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ORIGINAL PAPER

Influence of carbon-containing and mineral sorbents on the toxicity of soil contaminated with benzo[a]pyrene during phytotesting

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Abstract Benzo[a]pyrene (BaP) is a member of polycyclic aromatic hydrocarbons known for high persistency and toxicity. Technologies of BaP sorption through solid matrixes have received relatively more attention. The present study was devoted to the phytotesting investigations of two different groups of sorbents, such as carbonaceous, including biochar and granulated activated carbon (GAC), and mineral, including tripoli and diatomite. Evaluation of the BaP removing efficiency was carried out using the phytotesting method with spring barley in Haplic Chernozem contaminated with different levels of contamination (200 and 400 μg kg^{-1} BaP). The sorbents' efficiency for BaP remediation was estimated in the sorbents doses from 0.5 to 2.5% per kg of soil. It was shown that biochar and GAC decreased the soil toxicity class to a greater extent than mineral sorbents ones. The effect intensified with an increase in applying sorbents doses. The optimal dose of carbonaceous sorbents into the soil contaminated with 200 μg kg^{-1} was 1%, decreasing the BaP content up 57–59% in the soil. Simultaneously, the optimal dose of the mineral sorbents was found to be 1.5%, which decreased the BaP content in the soil up 41–48%. Increasing the BaP contamination level up to 400 μg kg^{-1} showed the necessity of a sorbent dose increasing. In these conditions, among all applied sorbents, only 2% GAC could reduce the soil toxicity class to the normal level up to 0.91–1.10. It was shown that BaP tended to migrate from the soil to the roots and further into the vegetative part of barley.

Keywords Phytotesting · Carbon-containing sorbents · Mineral sorbents · Model experiment · Remediation of soil · Soil toxicity class

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Introduction

Benzo[a]pyrene (BaP) is one of the most dangerous compounds in the polycyclic aromatic hydrocarbons (PAHs) group, belongs to the xenobiotics (IARC, 2020). BaP is a high molecular weight organic compound ($C_{20}H_{12}$) formed from five condensed benzene rings with a molecular weight of 252.31 gmol^{-1} (ATSDR, 1995) and has relatively high stability in all environments. One of the main depositors of BaP is soils (Mackay et al., 2006) which accumulate the most part of PAHs emitted into the environment. The main sources of BaP in soils under the anthropogenic impact are the combustion of fossil fuels during the transport operation, the electricity production using coal or oil products, stove heating, cement and asphalt production, and waste incineration (ATSDR, 1995; Tsibart and Gennadiev, 2013; Kuppusamy et al., 2017).

Compounds of the PAHs group are classified as persistent organic pollutants due to their resistance in the landscape components, the ability to bioaccumulate, high toxicity, potential mutagenic, teratogenic and carcinogenic effects on living organisms (ATSDR, 1995; Abdel-Shafy & Mansour, 2016; Schwarzbauer and Jovančićević, 2015). In the international regulation practice, the 16 priority PAHs compounds are subjected to the independent obligatory control and regulation (ATSDR, 2020; CCME, 2020; US EPA, 2020). However, according to Russian Federation standards, only one BaP is subjected to regulation as the most toxic and carcinogenic compound to humans (IARC, 2020). According to the Russian legislation, the maximum permissible concentration (MPC) of BaP in the soil is 20 μg kg^{-1} (GN 2.1.7. (2041)-06. 2.1.7. (2006). The negative effects of PAHs on human health can arise from the consumption of contaminated food. Crops grown on PAH-contaminated soils can have intensive bioaccumulation (Sushkova et al., 2019). For example, according to the sanitary and epidemiological standard in Russia, the MPC for BaP in cereals should not exceed 1 μg kg^{-1} SanPiN (2001).

Currently, the mechanisms of the PAHs, including BaP, uptake by plants, are not well investigated. PAHs are sorbed on the walls of root cells, and their uptake by the root, as reported by Pretorius et al. (2018), is inversely proportional to the lipophilicity of the molecule (Kang et al., 2010). It is noted that BaP diffusion into the plant root is very slow (Li et al., 2015). Despite this, many authors report that the content of BaP in cereals exceeds 1 μg kg^{-1} (Li and Ma, 2016; Liu et al., 2017; Tian et al., 2018), which is largely due to the level of soil pollution by this dangerous ecotoxicant (Ni et al., 2017; Chen et al., 2019). Plant families have different tolerances to BaP. Cereals accumulate PAHs up to 30–40% of the total PAHs content in the soil (Roszko et al., 2020). For example, in the study of Wu et al. (2018), it was shown that the BaP bioaccumulation by agricultural crops decreases in the following order: *Spinacia oleracea L.* > *Cucurbita moschata* > *Cucumis sativus L.* > *Zea mays L.* The selectivity of pollutants uptake complicates the assessment of soil toxicity by plants. In crop rotation, the same level of BaP content provides a different degree of soil toxicity for each agricultural crop. Accordingly, the costs of remediation of such soils may be unjustifiably overestimated or, on the contrary, underestimated.

Soils are capable of natural regeneration through self-cleaning. However, the restorative capacity of soils is limited and possible at a relatively low pollution level during a long period of time (Manzetti, 2013; Schwarzbauer & Jovančićević, 2015). The application of natural and artificial sorbents can be used as a method for soil remediation. This soil remediation technology is not only low-cost, easy to use but highly effective both in terms of selective removal of pollutants and in terms of restoring soil quality (Sophia and Lima, 2018). Carbon sorbents, such as GAC and biochar, are the most often used for soil remediation (Vardhan et al., 2019). The global production of GAC alone reaches hundreds of thousand tons per year (Eeshwarasinghe et al., 2018). A large specific pore surface area and high stability in the soil determine the sorption potential of sorbents such as GAC (He and Wang, 2011). Biochar has sorption properties similar to GAC, but its production is much cheaper (Huggins et al., 2016; Liu et al., 2017; Qin et al., 2013).

The efficiency of the GAC application and biochar into the soil contaminated with oil products has been proven by activating natural microorganisms-destructors of hydrocarbons, and the foundations of sorption bioremediation of oil-contaminated soils have been developed (Vasilyeva et al., 2020; Liu et al., 2017; Zhang et al., 2016; Li et al., 2020; Igun et al., 2019). It has been found that carbon sorbents promote the removal of PAHs from the soil and wastewater sludge (Kołtowski and Oleszczuk 2016; Kołtowski et al., 2016, 2017; Zheng et al., 2018; Bonaglia et al., 2020; Li et al., 2020). In addition to stimulating the microbiological destruction of PAHs, GAC and biochar have a high ability to firmly bind organic pollutants in the soil (Chen and Chen, 2009; Hale et al., 2011). Therefore, they would limit the bioavailability of PAHs to plants. However, the rate of mineralization of these compounds in the soil in the presence of sorbents can decrease (Zhang et al., 2016).

Mineral sorbents such as diatomite or tripoli also have a large specific surface area and are characterized by the presence of a large number of carboxyl groups capable of physical sorption of PAHs (Danil de Namor et al., 2012; Ma et al., 2015). However, there are very few works devoted to the remediation of soils contaminated with PAHs. There was a trend towards decreasing oil products in the soil when diatomite was applied at a dose of 4–12% (Vasilyeva et al., 2020). The high sorption potential of diatomite in relation to phenanthrene, which is also a representative of PAHs from the list of priority pollutants (US EPA), was established by Zhao et al. (2019) and da Silva et al., (2015). It is promising to use tripolite as a sorbent for the treatment of drainage effluents of solid waste landfills (Gogina and Pelipenko, 2016), as well as for the treatment of liquid radioactive wastewater (Abdel Rahman et al., 2011).

It is known that carbonaceous and mineral sorbents are capable of treating the PAHs by sorption from soils, including BaP. Simultaneously, the optimal doses of sorbents can vary significantly depending on the type of pollutant and the conditions of the environment to be restored. Most often, the application rates of carbonaceous and mineral sorbents vary from 1.0 to 7.5%, depending on the level of soil contamination. However, the optimal doses of most sorbents are in the range from 0.5 to 3.0%, since the application of higher doses of sorbents can lead to a decrease in the availability of nutrients to plants (Ali et al., 2017; Gao et al., 2019; Meier et al., 2017; Zhu et al., 2018). Existing studies devoted to the remediation of soils contaminated with PAHs are rather scattered since they often describe the results of using only one sorbent. This does not allow a qualitative comparison of the effect of using carbon-containing and mineral sorbents in contaminated soils. In addition, the assessment of the one or another sorbent application effectiveness is often made only based on a decrease in the pollutant content in the soil, which does not fully reflect the level of soil toxicity for various crops, and subsequently for humans.

Therefore, the purpose of this work was to study the effect of carbon-containing and mineral sorbents on the toxicity of soil contaminated with BaP during phytotesting, with a special focus on identifying the optimal doses of sorbent application.

Materials and methods

Model experiment design

To study the effect of sorbents on the phytotoxicity of soil contaminated with BaP, a model laboratory experiment was laid. The soil (0–20 cm) of the specially protected natural area "Persianovskaya reserved steppe" was used, which is represented by Haplic Chernozem (Table 1). Haplic Chernozem soil occupies a significant area in the large agro-industrial regions of southern Russia, such as the Rostov Region and Krasnodar Krai territory. Most of the Haplic Chernozem is in agricultural use, closely adjacent to industrial enterprises, which significantly increases the anthropogenic pressure.

The selected soil was cleaned of plant residues and other inclusions, grounded in a porcelain mortar, and passed through a sieve with a hole diameter of 1 mm. Air-dry soil 50 g as determined by GOST RISO 22,030–2009 (2009) was placed in the Petri dishes, and an aqueous solution of BaP in acetonitrile (200 and 400 μg kg^{-1}) was added to the soil surface. The choice of doses of pollutants was determined by the existing levels of soil pollution in the Rostov Region (Sushkova et al., 2018, 2019). After applying pollutants, the soil was incubated for one week. According to the experiment scheme, carbonaceous and mineral sorbents were added in doses from 0.5 to 2.5% of the total soil volume (Table 2).

The moisture content was maintained at 60% of the total field moisture capacity during the entire incubation period in the soil of the phytotoxicity model laboratory experiment (GOST RISO, 22,030–2009). After a week of incubating the soil with sorbents, the seeds of spring barley of the two-row variety Ratnik (*Hordeum Sativum Distichum*) of the Poaceae Family, one of the main grain crops grown in the Rostov region, were sown in the amount of 15 seeds per cup. The seed germination energy was calculated 72hours after seed germination GOST (1096)8–88 (2009). Germination energy is equal to the proportion of seeds germinated after three days from the moment of sowing. Plants were sampled one week after sowing, and the length of the roots and the height of the seedlings of the test culture were measured GOST (1203)8–84(2004). The experiment was settled in 4 replications.

Table 1 Physical and chemical properties of the model experiment soil

Physical clay content (%)		Organic carbon content (%)	$CaCO_3$(%)	pH_{water}
< 0.01	< 0.001			
52.2	30.0	2.5	0.4	7.5

Table 2 Phytotoxicity scheme

Name of the sorbent	Sorbent application dose, %	BaP concentration	Name of the sorbent	Sorbent application dose, %	BaP concentration
Without sorbent	without BaP (control)	–	Without sorbent	without BaP (control)	–
	0.0%	200 BaP μg kg^{-1}		0.0%	400 BaP μg kg^{-1}
Biochar	0.5		Biochar	0.5	
	1.0			1.0	
	1.5			1.5	
	2.0			2.0	
	2.5			2.5	
GAC	0.5		GAC	0.5	
	1.0			1.0	
	1.5			1.5	
	2.0			2.0	
	2.5			2.5	
Diatomite	0.5		Diatomite	0.5	
	1.0			1.0	
	1.5			1.5	
	2.0			2.0	
	2.5			2.5	
Tripoli	0.5		Tripoli	0.5	
	1.0			1.0	
	1.5			1.5	
	2.0			2.0	
	2.5			2.5	

Brief description of sorbents

As the carbon sorbent, crushed GAC was made by VEKTON, BAU-A, Russia, according to GOST 6217–74 (2003). Moreover, biochar was made from sunflower husks at a pyrolysis temperature of 500 °C. The studied biochar was made by authors in the conditions by a slow pyrolysis at the different temperature gradient to safe a pore structure for a selective PAHs sorption. The temperature was settled up for producing the biochar without any PAHs mixture and additional phytotoxicity. Diatomite was obtained from the Kamyshlovsky diatomite deposit located in the northeastern outskirts of Kamyshlov, Russian Federation. The tripoli was obtained from the Brusyan-Log of the Lunacharsky tripoli section, Russian Federation.

Extraction of BaP from soil and plant samples

BaP was extracted from soils and plants using an innovative subcritical water extraction (Sushkova et al., 2016). A one g weighed portion of the soil was placed in an extraction cartridge. Eight milliliters of bidistilled water was added after screwing both sides tightly with screws. A pressure gauge with a built-in emergency pressure relief valve was connected to the cartridge so that the pressure inside the cartridge did not exceed 100 atm. The cartridge was installed in a thermostat and heated to 250 °C for 30 min. After cooling the system, the cartridge was unscrewed, and the contents were filtered three times through a paper filter with a blue ribbon into a conical glass flask to obtain a clear solution. From the resulting aqueous extract, BaP was re-extracted three times with n–hexane (analytical grade). For this purpose, 5 ml of hexane was poured into the flask, closed with a glass stopper and shaken on a shaker for 15mins. Separation of layers was carried out on a 50 ml separating funnel sequentially in three stages with the next portion of hexane. The combined hexane extract was passed through a funnel with calcined anhydrous sodium sulfate. The extract was evaporated in a pear-shaped flask on a rotary evaporator at a water bath temperature of 40 °C to a dry residue. The resulting residue was dissolved in 1 ml of acetonitrile with stirring for 30mins, and the concentration of BaP in the extract was determined by HPLC. The completeness of BaP extraction was determined by the addition method, for which a soil sample of 1 g was placed in a flask for a rotary evaporator and a certain amount of a standard BaP solution in acetonitrile was added based on the creation of a BaP concentration in the sample of 2, 4, 6, 8, 16, or 32 μg kg^{-1}. After evaporation of the solvent for 30 min under room conditions, the analyte was kept at 7 °C for 24hours, and then the samples were analyzed by high-performance liquid chromatography (HPLC) according to the certified procedures (MUK 4.1. (1274)-03. 4.1. (2003); ISO 13,877–2005) using the system with fluorometric detection 1260 Infinity Agilent (USA). The HPLC system was coupled to reversed-phase column Hypersil BDS C18 (150 × 4.6 mm, 5 μm) with a mixture of acetonitrile and ultrapure water as the mobile phase. Compounds were identified according to the retention time recorded by the corresponding analytical standard samples. HPLC grade acetonitrile (99.9%, analytical grade), anhydrous Na_2SO_4, n–hexane (99%, analytical grade), ethanol (96%, analytical grade), potassium hydrate (98%, analytical grade), and NaOH (97%, analytical grade), were used in the analysis. All research results were performed in threefold analytical replication.

Statistical analysis

Sigmaplot 12.5 and Statistica 10 were used for processing data. The reliability of differences between the experimental variants was assessed using the Student's *t* test, with a fixed p-level < 0.05. The relationships between the variables were estimated using linear regression with a fixed p-level < 0.001.

Results and discussion

BaP content in the soil of the model experiment

The content of BaP in the Haplic Chernozem in the control variant did not exceed the MPC and amounted to 17.1 ± 0.7 μg kg^{-1}. The application of the pollutant in the concentrations of 200 μg kg^{-1} and 400 μg kg^{-1} led to an increase in the BaP content in the soil to 215 ± 10 μg kg^{-1} and 406 ± 19 μg kg^{-1}, respectively. The use of carbonaceous and mineral sorbents led to decreased BaP content in all studied variants. Simultaneously, with an increase in the dose of the applied sorbent, the content of the pollutant in the soil decreased (Fig. 1a, 1b).

The application of biochar or GAC at a dose of 1% into the soil contaminated with 200 μg kg^{-1} BaP was accompanied by a decrease in the pollutant content by 82–83%. A further increase in the dose of the applied carbonaceous sorbents to 2.5% led to the decline in the

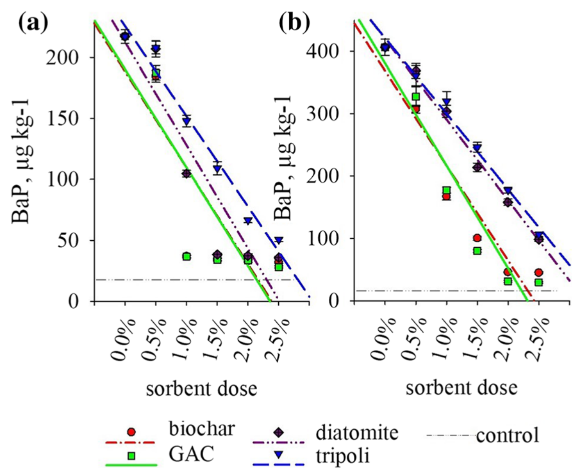

Fig. 1 Benzo[a]pyrene content in soil contaminated by 200 μg kg^{-1} (**a**) and 400 μg kg^{-1} (**b**) with different sorbents doses application

BaP content by 85–86%. However, there were no significant differences with the results obtained at a lower dose of biochar or GAC. Accordingly, the application of 1.0% of carbonaceous sorbents into the soil contaminated with 200 μg kg^{-1} BaP can be considered optimal. The optimal dose of diatomite applied into the soil contaminated with 200 μg kg^{-1} BaP can be regarded as 1.5%. This amount of diatomite in soil contaminated with 200 μg kg^{-1} BaP contributes to a decrease in the BaP content by 82%. It could be concluded that the application of tripoli into the soil contaminated with 200 μg kg^{-1} BaP is less effective than other studied sorbents. Although the proportion of the pollutant in the soil of the experimental variants significantly decreased when using the optimal doses of various sorbents, the BaP content exceeded the MPC, which may affect other studied parameters (Fig. 1a).

The rate of BaP destruction increased with an increase in the content of the pollutant in the soil (Sushkova et al., 2018). This hypothesis is confirmed by the fact that under conditions of sorbents equal doses, the degree of BaP reduction in the soil was higher in those variants of the experiment, where the initial application of the pollutant into the soil was higher and amounted to 400 μg kg^{-1}.

The optimal dose of biochar or GAC application in the soil contaminated with 400 μg kg^{-1} BaP was 2%, where the pollutant content decreased by 89% for biochar amended soil and 92% for GAC amended soil. Diatomite and tripoli were less effective in soil remediation for the soil that had been contaminated with 400 μg kg^{-1} BaP. A decrease in BaP content by 69–74% was established only when mineral sorbents were added to the contaminated soil at a dose of 2.5% (Fig. 1b).

Accumulation of BaP in the root and stem of spring barley

As given in Table 3, the BaP content in the root part of the spring barley was lower than in the soil, and in general, the accumulation of the pollutant in the plant can be attributed to the acropetal type. In the control variant, the content of BaP in the vegetative part of the plant and the root were 0.4 ± 0.1 μg kg^{-1} and 0.9 ± 0.1 μg kg^{-1}, respectively, which did not exceed the MPC of the content of BaP in plants. The BaP contamination at a dose of 200 μg kg^{-1} into the soil contributed to an increase in the pollutant content to 115.2 ± 5.1 μg kg^{-1} in the root and 36 ± 1.4 μg kg^{-1} in vegetative parts of the plant. At 400 μg kg^{-1} BaP, the accumulation of 209.4 ± 10.1 μg kg^{-1} and 87.9 ± 4.2 μg kg^{-1} were found in the root and vegetative parts, respectively. The use of sorbents was observed to reduce the content of pollutants in the soil of the model experiment and decrease the degree of BaP accumulation in spring barley. Simultaneously, the effect was enhanced by increasing the dose of the applied sorbent (Table 3).

Barley seedlings in the experiments with the carbonaceous sorbents showed that the BaP was accumulated to a lesser extent than those grown on the contaminated soil amended with mineral sorbents. This effect is primarily, because the application of biochar or GAC enhanced the BaP removal from the soil to a greater extent than the experimental variants where diatomite or tripoli was used (Table 3).

The BaP content in the root part of barley decreased by 1.1–4.3 times, and in the vegetative part by 1.2–5.9 times, in the variants of the experiment with the initial dose of pollutant concentration equal to 200 μg kg^{-1}, when using biochar or GAC, depending on the dose of the applied sorbent. The initial dose of diatomite or tripoli was 1.0% in soil contaminated with 200 μg kg^{-1} BaP at which a statistically significant decrease in the pollutant content in the plant was observed. The BaP content was reduced in the root part by 1.2–2.5 times and in the vegetative part by 1.4–4.6 times, compared to the content of the pollutant in barley grown from the variant of the experiment without adding sorbents to the contaminated soil (Table 3).

In general, a statistically significant decrease in the BaP content in the roots of barley seedlings was observed starting from the dose of 1.0% carbon sorbents and 1.5% mineral sorbents compared to the pollutant content in plants growing on soil contaminated with 400 μg kg^{-1} BaP without adding sorbents. Thus, the use of biochar or GAC for soil contaminated with 400 μg kg^{-1} BaP contributed to a decrease in the pollutant content in barley roots by 1.2–1.6 times. The use of diatomite or tripolite contributed to reducing the pollutant content in barley roots by 1.2–1.4 times. The content of BaP in the vegetative part of the plant significantly decreased by 1.3–3.3 and 1.3–2 times after using carbonaceous and mineral sorbents, respectively (Table 3).

Table 3 BaP content in the soil of the model experiment with various combinations of sorbents and pollutants

Name of the sorbent	Root length, mm							Stem height, mm						
	Control	0.0%	Sorbent dose					Control	0.0%	Sorbent dose				
			0.5%	1.0%	1.5%	2.0%	2.5%			0.5%	1.0%	1.5%	2.0%	2.5%
200 BaP µg kg^{-1}														
Biochar	0.9 ± 0.1	115.2 ± 5.1	104.9 ± 4.8	85.3 ± 4.6	61.2 ± 3.0	30.5 ± 1.4	28.4 ± 1.4	0.4 ± 0.1	46.0 ± 2.4	41.5 ± 2.0	29.0 ± 1.4	21.5 ± 1.0	9.2 ± 0.5	8.5 ± 0.4
GAC			100.6 ± 5.2	86.5 ± 4.3	58.4 ± 2.5	30.9 ± 1.4	27.5 ± 1.2			41.0 ± 2.1	30.2 ± 1.5	20.3 ± 1.1	10.0 ± 0.4	8.2 ± 0.5
Diatomite			110.8 ± 5.4	93.5 ± 4.5	73.5 ± 3.5	47.2 ± 2.2	46.9 ± 2.3			43.2 ± 2.1	33.4 ± 1.5	25.1 ± 1.1	19.4 ± 0.9	10.0 ± 0.4
Tripoli			112.7 ± 5.6	93.2 ± 4.0	78.4 ± 3.6	49.5 ± 2.0	48.4 ± 2.5			42.8 ± 1.9	33.9 ± 1.6	26.8 ± 1.2	20.1 ± 0.8	11.2 ± 0.5
400 BaP µg kg^{-1}														
Biochar	0.9 ± 0.1	209.4 ± 10.1	202.0 ± 9.5	184.2 ± 9.2	171.4 ± 8.4	165.5 ± 7.8	147.4 ± 7.0	0.4 ± 0.1	77.9 ± 4.3	60.6 ± 3.0	55.4 ± 2.5	49.3 ± 2.3	42.1 ± 2.0	34.1 ± 1.5
GAC			199.0 ± 8.7	180.1 ± 9.0	168.3 ± 7.5	159.1 ± 7.5	132.0 ± 6.2			59.8 ± 2.9	54.0 ± 2.1	50.49 ± 2.5	48.2 ± 2.1	34.9 ± 1.5
Diatomite			204.1 ± 10.0	190.6 ± 8.6	176.6 ± 8.0	169.4 ± 8.3	153.4 ± 7.5			61 ± 3.1	59.4 ± 3.0	54.4 ± 2.6	47.9 ± 2.2	38.4 ± 1.6
Tripoli			203.7 ± 9.8	188.9 ± 8.7	179.2 ± 8.2	170.0 ± 8.4	161.1 ± 7.5			60.5 ± 2.8	57.2 ± 2.8	51.0 ± 2.0	50.1 ± 2.4	40.0 ± 1.9

The statistical analysis showed a linear relationship between the content of BaP in the soil and its accumulation in different parts of the plant, as confirmed by the coefficient of determination (R^2). The decreasing order in the content of BaP was observed as follows: soil > root > stem. The linear relationship was calculated between "content of BaP in soil" and "content of BaP in barley roots", as shown in Eq. (1). Moreover, the relationship between "content of BaP in barley roots" and "the content of BaP in barley vegetative part" could be expressed by Eq. (2). In the first case, R^2 was found to be 0.54, and in the latter, 0.67, at a p-level < 0.001.

$$\text{BaP content in the soil} = 65.6 + (0.4 \times \text{content of BaP in barley roots}), R^2 = 0.54 \tag{1}$$

$$\text{Content of BaP in barley roots} = 18.3 + (0.1 \times \text{BaP content in the barley vegetative part}), R^2 = 0.67 \tag{2}$$

Changes in the sowing qualities of spring barley seeds

BaP is a plant growth inhibitor, and its content in soil reduces the sowing qualities of seeds, such as germination capacity and seed germination energy (Sushkova et al., 2017). The proportion of germinated seeds planted in the control soil was 99%, as shown in Fig. 2a–d. Of these, 99% of seeds germinated on the third day after sowing. A decrease in the number of germinated seeds was observed by 29% and the seed germination energy by 33% in the variant of the experiment with the 200 μg kg^{-1} BaP. An increase in the BaP concentration dose to 400 μg kg^{-1} had a greater toxic effect, where the germination capacity and the seed germination energy decreased by 49% and 57%, respectively (Fig. 2a–d).

The use of sorbents contributed to the improvement of the seeds sowing quality. It should be noted that at the same application rates of various sorbents into the soil contaminated with 200 μg kg^{-1} or 400 μg kg^{-1} BaP, their effect on the sowing qualities of spring barley was similar and insignificant differences found between the options. In general, with an increase in the dose of sorbent application into the contaminated soil, the germination capacity and seed germination energy increased. Values comparable to the control sample were obtained only using a 2% sorbent on a soil contaminated with 200 μg kg^{-1} BaP. The germination capacity in these variants was 93–96%, and a seed germination energy of 91–93% (Fig. 2a, b). The use of sorbents in the same amount also promotes an increase in the sowing qualities of seeds compared with the variant of the experiment without their application for the soil contamination of 400 μg kg^{-1} BaP. However, the obtained values were not comparable with the control variant and corresponded to 84–92% of the germination capacity and 81–90% of the seed germination energy (Fig. 2c , d).

Morphometric characteristics of spring barley

In the control variant of the experiment, the barley root length was 106 ± 5 mm, and the stem height was 108 ± 5 mm. Contamination by the BaP at a dose of 200 μg kg^{-1} contributed to decreasing the root length and stem height to 4.8 and 4.0 times, respectively. The suppression of the root part of the plant increased, and the length of the roots decreased by 13.2 times, as well as the length of the vegetative part of the plant decreased by 9.0 times with an increase in the dose of the pollutant concentration to 400 μg kg^{-1}. It should also be noted that the use of carbonaceous sorbents in the soil of the phytotoxicity model experiment with different pollutant concentrations had a more significant effect on the growth of the root and stem parts of barley compared with the use of mineral sorbents.

The use of sorbents contributed to the improvement of the morphobiometric parameters of spring barley seedlings, and with an increase in the dose of the sorbent applied, the effect intensified. However, only in the variants with the use of 2–2.5% carbonaceous sorbents in the soil contaminated with 200 μg kg^{-1} BaP, the length of barley roots and vegetative part did not significantly differ from the plants from the control sample. The use of different doses of mineral sorbents at the same level of soil contamination increased the length of barley roots by 1.7–4.2 times compared to the samples of plants growing on contaminated soil without the addition of sorbents. However, the obtained values of the root length are not comparable with the plants of the control variant. The height of the barley vegetative part increased 1.4–3.9 times as

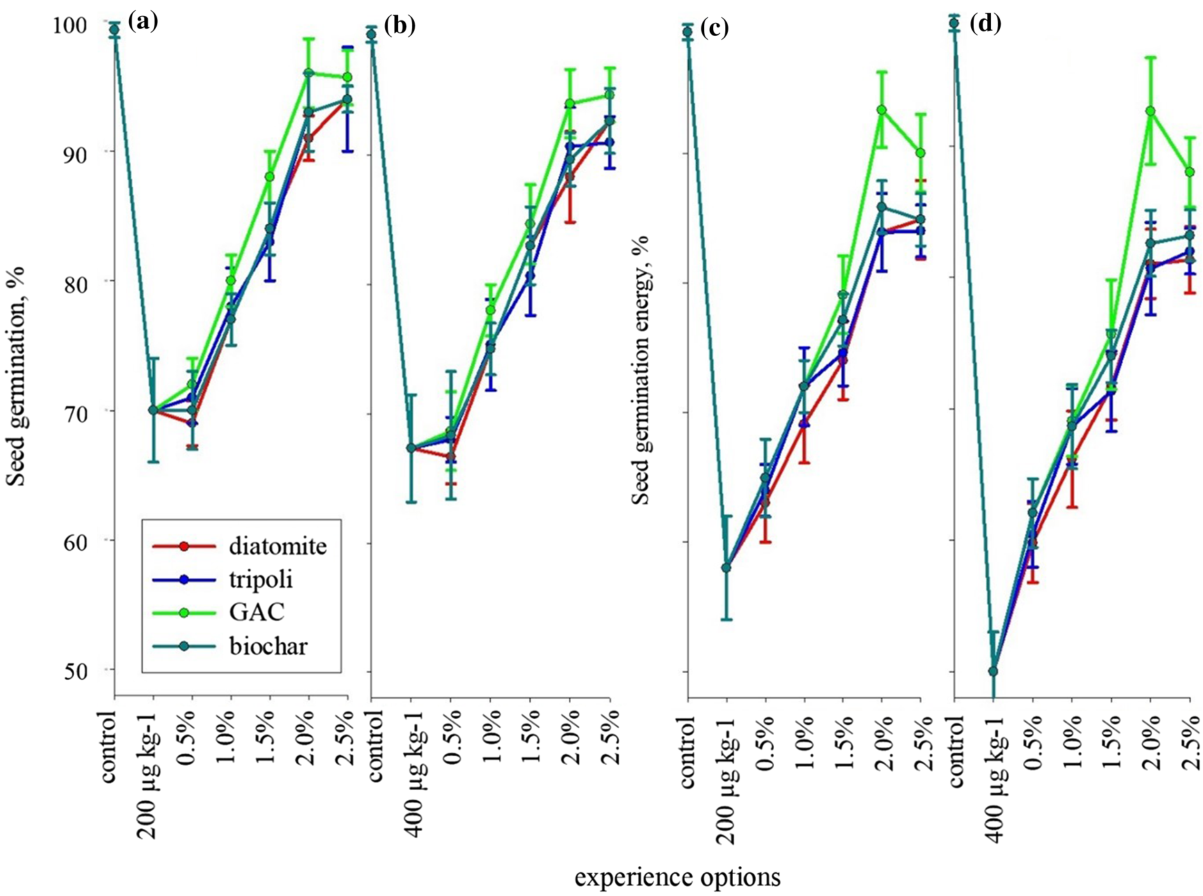

Fig. 2 Dynamics of spring barley seeds germination number (**a**) and germination energy (**b**) under soil contamination with 200 μg kg^{-1} of benzo[a]pyrene, and germination capacity (**c**) and seed germination energy (**d**) under soil contamination with 400 μg kg^{-1} of benzo[a]pyrene

compared to plants growing on contaminated soil without applied sorbents. The results of the vegetative part height comparable to the control sample were obtained for barley plants growing in contaminated soil 200 μg kg^{-1} BaP with the addition of 1.5–2.5% sorbent, in contrast to the root part (Table 4).

In general, the various sorbents application into the soil contaminated with 400 μg kg^{-1} BaP contributed to improving morphobiometric parameters. Still, the results obtained did not correspond to the plants from the control samples. The application of carbonaceous sorbents was accompanied by an increase in the length of barley roots by 2.1 times at 0.5% and 11.6 times at 2.5% of the applied sorbent. Simultaneously, the height of the plant vegetative part increased 1.4 times at 0.5% and 8.2 times at 2.5% sorbents doses in the contaminated soil compared to the variants of the experiment without adding sorbents. Mineral sorbents were less effective and their use in contaminated 400 μg kg^{-1} BaP led to an increase in the root part of barley to 1.9 times at 0.5% and 6.8 times at 2.5%. Simultaneously, the increase in the vegetative part of barley was 1.3 times at 0.5% and 7.3 times at 2.5% content of diatomite or tripoli in the contaminated soil compared to plants growing in the soil without sorbents (Table 4).

The optimal dose of the applied sorbents at different levels of soil contamination with BaP

To assess the effectiveness of the sorbents for remediation and their optimal dose of application into the soil contaminated with BaP, the soil toxicity class (STC) was calculated for each variant of the experiment (Kołtowski and Oleszczuk, 2016):

Table 4 Morphobiometric indicators of spring barley growing in the soil of a model experiment under the conditions of applying various doses of sorbents and pollutants

Name of the sorbent	Root length, mm							Stem height, mm						
	Control	0.0%	Sorbent dose					Control	0.0%	Sorbent dose				
			0.5%	1.0%	1.5%	2.0%	2.5%			0.5%	1.0%	1.5%	2.0%	2.5%
200 BaP μg kg^{-1}														
Biochar	106 ± 5	22 ± 1	50 ± 2	91 ± 5	92 ± 5	99 ± 5	98 ± 4	108 ± 5	27 ± 1	55 ± 3	102 ± 5	101 ± 5	100 ± 4	97 ± 5
GAC			45 ± 2	88 ± 4	92 ± 4	105 ± 5	103 ± 4			45 ± 3	99 ± 5	99 ± 5	101 ± 5	100 ± 6
Diatomite			43 ± 2	75 ± 3	90 ± 4	93 ± 4	93 ± 4			37 ± 2	84 ± 5	104 ± 5	102 ± 5	101 ± 6
Tripoli			39 ± 2	74 ± 3	84 ± 4	90 ± 4	92 ± 4			40 ± 2	80 ± 4	89 ± 4	104 ± 5	105 ± 6
400 BaP μg kg^{-1}														
Biochar	106 ± 5	8 ± 1	18 ± 1	45 ± 2	53 ± 2	88 ± 5	91 ± 5	108 ± 5	12 ± 1	18 ± 1	41 ± 3	60 ± 3	94 ± 5	94 ± 4
GAC			17 ± 1	47 ± 2	80 ± 4	94 ± 5	93 ± 5			17 ± 1	53 ± 3	67 ± 4	95 ± 4	98 ± 4
Diatomite			16 ± 1	40 ± 2	46 ± 2	72 ± 3	82 ± 4			15 ± 1	39 ± 2	41 ± 2	80 ± 4	88 ± 4
Tripoli			15 ± 1	41 ± 2	40 ± 2	64 ± 3	81 ± 4			15 ± 1	37 ± 2	40 ± 2	71 ± 3	86 ± 4

$$\text{Soil Toxicity Class (STC)} = (T_1/T_{c1} + T_2/T_{c2} + T_3/T_{c3} + T_4/T_{c4})/n \quad (3)$$

where T_1—the length of the barley root part in the test variant of the experiment, T_{c1}—the length of the root part of barley growing on the control variant, T_2—the height of the barley vegetative part in the studied variant of the experiment, T_{c2}—the height of the barley vegetative part growing on the control variant, T_3—germination of barley seeds in the test variant of the experiment, T_{c3}—germination of barley seeds in the control variant of the experiment, T_4—germination energy of barley seeds in the studied variant of the experiment, T_{c4}—germination energy of barley seeds in the control variant of the experiment, n—number of factors.

To assess the STC, the following scale was used: VI toxicity class (stimulation)—STC > 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)—0.50–0.30; I—< 0.3 (ultra-high toxicity)—the environment is not suitable for the life of the test object.

The soil is characterized as highly toxic during contamination by BaP concentration at a level of 200 μg kg^{-1}. A concentration of 400 μg kg^{-1} was found to be unsuitable for the existence of the test object (in this case, the spring barley). The application of 0.5% of any of the tested sorbents into the soil contaminated with 200 μg kg^{-1} BaP reduced the STC to medium. An increase in the sorbent application dose to 1.0–1.5% reduced the STC to a low level, and 2–2.5% doses of the sorbent application eliminated the toxic effect of the contaminated samples and transferred the soil of the model experiment to the norm class. For the soil contaminated with 400 μg kg^{-1} BaP, the use of sorbents with a dose of 0.5% reduced its STC to high, 1.0–1.5% sorbent application transferred the STC to the medium, and 2–2.5% sorbent application led to decrease the STC to a low-toxicity soil. An exception was the variant of the experiment with the GAC application at a dose of 2% into the soil contaminated with 400 μg kg^{-1} BaP. Under these conditions, the soil of the model experiment variants had almost no toxic effect on spring barley and belonged to the "norm" class (Fig. 3).

In general, there is a decrease in the STC with an increase in the dose of applied sorbents. Still, in Fig. 3,

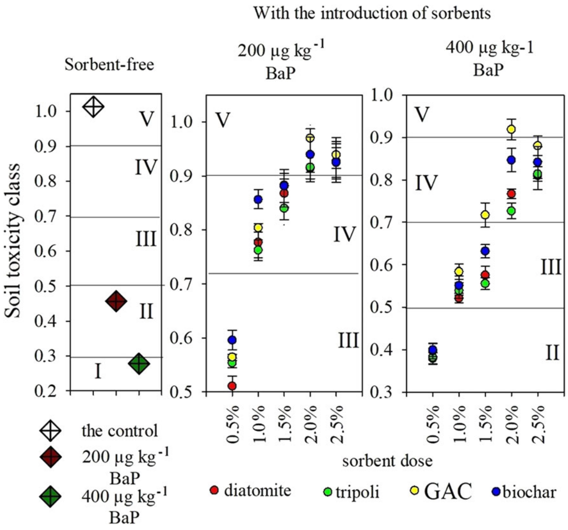

Fig. 3 The changes in soil toxicity class under the different applications of carbonaceous and mineral sorbents

there was a tendency to a reduction in the STC as carbon sorbents were added to the contaminated soil at a dose of 2.5% compared to a 2% dose of biochar or GAC (Fig. 3). A decrease in STC, in this case, occurred mainly due to a slight decrease in the germination and germination energy of spring barley seeds in the variants of the experiment with the biochar or GAC application at a dose of 2.5% into the soil with different levels of contamination (Fig. 2a, 2b, 2c, 2d). This might be due to the fact that the content of carbon sorbents in the soil at a dose of 2.5% led to the adsorption of nutrients in the soil (Gao et al., 2019; Palanivell et al., 2020; Song et al., 2019), which are necessary for normal growth and development of spring barley.

It can be concluded that the optimal dose of carbonaceous sorbents is 2% for soils contaminated with 200 μg kg^{-1} BaP. Also, at a given level of soil contamination, the possibility of using carbonaceous sorbents with a dose of 1.0% should be considered for using biochar or GAC. Since the application of sorbents in such an amount into the contaminated 200 μg kg^{-1} BaP promoted reducing soil toxicity, the STC index significantly increased. Also, some authors have effectively applied GAC or biochar from other materials to soils contaminated with various toxic compounds at a dose of 1.0% (Ali et al., 2017; Meier et al., 2017; Zhu et al., 2018). It should be noted that the GAC addition had a slightly better effect in comparison with biochar and under the condition of the same sorbents doses.

The difference between these sorbents for several indicators was not reliable. Taking into account that the economic efficiency of biochar is higher than that of GAC (Lyu et al., 2016), biochar with a dose of 2% should be recommended as a possible sorbent for soil remediation contaminated with 200 μg kg^{-1} BaP. Increasing the BaP concentration in the soil to 400 μg kg^{-1} demonstrated the possibility of GAC using a dose of 2% with higher effectiveness since only in this variant of the experiment the STC decreased to the norm. Mineral sorbents were significantly less effective than carbonaceous sorbents according to all the studied criteria. However, at 2% diatomite application into the soil contaminated with 200 μg kg^{-1} BaP, the STC decreased and was close to the carbonaceous sorbents results, which made soils possible to use for green agriculture (Fig. 3).

Conclusions

The phytotesting method with spring barley in the Haplic Chernozem contaminated with different levels of contamination showed that the BaP at a concentration of 200 μg kg^{-1} inhibited the growth and development of spring barley plants. The toxic effect originated from BaP intensified with an increase in pollutant concentration. A positive linear relationship was established between the content of BaP in the soil and the BaP content accumulated in the root part of spring barley (R^2 = 0.54), as well as between the root and vegetative parts of spring barley (R^2 = 0.67), at a significant p-level of 0.001. In general, the accumulation of BaP in spring barley could be attributed to acropetal type, as BaP was migrated from the soil to the root and then to the vegetative part.

STC corresponded to the level of high toxicity (at 200 μg kg^{-1}) and ultra-high toxicity (at 400 μg kg^{-1}) of soils. All types of the applied carbonaceous and mineral sorbents declined the STC values, which ultimately led to a decrease in the BaP accumulation in spring barley. Consequently, an improvement was observed in the morphobiometric parameters of the plant and the sowing qualities of seeds. Under similar conditions, carbonaceous sorbents were more effective than mineral ones. An increase in the applied dose of sorbents increased the positive effect of remediation, thus leading to a decline in STC.

The optimal doses of carbonaceous and mineral sorbents were determined to be 2.0% for soil contamination with BaP in concentration 200 μg kg^{-1}. The optimal dose of mineral sorbent was 1.5% for soil contamination with BaP in concentration 200 μg kg^{-1}, at which STC corresponds to the normal class. In soil contaminated with 400 μg kg^{-1} BaP, it was more suitable to apply a dose of 2.0% GAC since only using this sorbent contributed to a decrease in STC to the normal class.

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Author contributions SS was responsible for conceptualization and formulation of a research problem. TM was responsible for data curation and writing—reviewing. TD and SS were responsible for writing. EA performed analytical work, HPLC and data performing. VR and RK performed data processing. AB and IL were responsible for conducting experiments. MM was responsible for visualization, statistical processing and writing–review and editing. NC and RK performed methodology. IL was responsible for creating data. ID performed experiments design. RK involved in discussion.

Data availability The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declarations

Conflict of interest The authors declare there is no conflict of interest in this work.

Ethical approval It is not applicable since the manuscript has not been involved in the use of any animal or human data or tissue.

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