(dW/dT) | W2(dW/dT) | W1-W2 |
|-----------|-----------|-----------|-------|
| K         | 16.5 (0.4)| 32 (0.4)  | 15.5  |
| L         | 13.4 (0.32)| 26.9 (0.32)| 13.5  |
| PG        | 14.3 (0.33)| 29.1 (0.33)| 14.8  |
| HS        | 14.1 (0.28)| 35.0 (0.28)| 20.9  |
| BC        | 12.7 (0.34)| 35 (0.34)  | 22.3  |

According to these observed features we can suggest improvement of water-retention ability of soils after application of coal humate and biochar, which can potentially lead to the formation of micro- and macrostructure through active sorption centers. This analysis can prove an important idea that the quality, and not the quantity, of the organic amendment is crucial both for HM behavior and for the soil properties itself.

**4. Conclusions**

Organic amendments may be recommended for remediation of contaminated soils because for enrichment of soils by carbon, decreasing of acidity, promotion of heavy metals’ stabilization, nutrients uptake and test-culture growing. Potential advantage of organic amendments – coal humate and biochar – comparing to mineral ameliorants is their potential positive influence on physical soil properties which may be crucial in harsh climatic conditions and water and wind erosion. These features in combination with the resumption of fresh plant litter may favor to enhanced restoration of ecosystem functions of soils due to renewal of humus matrix and improvement of soil hydrological properties.
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