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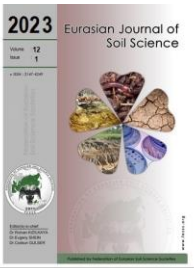

Role of sorbents in early growth of barley under copper and benzo(a)pyrene contaminated soils

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Abstract

In modern economic and industrial realities, agricultural lands are often located next to industrial areas, which leads to soil contamination and, as a result, agricultural products with pollutants. Pollution of soils and plants by several pollutants of various nature has acquired huge proportions. There is a threat of migration of dangerous ecotoxicants, including heavy metals and benz[a]pyrene, one of the main persistent compounds, a marker of PAH soil contamination, along trophic chains that may be dangerous to public health. This study examines the use of various types of mineral sorbents (Tripoli, Brown coal, Diatomite) and mineral sorbents (Biochar, Granular activated coal) to reduce the toxic effects of pollutants on the sources of anthropogenic emissions of heavy metals and polycyclic aromatic hydrocarbons adjacent to the sources. Using scanning electron microscopy, it was found that the sorbents have a high specific surface area. With the help of phytotesting in combined contaminated soils, the optimal dose of sorbent administration was determined at the level of 1% and 2% for various pollution variants. In addition, the analyzed sorbents are ordered by the effect of reducing the phytotoxicity of combined soil pollution. It was found that the introduction of sorbents into contaminated soil contributed to an increase in the morphometric parameters of the test culture - barley (Hordeum sativum distichum), which confirms the effectiveness of the sorption remediation of jointly contaminated soils with heavy metals and benz(a)pyrene.

Keywords: Heavy metals, polycyclic aromatic hydrocarbons, remediation, sorbents, biochar, germination energy.

Introduction

Heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) are among the most hazardous soil pollutants. The combined pollution of soils by HMs and PAHs constitutes a significant threat to the environment and human health. In the last decades, among HMs, copper (Cu) got a great deal of environmental and toxicological concern (Ben-Ali et al., 2017; Sushkova et al., 2017; Li et al., 2020). Copper compounds are among the most widely distributed contaminants; nonetheless, copper is a trace element that is required by plants to function properly. Now coming to PAHs, benzo(a)pyrene (BaP) is one of the most harmful members of this class of chemicals. BaP is subject to statutory control around the world and is a critical indication of contamination of soil with organic pollutants (Skłodowski et al., 2006; Abdel-Shafy and Mansour, 2016; Eeshwarasinghe et al., 2019). There is no universal method for restoring soils contaminated with heavy metals and polycyclic aromatic hydrocarbons. The effectiveness of the methods used depends on the soil properties,

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the degree of adaptation, and the stability of the plants growing on it. The main approach for the restoration of combined contaminated soils lies mainly in either reducing the content of pollutants to a safe level or stabilizing and immobilizing pollutants to reduce their bioavailability.

Hence, the introduction of natural and artificial sorbents can be used as an independent method of soil remediation. While this soil reclamation method is economic and straightforward in its application, it is exceptionally effective in both the selective removal of contaminants and the restoration of the soil's natural condition. For soil remediation, the common sorbents based on natural resources and mineral raw materials (diatomites, tripoli), or obtained because of pyrolysis of biomass (activated carbon, biochar) (Ding and Luo, 2005; Gutiérrez-Ginés et al., 2014; Smirnov and Konstantinov, 2016; Smirnov et al., 2017; Singh et al., 2017; Xu et al., 2021). The current work is designed, and the scientific novelty of this work is in the choice of sorbents and the doses of their introduction into soils under the combined contamination of Cu and BaP has been substantiated. This work aims to study the transformation of Cu and BaP in the soil, as well as the effect of combined pollution on the growth and development of barley *(Hordeum sativum* distichum*).*

Material and Methods

The experiment was carried out in a climate chamber at the Academy of Biology and Biotechnology of the Southern Federal University. The soil (0-20 cm) of the specially protected natural area "Persianovsky reserved steppe", which is represented by Haplic chernozem, was used. Vegetative vessels with a closed drainage system with a volume of 3 l were loaded with soil sifted through a 2 mm sieve. The mass of soil in the vessels was 3 kg. Added an aqueous solution $Cu(CH_3COO)_3$ (275 and 550 mg/kg, which corresponds to 5 and 10 maximum permissible concentration (MPC) of the metal, and BaP solution in acetonitrile (200 and 400 mg/kg BaP), which corresponds to 10 and 20 MPC of polyarene. The selection of pollutant doses is carried out based on the degree of soil destruction in the Rostov region (Minkina et al., 2009; Sushkova et al., 2016; Bauer et al., 2020).

After 30 days from the moment the pollutants were introduced into the soil, sorbents were introduced according to the experimental scheme: 1) Control; 2) Control + 0.5% sorbent; 3) Control + 1% sorbent; 4) Control + 1% sorbent; 5) Control + 2% sorbent; 6) Control + 2.5% sorbent; 7) 10 MPC BaP + 5 MPC Cu (Background 1); 8) Background 1 + 0.5% sorbent; 9) Background 1 + 1% sorbent; 10) Background 1 + 1.5% sorbent; 11) Background 1 + 2% sorbent; 12) Background 1 + 2.5% sorbent; 13) 20 MPC BaP + 10 MPC Cu (Background 2); 14) Background 2 + 0.5% sorbent; 15) Background 2 + 1% sorbent; 16) Background 2 + 1.5% sorbent; 17) Background 2 + 2% sorbent; 18) Background 2 + 2.5% sorbent (Figure 1).

Figure 1. Growing experiment with spring barley (*Hordeum sativum distichum*)

The sorbents used were granular activated carbon (GAC), biochar produced at the Academy of Biology and Biotechnology of the Southern Federal University, diatomite from the Kamyshlov deposit, brown coal, and tripolite from Razrer Brusyan. The doses of sorbents were selected based on previous studies (Bolan et al., 2014; Minkina et al., 2016; Pinskii et al., 2018; Gholizadeh and Hu, 2021). In total, there were 53 variants in the experiment in 3-fold repetition. Soil incubation with sorbents lasted 30 days, after which a test culture was sown - two-row barley of the Ratnik variety (Hordeum sativum distichum) in the amount of 20 pieces per 3-liter pot. Plants were grown for 45 days - until the booting phase. Based on the previously obtained results of photo-testing, the choice of sorbents and their application rates were substantiated

Scanning electron microscopy (Carl Zeiss EVO-40 XVP microscope) was used to analyze the topography and morphology (microgeometry) of carbon sorbent fragments (Figure 2) (Bain et al., 2010; Rajput et al., 2021a,b). GAU consists of cylindrical granules 0.5-3 mm in size. Microscopic examination showed that it is heterogeneous in its dispersed and morphological composition and contains both rhombohedral fragments up to 20-25 microns in length and particles several hundred microns in size (Figure 2). Large particles are sieve-like structures with through cylindrical holes with a diameter of approximately 10-20 microns and 1-2 microns. These formations in their shape and structure repeat the capillary structure of the wood from which they were obtained as a result of incomplete combustion of the feedstock. The biochar sample is a coarse-grained, highly porous material with a large surface area. The size and structure of the particles is determined by the characteristics of the feedstock.

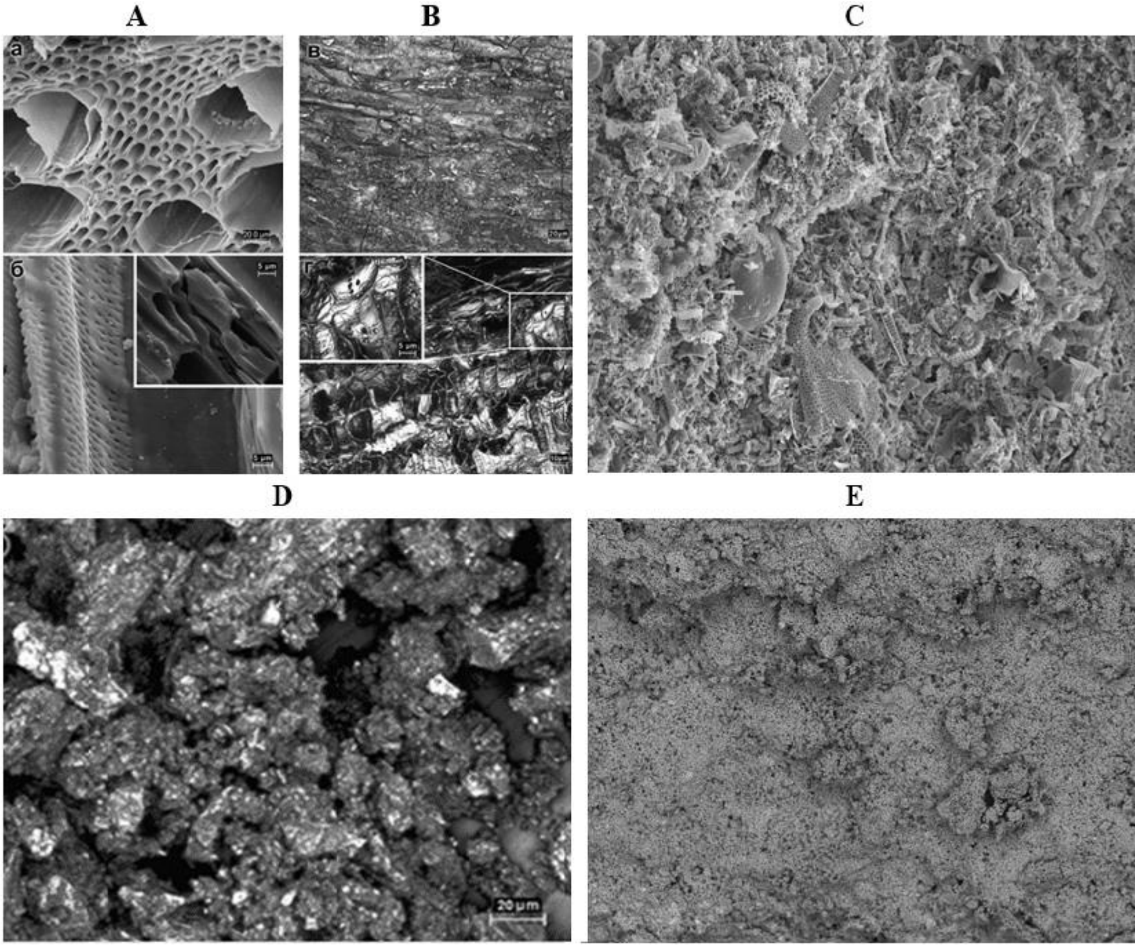

Figure 2. Images of the surface of the sorbents were made using scanning electron microscopy, microphotograph of A-granulated activated carbon, B – biochar from sunflower husk, C - surface of diatomite from the Kamyshlovskoye deposit, D - brown coal, E - surface of Brusyan-Logacharsky tripolite

Microscopic examination showed that, as in the GAC sample, biochar particles have an anisotropic structure of pores, which are long cylindrical cavities located along the longitudinal axis of sunflower husk particles (Minkina et al., 2013; Chen et al., 2020; Wang et al., 2020; Cheng et al., 2021). On the sagittal view (Figure 3), a developed surface is visible with many cracks and slit-like pores 1-2 microns wide. A segmental cleavage contains many rounded pores 10–30 µm in size, as well as pores 0.5–1 µm in size (Table 1). A brown coal sample consists of particles 0.1-1 mm in size. Microscopic examination showed the homogeneity of the sample. Most of the material has a loose texture and granular structure, irregularly shaped pores (Figure 2). The particles predominantly have an isomorphic, close to rounded shape. The total mass of the samples can be divided into the skeletal part and the finely dispersed component. Dust consists of both aggregates and individual particles (Figure 2). Aggregates are formed not only from small particles (<5 µm), they include large mineral grains, on the surface of which smaller particles adhere. The aggregates have sizes from tens of micrometers to 1 mm. Microaggregates of size from 20 to 70 µm prevail.

Table 1. Physical characteristics of the private surface and porosity of sorbents

Sorbent brand	Feedstock	Sorbent form	Granule size (mm)	Specific surface area (m2/g)	Pore volume (cm3/g)			
					General	Macro >500 nм	Mezo2-500 nм	Micro >2 nм
GAU	Wood	Granules	0,5-3	950	0,98	0,4	0,19	0,39
Biochar	Husk	Records	1-5	640	0,81	0,14	0,04	0,63
Brown coal	Brown coal	Powder	0,1-1	451	0,17	0,03	0,05	0,09

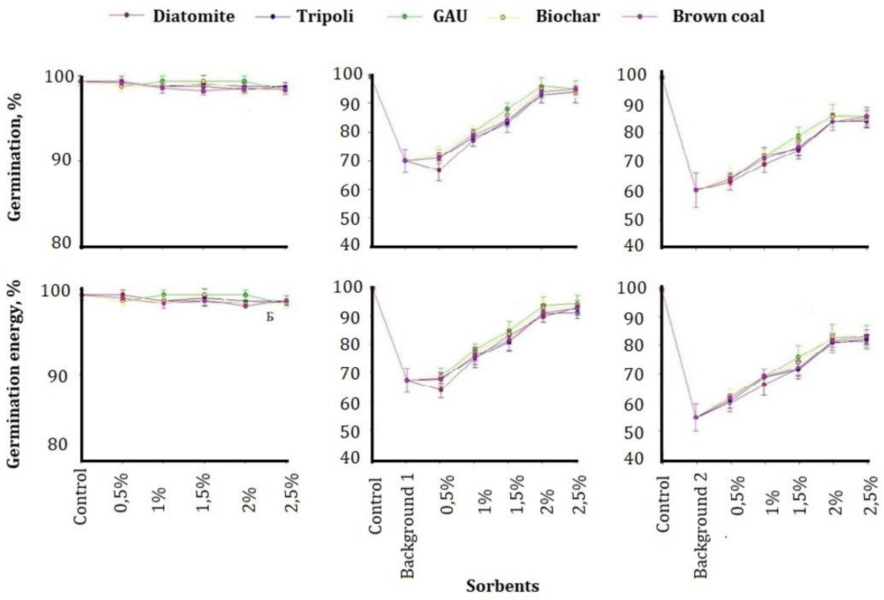

Figure 3. Germination and germination energy of the test culture of *Hordeum sativum distichum* in a model laboratory experiment

The Kamyshlovskoye deposit of diatomites is located on the northeastern outskirts of the city of Kamyshlov, Sverdlovsk region, 2 km from the Kamyshlov railway station, and is a large sheet-like deposit of diatomites. The thickness of diatomites within the deposit does not change significantly, except for the eastern part of the deposit, where the thickness of the deposit increases significantly. Within the boundaries of the explored area, the deposit is composed of diatomites of the Irbit Formation and opoks of the Serov Formation. Diatomites over the entire area are overlain by Pliocene-Quaternary sediments with a maximum thickness of 6 m or more. The diatom complex in the rocks of the productive strata of the Kamyshlovskoye deposit is represented by Coscinodiscus payeri (lower part of the Lower Eocene) - large isometric diatoms with dense and thick valve walls predominate (Figure 2).

Diatomites (mainly from Eastern Europe) with a relatively low SiO2 content of about 50% are effective as soil additives, including pollutant immobilization. At the same time, in the diatomites of the Trans-Urals, the average content of SiO_2, as a rule, ranges from 75 to 80%. In addition, there are numerous, relatively simple and cheap methods for their mechanical, thermal and chemical treatment, which make it possible to reduce the content of the clay component and bring the content of SiO_2 to 95% or more, as well as increase the specific surface area. Chemical properties, granulometric and mineral composition of the used sorbents are presented in Table 1 (Figure 2) (Fedorenko et al., 2021).

Methods

The toxic effect of pollutants is evaluated by such indicators as germination energy, germination, shoot length, root length. Germination energy was observed on the third day. Then, on the seventh day, germination was determined. At the end of the experiment, the experimental plants were collected and their morphometric characteristics were determined: the length of the shoots and the length of the roots. Next, the toxicity index was calculated for each factor in order to determine the toxicity of the studied soil before and after pollution. The toxicity index of the evaluated factor for each biological test object was determined by the formula (Kotyak, 2019; Kotyak et al., 2019): TF = TF0 /TFk, where is TF0 – the value of the measured indicator in the studied variant, TFk – on control. To assess the toxicity of the factor, the following scale was used: VI toxicity class (stimulation) –ITF >1.10; V (norm) - 0.91 – 1.10; IV (low toxicity) - 0.71 – 0.90; III (medium toxicity) - 0.50 – 0.70; II (high toxicity) - <0.50; I (ultrahigh toxicity) - the environment is not suitable for the life of the test object.Statistical data processing was carried out using the software package Microsoft Excel 2016, STATISTICA 2010. The average value of the indicator was determined, the standard deviation and validation of the samples were performed using a comparative Student's test.

Results

Germination and germination energy in uncontaminated soil amounted to 99%, which indicates high sowing qualities of the test crop. The average length of the roots varied in the range of 104-110 mm, and the stems - 106-112 mm (Figure 3, 4). The combined contamination of the soil with Cu and BaP has a toxic effect on the growth and development of the test culture. So, in the variant with the introduction of 275 mg/kg of Cu into the soil (corresponds to 5 MPC) together with 200 mcg / kg of BaP (corresponds to 10 MPC), root length and stem height are suppressed by 79% compared to the control sample, in addition, germination and seed germination energy are reduced by 29% and 33% (Figure 4).

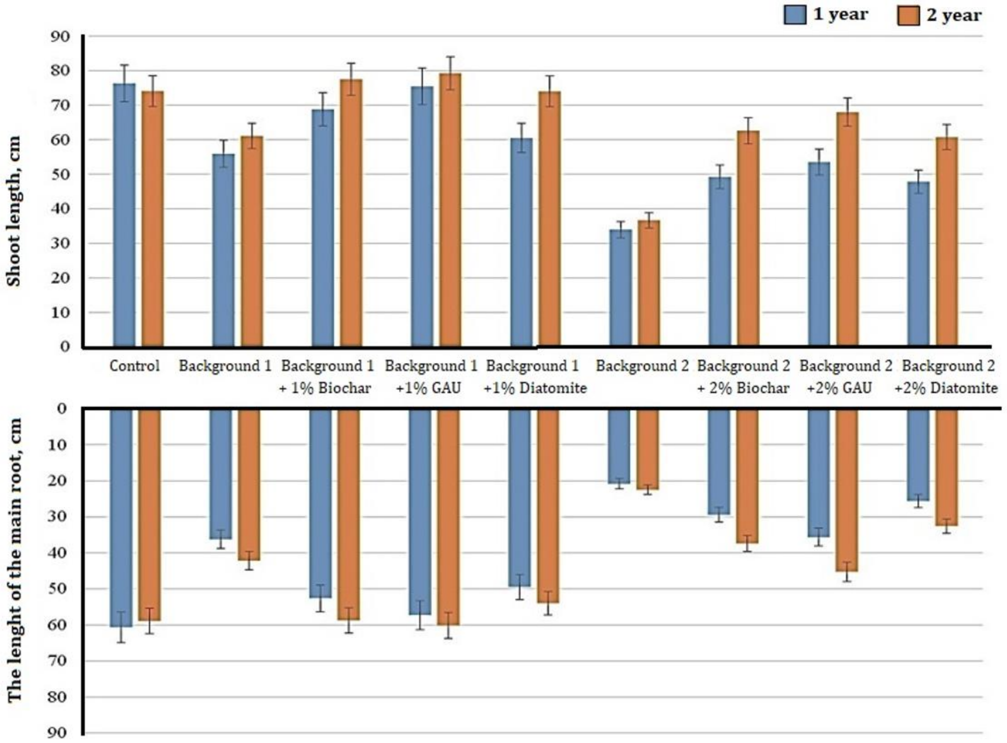

Figure 4. The effect of sorbents on the morphometric parameters of double row spring barley (*Hordeum sativum distichum*) in the tubulation phase (45 days), expressed in the variant with 5 MPC Cu and 10 MPC BaP (Background 1) and with 10 MPC Cu and 20 MPC BaP (Background 2)

Accordingly, with an increase in the content of introduced pollutants to 550 mg/kg Cu (10 MPC) and 400 mcg/kg BaP (20 MPC), the negative effect on the growth of roots and stems increases by 90%, as well as on germination and germination energy by 39% and 46% compared to plants (Figure 3), growing on unpolluted soil. Effective dose also remained 2.5%, but its effect is noticeably lower than that of the two previous sorbents: the length of the roots reached 79 mm, and the shoots – 73.

In the study results, the germination energy of spring barley seeds in uncontaminated soil was length of the roots varied between 104-110 mm, and for the stems between 106-112 mm. The combined soil contamination with Cu and BaP had toxic effect on the growth and development of the test culture. So, in the variant with 275 mg/kg Cu in soil (corresponds to 5 MPC) together with 200 µg / kg BaP (corresponds to 10 MPC), the root length and stem height were inhibited by 79% in comparison to the control. Additionally, the germination rate and seed germination energy decreased by 29% and 33%, respectively. As the pollutants' concentration increased to 550 mg/kg Cu (10 MPC) and 400 µg / kg BaP (20 MPC), the rate of stem and root growth decreased by up to 90%, as well as the germination energy by 39% and 46 % compared to plants growing in uncontaminated soil. It is noted that the joint soil contamination with organic and inorganic pollutants has a maximal toxic effect on plants as compared to the effects of individual pollution. Plant morpho-biometric parameters were not significantly affected by the introduction of mineral and carbonaceous sorbents into uncontaminated soil for shorter duration; however, in several studies involving a longer vegetation experiment, a positive effect on plant growth and productivity was observed. The use of mineral sorbents in contaminated soil had a positive effect on the morpho-biometric parameters of plants (Dietz et al., 1999; Kabata-Pendias, 2011; Mousavi et al., 2018).

Discussion

Germination and germination energy in variants with the introduction of different doses of diatomite was 70-94% and 66-90%, and in variants with tripoli - 71-94% and 67-91%, respectively (Figure 3). The introduction of diatomite into the soil with artificial pollution of 10 MPC BaP + 5 MPC Cu in doses of 0.5-2.5% increased the length of roots and stems in comparison with the contaminated soil. The best morpho-biometric indicators of plants grown on contaminated soil were established with the introduction of 1.5% diatomite and 2% tripoli. With an increase in the content of pollutants in the soil to 20 MPC BaP + 10 MPC Cu, the efficiency of the introduced doses of mineral sorbents slightly decreases. Germination and germination energy with different doses of diatomite in the soil observed to be 63-85% and 59-81%, and for tripoli - 64-84% and 60-83%. A dose of 0.5% diatomite and tripoli improved the parameters of the root length only by 1.5, 1.4 times, and the stem height by 1.4 times. With an increase in the doses of sorbents introduced into the soil, their effectiveness increases (Bauer et al., 2018; Rajput et al., 2021a,b; Kumar et al., 2021). The amendments efficiency was visible at 2.5% diatomite and tripoli. Similar phytotoxic effects were shown by diatomite and tripoli on the in regard to their physicochemical properties. The addition of carbon sorbents to the contaminated soil (10 MPC BaP + 5 MPC Cu) led to an improvement in the morpho-biometric parameters of plants. High germination (≤95%) of the test culture was recorded when 2–2.5% carbon sorbents were used, the germination energy varied within 90–94%. On variants of contamination of 10 MPC BaP + 5 MPC Cu at application rates> 1% GAU and biochar, the morpho-biometric parameters of plants reach the control sample. The lowest efficiency was found when using brown coal: 2.5% of brown coal, which contributed to an increase in root length, stem height by 3.7, and 4.0 times compared to the contaminated version (soil), however, the growth and development of plants do not reach control. The content of carbon sorbents in the contaminated soil 20 MPC BaP + 10 MPC had a positive effect on the growth and development of plants, whereas the sorbent concentration increased their efficiency become more evident. The use of GAU in doses 0.5-2.5% increases the length of the roots and the height of plants up to1.6-9.2 times, and biochar – up to 1.7-8.9 times.

The optimal dose of GAU and biochar application was 2% since with the introduction of 2.5% mathematically (statistically) reliable changes in morpho-biometric parameters were not observed GAU and biochar, in comparison with brown coal, were the most effective, which is associated with their characteristics especially specific surface area and pore volume. Thereby, in 2% brown coal concentration in soil, the root length increased by 7.1 times and the stem height by 6.1 times, while in the case of GAU and biochar, the increase was approximately 9 times (Chikhi et al., 2011).

With combined contamination, the morphometric parameters of spring barley deteriorated compared to the control (Figure 4). One of the most sensitive characteristics is the length of barley roots, which showed a significant impact on the formation of yield. It was found that the length of the roots decreased with combined contamination by 40% in the variant with 10 MPC BaP and 5 MPC Cu (Background 1) and by 66% with a doubling of the dose of pollutants compared with the control. This may be caused by the high carcinogenicity and mutagenicity of BaP, as well as other metabolites, which are the representatives of PAHs, and their carcinogenic metabolites formed during the degradation of BaP. It is generally recognized that the negative influence of heavy metals on growth processes, the development of stem meristems and roots increases with an increase in the concentration of metal in the soil.

The height of cereal plants reflects the general condition of plants when the main biomass is growing and forming, and reveals their reaction to nutritional conditions and soil toxicity. Based on current research outcomes, it was found that the length of the stems decreased by 27% and 56%. The inhibition in the growth and development of plants was not only reported in cultivated, but also in wild conditions under combined pollution by many researchers (Matsumoto et al., 1979; Zhou et al., 2021). Such processes may be related with a disruption of the antioxidant enzyme functions of plants as a result of the harmful effect of BaP's influence on these enzymes' activities. In the work of Bernard (Bernard et al., 2015), it was shown by the example of broccoli (*Brassica oleracea*) and white clover (*Trifolium repens*) that the level of resistance to oxidative stress (reactive oxygen species) at the biochemical level is directly associated with disturbed morphological characteristics of the plants.

There is an increase in the length of the barley root by 37% compared to the contaminated version of 20 MPC BaP and 10 MPC Cu (Background 2) with the introduction of 1% diatomite, and the length of the stem - by 8% and 7%, respectively. In the variants with higher pollution, a similar increase in the growth of spring barley is observed. The reduction of the toxic effect of pollutants during the introduction of diatomite occurs due to the fixation of bioavailable Cu compounds and the strengthening of the transformation of BaP. The maximum decrease in the morphobiometric parameters of plants on polluted soil (Background 1) was recorded when 1% of GAU is applied: the length of the barley root increased by 58%, and the root by 35% (Figure 4). The decrease in phytotoxicity might be due to a decrease in Cu mobility and BaP transformation (clause 1.3). GAU also has a stimulating effect on the development of agricultural crops (Feng et al., 2016; Bauer et al., 2020a,b).

In the second year of research, the effect of sorbents increases, which leads to better growth and development of test cultures, but the trends observed in the first year of research persist (Figure 4, 5, 6). Thus, the combined introduction of Cu and BaP into the soil has a negative impact on the morphometric parameters of barley. The most sensitive indicators of combined contamination are the length of the roots and stem. Further, the inhibition of the growth and development of test crops depends on the degree of contamination. When mineral and carbon sorbents are applied, morphometric parameters of spring barley are improved by reducing the content of BaP and mobile Cu compounds. The best effect is observed when applying GAU. In the second year of research, there is a tendency to reduce the toxic effect of pollutants on the growth of test cultures. An increase in the effect of mineral and carbon sorbents was found as a result of greater fixation of Cu compounds and transformation of BaP.

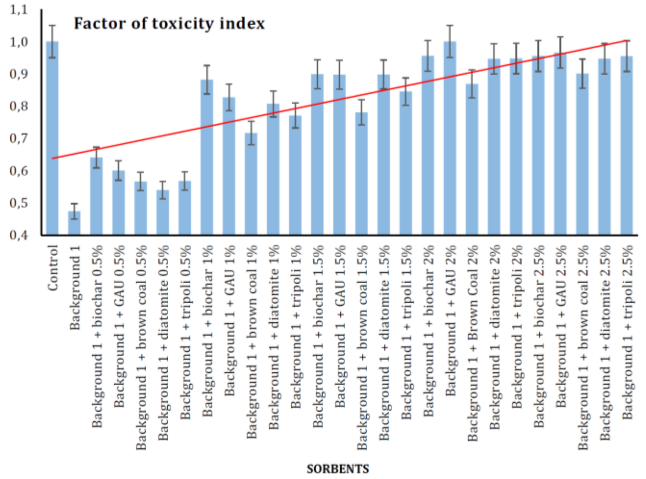

Figure 5. The effect of sorbents on on factor of toxicity index of double row spring barley (*Hordeum sativum distichum*), expressed in the variant with 5 MPC Cu and 10 MPC BaP (Background 1)

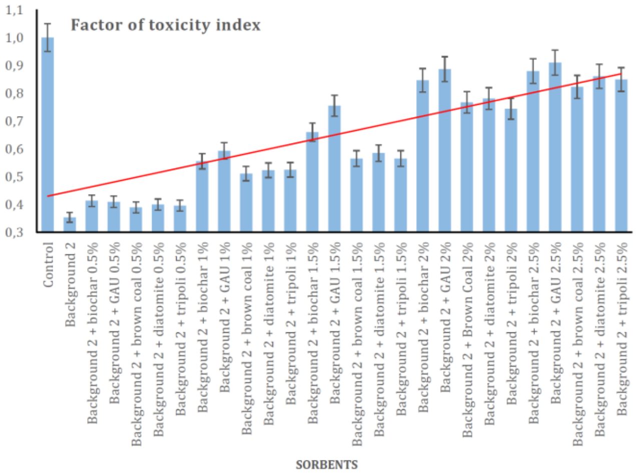

Figure 6. The effect of sorbents on factor of toxicity index of double row spring barley (*Hordeum sativum distichum*), expressed in the variant with 10 MPC Cu and 20 MPC BaP (Background 2)

Conclusion

It was shown that the introduction of mineral and carbonaceous sorbents into uncontaminated soil did not significantly affect the morpho-biometric parameters of plants. Germination energy was almost the same between different types of carbon sorbents. By reducing the phytotoxicity of the combined contamination of soil, the analyzed sorbents can be sequenced (sequenced) as follows: GAU> biochar> diatomite> tripoli> brown coal. In Haplic chernozem, combined contamination with Cu and BaP, the introduction of GAU, biochar, and diatomite to reduce the phytotoxicity of the soil showed the most noticeable changes when adding sorbents at a dose of 1% in the variant 10 MPC BaP + 5 MPC Cu and 2% in the variant 20 MPC BaP + 10 MPC Cu. Thus, these research outcomes will be helpful for remediation of combined polluted soils by heavy metals and benzo(a)pyrene and leveling the negative impact of pollutants on plant growth and development.

Acknowledgements

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