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The efficiency of the hard wood origin biochar addition on the PAHs bioavailability and stability in sediment

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ABSTRACT

Polluted sediments with organic pollutants like PAHs represent a potential danger to environment, human health and potential obstacle to water management. Removal of polluted sediment provides the potential for reuse of nutrients from sediment, for crop production or for materials in building industry. The purpose of this study was to determine the efficacy of using hard wood biochar for the immobilization of bioaccessible polycyclic aromatic hydrocarbons (PAHs) in historically polluted sediment. The main question is would carbon materials' presence (in this case biochar) have influence on PAH bioavailability and their stability in sediment. This is important because the world trend is to go for sediment reuse in agriculture purposes, and biochar is proven to be good amendment for increasing soil organic carbon (SOC) stabilization and increasing soil carbon stock. The manuscript provides a detailed consideration of the supersorption performance of the biochar and PAH sequestration in different types of PAHs with aging period up to 6 months in *ex situ* treatment. The efficiency of biochar to sequester the PAHs was evaluated by assessing the bioavailable fraction (F_{rap}) using desorption method with Amberlite XAD4 resin assistance. In untreated sediment, F_{rap} ranged from 22% up to 42% for 2–4 rings, and around 9% for 5–6 rings PAHs. 180-days amendment of biochar led to a further decrease in the bioavailable portion of PAHs. The results of this laboratory study shown that biochar produced from hard wood gave promising results for binding and further stabilizing PAH in historically polluted sediments.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are among the most common groups of organic compounds present in the sediment and have drawn much public concerns due to their carcinogenic, toxic and mutagenic potentials (Xiong et al., 2017; Ni et al., 2018; Maletić et al., 2019; Li et al., 2020). Consequently, a great number of scientific papers have dealt with the subject of developing appropriate techniques to lower the risk of PAHs associated in sediment (Lamichhane et al., 2016; Yang et al., 2018; Albarano et al., 2020; Maletić et al., 2021). Dredging and *ex-situ* treatments by chemical and biological technologies is recognized expensive and suitable for small volume and highly polluted sediment. A new approach that implies treating the pollutants *in situ* using carbonaceous adsorbents is considered less disturbing to the ecosystem compared to traditional remediation methods. These materials are used not only to remove pollutants from the medium but also in order to improve quality of the soil/sediment, and reduce the negative pollution's consequences on human health and the environment reducing the available proportion that is directly harmful to organisms (bioavailable/bioaccessible fraction) (Yin et al., 2019; Maletić et al., 2019).

Carbonaceous materials such as biochars (BC) have shown high effectiveness in reducing bioavailable contaminant concentrations and toxicity in sediments due to the huge surface area particular associated to their porous structure and carbon content, and consequent high adsorption capacity to organic pollutants (Zhang et al., 2017; Li et al., 2020). Biochar produced by temperature pyrolysis higher than 400 °C has a high affinity for PAHs due to a - electron donor-acceptor interaction and possesses more condensed aromatic clusters (Zhu and Pignatello, 2005; Wang et al., 2017a) as well as the high porosity with well-developed nano- or micro-pores accessible for low molecular weight PAH sorption (LMW-PAHs) (Yang et al., 2021; Chen et al., 2018). In the last decades there have been a great number of research papers that deals with the subject of applications of BC and other carbonaceous sorbents to soil, sediment, and water as immobilization agent, however, there are still some lacks and gaps in knowledge on mechanisms and stability of sediment treated this way (Li et al., 2020). In the

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natural environment, soil and sediment serves as a storage and transit station for PAHs, which account for more than 90% of the environmental burden. Ailijiang et al. (2022) reported Σ16PAHs concentration in urban parks of Northwest China ranged from 0.135 to 12.427 mg/kg; Deelaman et al. (2023) in sediment cores from Phayao Lake, Thailand concentration of Σ16PAHs ranged from 77.6 to 1251.1 mg/kg, while Froger et al. (2021) measured PAHs concentration in 2154 soils in France, and detected ranges from 0.0051 to 31.2 mg/kg. In terms of toxicology, PAHs have both threshold and nonthreshold effects, and therefore the fate and diffusion represent one of the main concern and subject of scientific community. Biochar has been used in various papers like Ahmad et al. (2014); Chen et al. (2018); Dong et al. (2018) and Fuentes et al. (2020) for remediation or quality improvement of the soil/sediment, but it is important to emphasize that biochar can have a toxic effect on organisms due to the presence of dangerous chemicals (like PAHs) in it (Godlewska et al., 2021). Therefore it is crucial to do lab experiment in order to see how the biochar presents affect on PAH stability and fate of this pollutant. Till now, most studies have been concentrated on the influences of pyrolyzing temperature on biochar properties and on the sorptive efficiency of PAHs associated sediment under spiked sediment (Qiao et al., 2018; Zhang et al., 2019; Yang et al., 2021). In addition, most of the published sediment deals with representative compounds of PAHs, like naphthalene or phenantrene (Yang et al., 2021), and there is a need to look at the effects of biochar addition if there are more PAH compound present in the sediment sample.

Therefore, the overreaching goal of this research paper was to investigate whether biochar made from hard wood can be a good stability amendment for treatment of historically contaminated sediments with PAHs. This paper evaluates the biochar application for sequestration and further stabilization of PAHs present in a water/sediment historically polluted system and his potential bioaccessible fraction using XAD4 assisting desorption technology. The study's more precise goals were as follows:: (1) to investigate effects of sediment geochemistry (different characteristics of sediment) and biochar properties on the sequestration efficiency and stability of PAHs; (2) to assess the optimal dose of biochar amendment and potential for reuse of sediment with historically pollution; (3) to look at the short- and long-term consequences of biochar amendment in polluted sediment on PAHs bioavailability/bioaccessibility and (4) to identify possible problems during practice and make recommendations for further research .

2. Materials and methods

2.1. Biochar

Biochar (BC) was produced with a KonTiki system with hard wood and charring temperatures ranging from 680 °C to 740 °C. In brief, fire was created within the kiln using little branches with diameters of around 1 cm. After that initial phase, to the kiln were added new branches with diameter smaller than 4 cm. The kiln was regularly fed until all the selected biomass was consumed (Schmidt and Taylor, 2014). The temperature recorded before quenching was 740 °C. The biochar obtained in this way was filtering and drying at 105 °C for at least 48 h. The biochar had been crushed and sieved (Fuentes et al., 2020).

2.2. Contaminated sediment

The sample stations' positions were obtained using the Global Positioning System (GPS).Samples of sediment (S1, S2 and S3) consisted of excavated material from three locations in Autonomous Province of Vojvodina, in the north part of the Republic of Serbia. Locations Begej (S1 (N45°36´46.45´ and E20°45´21.31´´) and S2 (N45°26´31.34´´ and E20°27´33.62´´)) are under strong anthropogenic influence and currently represents a recipient of wastewater, sludge, and run-off from the agricultural land. Dubovina et al. (2018) assessed PAHs in this location's sediment and determined that the sediment requires thorough rejuvenation. As far as the sample S3 (N45°23´14.81´´ and E19°13´58.22´´) it was collected from the location of Danube–Tisa–Danube Canal (DTD). Pollution in the DTD Canal began in the twentieth century (about 1950) as a result of fast industrial expansion. Problem with DTD contamination is well known and already documented in some national and European documents (Serbian Environmental Protection Agency, 2011; European Commission, 2002). Sediment samples were collected according to standard method for sediment with a corer sampler (Beeker, Eijkelkamp, The Netherlands) and stored in appropriate containers (ISO 5667-12 2017).

2.3. Sorption kinetics

Kinetic studies for bioaccessibility measurements with and without XAD4 were carried out in 40 ml glass vials. Control tests were carried out without sediment to assess the loss of PAHs owing to sorption onto the surface of the glassware. PAH concentrations were basically constant. The vials containing 1 g of sediment were carefully filled with the 5 mmol $CaCl_2$, 0.2 g XAD4 resin and 0.8 g K_2CO_3. The vials were shaken at 20 °C and 150 rpm on an orbital shaker. After predetermined time intervals (0, 14, 30, 90 and 180 days), the vials were collected and centrifuged at 2500 rpm for 20 min. The concentration of PAHs in the sediment was analyzed. All experiments were run in triplicate.

2.4. Aging's influence on desorption kinetics

Desorption studies were carried out utilizing the solute-loaded sediments produced from the prior sorption experiments to explore the influence of age and contact duration between sediment and biochar on desorption kinetics. The 40 ml glass vials holding 1 g of sediments were filled with 1, 5, and 10% biochar, respectively. To suppress microbiological activity during the desorption studies; each vial received 1 mL of 300 mg L^{-1} $HgCl_2$ solution. The mixes were incubated in the dark for 0, 14, 30, 90, and 180 days to assess the immediate and long-term effects of biochar on pollutant (de)sorption in sediments. Following a predetermined incubation time point, the bioaccessibility of the chosen organic compounds was evaluated using methodologies described in our previous studies (Spasojević et al., 2015; Rončević et al., 2016; Grgić et al., 2019; Maletić et al., 2022). In brief, XAD-4 resin (Fluka) was purified for 30 h using ultra-pure water, methanol, hexane/acetone methanol, and ultra-pure water in that order. After aging, 5 mmol $CaCl_2$, 0.2 g XAD4 resin and 0.8 g K_2CO_3 in 40 mL water solution were added to the vials. PAHs associated with XAD4 resin (considered as bioaccessible fraction) were extracted by hexane and determined by GC–MS.

2.5. Data analysis

The sorbed organic pollutants are associated to different moieties in soil/sediment particles, which determine that desorption exhibits two stage kinetics: i.e., rapid desorption and slow desorption (Cornelissen et al., 1997). The ecological danger caused by PAHs linked with sediment is determined by their bioavailable fraction, which might be defined as the rapidly desorbed fraction from sediment samples (Spasojević et al., 2015; Rončević et al., 2016; Yang et al., 2018). PAH desorption kinetics from sorbent amended sediment were fitted based on the following two-compartment model (Eq. (1)) (Spasojević et al., 2015; Cornelissen et al., 1998a, 1998b):

$$\frac{S_t}{S_0} = F_{rap} \times e^{-k_{rap} \times t} + F_{slow+very\ slow} \times e^{-k_{slow+very\ slow} \times t} \quad (1)$$

S_t - amount of PAHs sorbed to the sediment (mg/kg dm) at desorption time t (h) and

S_0 - total amount of sediment-associated PAHs immediately prior to desorption (mg/kg dm)

F_{rap} - rapidly desorbing fractions (%)

F_{slow} ($F_{slow+very\ slow}$) - slowly desorbing fractions (%)
k_{rap} - rate constants of rapid desorption (h^{-1})
k_{slow} ($k_{slow+veryslow}$) - rate constants of slow desorption (h^{-1})

The desorption extent (F_{rap}) and rate constant (k_{rap}) in rapid period were considered as the indices for bioavailable fraction of PAHs associated in sediment. All results were subjected to one-way ANOVA (analysis of variance) using untransformed data. The threshold for statistical significance was set at $p < 0.05$. The procedure blanks and duplicate or triple samples were used to control data quality.

2.6. Sediment and biochar characterization

Before preparing the samples for analysis, sediment samples were held at 4 °C. To guarantee homogeneity, air-dried sediment was passed through a 2-mm filter and combined. The clay content in the sediments was determined using wet sieving method (ISO 11277:2009, 2009), while organic matter was determined by method of mass loss after ignition at 550 °C (SRPS EN 12879:2007, 2007). The mass of organic matter was converted into organic carbon content using a standard conversion ratio of 1.724 (Sauvé et al., 2003). An Autosorb iQ Surface Area Analyzer was used to calculate the multi-point BET specific surface area (SSA) of the sediment and bichar (Quantachrome Instruments). Mesopore volumes (V_{mes}) were determined using the BJH (Barrett-Joyner-Halenda) model using desorption isotherms. The sorbents' micropore volumes were determined using the *t*-test and the Horvath-Kawazoe (HK) technique. The surface carbon content was measured using an energy-dispersive spectrometer and scanning electron microscopy (SEM, Hitachi TM3030) (EDS, Bruker Quantax 70 X-ray detector system). The elemental composition of biochar (C, H, N, and S) was measured using a Vario EL III CHNS Analyzer across three repetitions.

2.7. PAH analysis

According to EPA3550b, 16 EPA PAHs were extracted using ultrasound and an acetone-hexane combination (1:1, v/v) (EPA, 2007). GC/MS analysis was carried out on an Agilent 7890 gas chromatograph with an MSD 5975C mass spectrometer on an HP-5MS column (J&W Scientific) according to method EPA8270C (EPA, 1996; Spasojević et al., 2015; Rončević et al., 2016). Phenanthrene-d-10 was used as internal standard. The following GC/MS conditions were used: a pulsed splitless mode with a split ratio of 50:1, an input temperature of 300 °C, initial oven temperature of 55 °C for 1 min, then 25 °C min1 to 300 °C for 3 min in splitless. The PAH concentrations were determined using the internal standard technique (target ion peak areas were used for the calculation). Quality control and assurance processes were carried out using the methods of full procedure blank, blank spike recovery, and soil matrix spike recovery and reference material comparison (Molnar Jazić et al., 2021).

3. Results and discussion

3.1. Biochar and sediment characterization

Biochar. The physicochemical characteristics and PAH contents of the examined biochar is given in Table 1. The sum of PAHs in the biochar used in this paper is 3.49 mg/kg, meeting the recommended EBC standard EBC 2012. The concentration of toxic 5–6 ring PAHs in our biochar is low (less than 10% of Σ16PAH), which is promising in terms of application wood biochar for sediment remediation. The surface area of the investigated biochar is 341 m^2/g. This value represents an important index to determine the effectiveness of sediment remediation (Ahmad et al., 2014; Yang et al., 2019; Li et al., 2020). It is consistent with the published findings for biochar generated at temperatures about 700 °C (Ahmad et al., 2014; Yang et al., 2019). For assessing aromaticity, the H/C molar ratio was employed, while the O/C molar ratio was used to assess the polarity. Aromaticity, or the H/C ratio, is a good predictor of biochar stability (Leng et al., 2019). The examined biochar had H/C value less than <0.3, which generally indicate highly condensed aromatic ring systems (Leng et al., 2019). Based on the O/C molar ratio value of 0.038, it can be concluded that this biochar is stable, with an estimated half-life of more than 1000 years (Spokas, 2010; Leng et al., 2019). In summary, based on the high C content, low atomic H/C ratio and O/C ratios, it can be concluded that this biochar consists mainly of unsaturated condensed aromatic carbon structure, which is like soot structure (Mahmud et al., 2018; Spokas, 2010). The SEM images of biochar (Fig. 1) showed the fibrous structure, indicating the formation of hard domains or soot structure.

Table 1
Physico-chemical characteristics of investigated biochar and sediments.

Biochar			
Parameter	Value		
BET SSA[a] (m^2/g)	341 ± 4.51		
Ash content (550 °C) (% (w/w))	6.40 ± 0.67		
N (% (w/w))	0.40 ± 0.04		
C (% (w/w))	89.8 ± 2.47		
H (% (w/w))	0.90 ± 0.05		
S (% (w/w))	< 0.03		
O (% (w/w))	4.50 ± 0.21		
H/C	0.12 ± 0.02		
H/C_{org}	0.12 ± 0.01		
O/C	0.038 ± 0.004		
Sediments			
Parameter	S1	S2	S3
Organic matter (%)	9.97 ± 0.47	14.9 ± 0.70	6.70 ± 0.43
Clay content (%)	37.4 ± 1.42	41.9 ± 1.31	20.6 ± 0.36
Organic carbon (%)	5.78 ± 0.34	8.64 ± 0.09	3.89 ± 0.08

Sediments. Table 1 shows the main physicochemical properties of the sediments. Organic carbon was calculated using standard conversion factor 1.724 to convert organic matter mass into organic carbon content (Sauvé et al., 2003). High molecular weight (HMW) PAHs with rings ≥ 4 were often prominent in the test sediments, which is consistent with the features of past PAH contamination, because light molecular weight (LMW) PAHs with rings ≤ 3 are significantly simpler to breakdown (Scott et al., 2012; Kanaly and Harayama, 2000).

3.2. Sorption kinetics

Mathematical fitting of desorption kinetics curves can provide information about the quickly desorbing fraction, which is commonly regarded as the bioavailable portion. In this study, two-component desorption model was used (Spasojević et al., 2018; Cornelissen et al., 1998a, 1998b) to account for the desorption kinetics to obtain the desorption percentage (F_{rap}) and desorption rate constants (k_{rap}) for different PAHs in rapid period (Table 2). Data presented in this section are related to samples without biochar addition. As the table showed that the k_{rap} of PAHs with 2–3 rings for all three sediments were similar, ranging from 0.239 h^{-1} to 0.257 h^{-1} (Table 2) (and are not significantly different from each other at $p < 0.05$). On the other hand, the k_{rap} of PAHs with 4- and 5–6 rings are smaller, ranging between 0.0535 h^{-1} and 0.144 h^{-1} for 4- ring (and are not significantly different from each other at $p < 0.05$) and 0.132 to 0.163 for 5–6 rings (and are not significantly different from each other at $p < 0.05$).

However, the rapidly desorbing fractions rate constant k_{rap} for 2–3 and 4-ring PAHs are higher (differ at $P < 0.05$) than rapidly desorbing fractions rate for PAHs with 5–6 rings. The reason for this phenomenon of PAH desorption could be due to higher values of $\log K_{ow}$ for PAHs with 5–6 rings compared to PAHs up to 4 rings. Namely, it is well known that organic compounds with lipophilicity have a considerable sorption affinity for organic materials in sediment/soil and hence

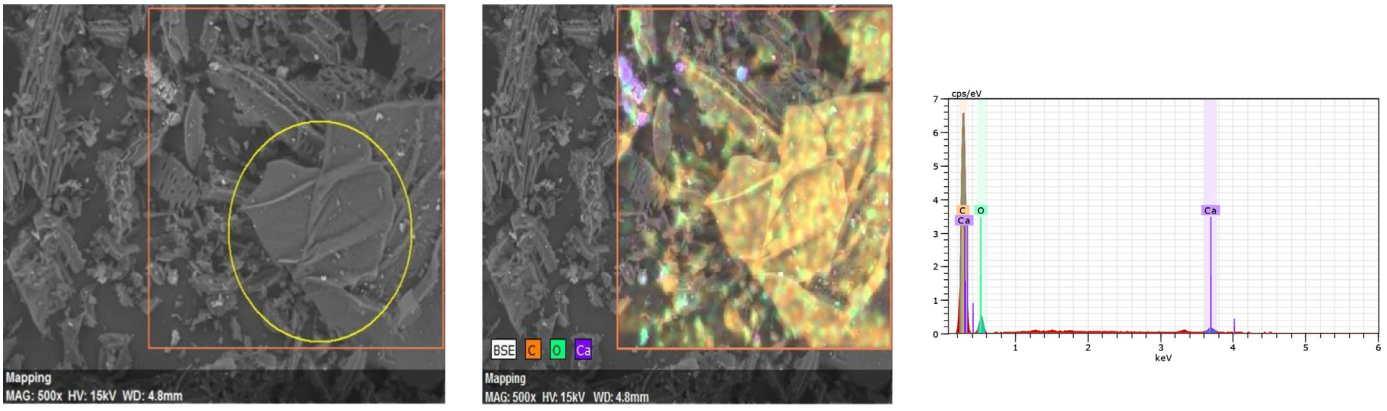

Fig. 1. Surface chemistry of investigated biochar (SEM images of the biochar surface (1A), elemental analysis of the marked part of the biochar surface (1B) with graph (1C)).

Table 2
Desorbing kinetic parameters for PAHs with different rings based on the two-fraction model.

Sediment	S1			S2			S3		
	2–3	4	5–6	2–3	4	5–6	2–3	4	5–6
F_{rap} (%)	32.8	40.9	10.5	24.4	23.4	7.3	41.9	22.3	9.56
k_{rap} (h^{-1})	0.239	0.144	0.132	0.248	0.0535	0.158	0.257	0.163	0.126
F_{slow} (%)	67.2	60.1	89.5	75.6	76.6	92.7	58.1	77.7	91.2
k_{slow} (h^{-1})	1.3×10^{-3}	1.7×10^{-3}	1.9×10^{-4}	1.4×10^{-3}	1.1×10^{-3}	4.8×10^{-4}	3.3×10^{-3}	1.3×10^{-3}	3.3×10^{-4}
R^2	**0.9384**	**0.9752**	**0.8855**	**0.9487**	**0.9978**	**0.9922**	**0.9517**	**0.9677**	**0.9268**

desorbs more slowly. Thus, as the hydrophobicity of PAHs increase, the sorption affinity increases (Čvančarová et al., 2013; Poot et al., 2014). It should be stated that k_{rap} for S2 sample behaves differently from samples S1 and S3. The k_{rap} values for PAHs with 5–6 rings are higher than the value for 4 ring PAHs. This can be explained by the fact that it is not always the amount of organic matter that matters, but its composition (Barnier et al., 2014; Nichols et al., 2008).

3.3. Effects of biochar addition/ effect of aging on desorption kinetics

The incorporation of biochar as a carbonaceous substance in polluted sediment may be able to lower the ecological danger of PAHs, making it a viable solution for practical remediation and possible sediment reuse (Dong et al., 2018; Yang et al., 2018; Chen et al., 2018). As previously indicated, the ecological risk caused by PAHs is determined by their bioavailability, which is defined by the quick desorbed portion. An important aspect of the biochar application is to maintain long-term positive effects. PAH bioavailability in the biochar amended sediment can: (1) decrease with time due to PAH sequestration in aged sediment or (2) increase due to changes of biochar characteristics as consequence of aging, oxidation, or degradation (Godlewska et al., 2017). When applying biochar it should have in mind not only the dose, but also contact time, possible negative environmental effects, and cost of used treatment (Godlewska et al., 2021). Fig. 2 shows stability of added biochar and desorption trend based on F_{rap}. All results show that added biochar is stable, have great PAH sorption and high sorption coefficients, and can be characterized as sink rather than a source of PAHs (Zhang et al., 2019). Only in case of S2 sample, regarding PAHs with 2–3 and 5–6 rings, there was slightly increase of PAH content in samples with 5 and 10% of biochar.

As far as S1 and S3 samples the use of biochar reduced the share of the bioavailable fraction of all investigated PAHs. S2 sample has a highest clay, organic carbon and organic matter content and therefore it is expected that bioavailable fraction is less than in other samples. However, results have shown that in system like that biochar is not stable and, in this case, biochar can be a secondary source of PAHs. The added doses decreased the PAH content in the examined sediment. The smallest reduction of desorbed amount of PAHs content was observed for 5–6 ring PAHs for all three sediments (Fig. 2). This information is relevant because, from the remediation point of view, these high molecular weight PAHs and their sequestration is important. These results are in line with high values of log K_{ow} for 5–6 ring PAHs. In general, the simultaneous sorption of organic compounds on organic matter and their adsorption on biochar explains the enhanced retention of PAHs in sediment in the presence of biochar (Silvani et al., 2017; Yang et al., 2018). In present study, the desorbed amount of all the investigated PAHs in the presence of biochar were smaller in comparison with desorbed amount from sediment only (Fig. 1), which most likely favors adsorption of PAHs on biochar and might explain the reduction in bioavailability fraction of PAHs in the presence of biochar. Biochar application onto organic contaminated sediments or soil is commonly recognized as a viable technique for carbon sequestration or soil quality improvement; nonetheless, it is critical to determine whether the employed biochar might be a potential source of PAHs..

The effectiveness of biochar amendment in stabilizing organic pollutants such as PAHs in soil varies depending on biochar source, amendment dosage, particle size, soil tipe and pollutant chemical nature and concentrations (Guo et al., 2020). It is assumed that the main mechanism used in this case is PAH adsorption methods on carbon adsorbents responsible for PAH adsorption and removal from contaminated sediment may be classified as having weak adsorption (hydrogen bond, hydrophobic and Van der Waals (VDW) interaction) and strong adsorption (π-π, π electron from BC, electrostatic interaction and π complexation). For example, Paszkiewicz et al. (2018) reported that VDW interactions are the key factor for stabilize adsorbed pyrene onto multiwalled carbon nanotubes. The electron-donor acceptor interaction is the primary mechanism for PAH sorption onto charcoal. Stable aromatic rings in PAHs with electrons can easily conjugate with aromatic rings or bonds

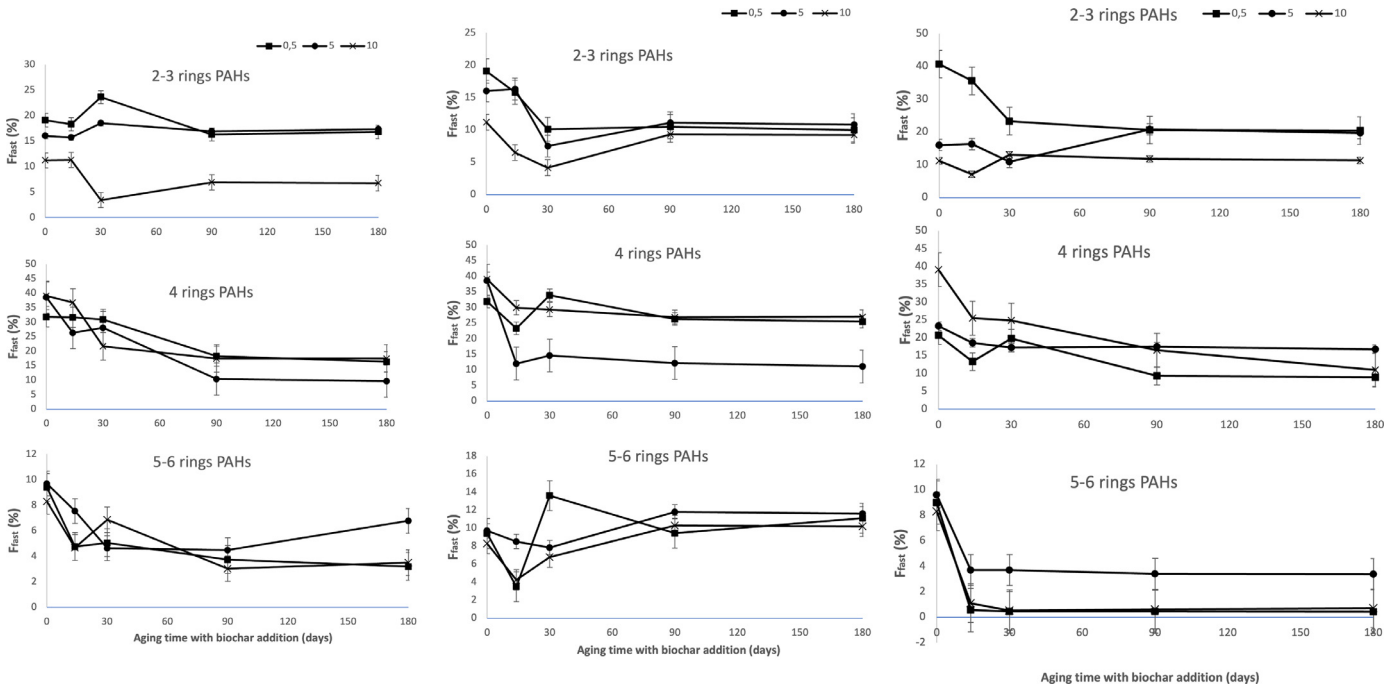

Fig. 2. The rapidly desorbing fractions rate for all samples S1, S2 and S3, respectively (doses 0.5%, 5% and 10%). Error bars represent SD of two replicates.

on charcoal. In, a detailed description of PAH adsorption processes on carbon adsorbents is provided in Li et al. (2020) and Guo et al. (2020). When considering all interactions in a system like this, we must include not just sorption onto biochar, but also PAHs permeate into sediment micropores, phenomena known as aging effects (Yang et al., 2018; Chen et al., 2018). These aging effects reduce PAH bioavailability and toxicity. Biochar can accelerate aging, which can be explained by its strong affinity for PAHs (Yang et al., 2018).

4. Conclusion and future remarks

According to the research, biochar amendment can stabilize organic pollutants in sediment and attenuate sediment contamination; however, efficacy is case specific and depends on individual sediment features. Organic contaminants are primarily absorbed by biochar through pore filling, partitioning, and the hydrophobic effect, while polar organic pollutants are absorbed by hydrogen bonding, electrostatic attraction, specific surface contact, and surface precipitation. The results of this laboratory study show that commercially available biochar made from hard wood can be used as potentially effective sustainable environmental immobilizing agent without negative effects on the environment. System biochar/historically polluted sediment is proven to be stable based on the reported results on lowering the bioavailable fraction of 16 USEPA PAHs with time. Based on our findings, we can infer that a biochar dose of 0.5% and an aging duration of 180 days provided good outcomes for this type of remediation therapy in terms of biochar and PAH stability. Undoubtedly, biochar used in this study can have strong implications not only because of his relatively small doses but also because it is cost-effective product. Though its stabilization efficacy may not be equivalent to that of activated carbon, biochar is more economically viable and, when used properly, can provide other environmental advantages such as carbon sequestration and soil health improvement. Higher doses of hard wood biochar can further decrease the bioavailability of PAHs in sediment by adsorbing them and reducing their mobility and bioavailability to plants and animals. The experiment showed that biochar produced this way is stable even in higher doses. However, before applying biochar directly to sediment, the qualities and influence of these materials on sediment features, as well as the long-term impacts on microbial ecology, should be thoroughly investigated, and the dose should be adjusted under realistic conditions. In future studies we are planning shifting to the field scale and conducting economic analysis of biochar usability in real system.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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References

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19–33.

Albarano, L., Costantini, M., Zupo, V., Lofrano, G., Guida, M., Libralato, G., 2020. Marine sediment toxicity: a focus on micro- and mesocosms towards remediation. Sci. Total. Environ. 708, 134837.

Ailijiang, N., Zhong, N., Zhou, X., Mamat, A., Chang, J., Cao, S., Hua, Z., Li, N., 2022. Levels, sources, and risk assessment of PAHs residues in soil and plants in urban parks of Northwest China. Sci. Rep. 12, 21448. doi:10.1038/s41598-022-25879-8.

Barnier, C., Ouvrard, S., Robin, C., Morel, J.L., 2014. Desorption kinetics of PAHs from aged industrial soils for availability assessment. Sci. Total Environ. 470-471, 639–645.

Chen, Z., Chen, J., Yang, X., Chen, C., Huang, S., 2018. Biochar as an effective material on sediment remediation for polycyclic aromatic hydrocarbons contamination. In: Proceedings of the 3rd International Conference on New Energy and Renewable Resources ICNERR 2018ISBN978-1-60595-608-4.

Cornelissen, G., Rigterink, H., Ferdinandy, M.M.A., Van Noort, P.C.M., 1998a. Rapidly desorbing fractions of PAHs in contaminated sediments as a predictor of the extent of bioremediation. Environ. Sci. Technol. 32, 966–970.

Cornelissen, G., Van Noort, P.C.M., Covers, H.A.J., 1998b. Mechanism of slow desorption of organic compounds from sediments: a study using model sorbents. Environ. Sci. Technol. 32, 3124–3131.

Cornelissen, G., Van Noort, P.C.M., Govers, H.A.J., 1997. Desorption kinetics of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: sediment extraction with Tenax and effects of contact time and solute hydrophobicity. Environ. Toxicol. Chem. 16, 1351–1357.

Čvančarová, M., Křesinová, Z., Cajthaml, T., 2013. Influence of the bioaccessible fraction of polycyclic aromatic hydrocarbons on the ecotoxicity of historically contaminated soils. J. Hazard. Mater. 254–255, 116–124.

Deelaman, W., Choochuay, C., Pongpiachan, S., Han, Y., 2023. Ecological and health risks of polycyclic aromatic hydrocarbons in the sediment core of Phayao Lake, Thailand. J. Environ. Expo. Assess. 2 (3). doi:10.20517/jeea.2022.29.

Dong, C.D., Chen, C.W., Kao, C.M., Chien, C.C., Hung, C.M., 2018. Wood-biochar-supported magnetite nanoparticles for remediation of PAH-contaminated estuary sediment. Catalysts 8, 73.

Dubovina, M., Krcmar, D., Grba, N., Watson, M.A., Radjenovic, D., Tomasevic-Pilipovic, D., Dalmacija, B., 2018. Distribution and ecological risk assessment of organic and inorganic pollutants in the sediments of the transnational Begej canal (Serbia-Romania). Environ. Pollut. 236, 773–784.

EBC, 2012. European biochar certificate - guidelines for a sustainable production of biochar. doi:10.13140/RG.2.1.4658.7043"> (Version 6.3E of 14th August 2017).

EPA, 1996. Method 8270C semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS).

EPA, 2007. Method 3550C ultrasonic extraction.

European Commission, 2002. Eutrophication and health; Office for Official Publications of the European Communities: Luxembourg.

Fuentes, A.L.B., Canevesi, R.L.S., Gadonneix, P., Mathieu, S., Celzard, A., Fierro, V., 2020. Paracetamol removal by Kon-Tiki kiln-derived biochar and activated carbons. Ind. Crops Prod. 155, 112740.

Froger, C., Saby, N.P.A., Jolivet, C.C., Boulonne, L., Caria, G., Freulon, H., Fouquet, C., Roussel, H., Marot, F., Bispo, A., 2021. Spatial variations, origins, and risk assessments of polycyclic aromatic hydrocarbons in French soils. Soil 7, 161–178. doi:10.5194/soil-7-161-2021.

Godlewska, P., Schmidt, H.P., Ok, Y.S., Oleszczuk, P., 2017. Biochar for composting improvement and contaminants reduction. A review. Bioresour. Technol. 246, 193–202.

Godlewska, P., Sik Ok, Y., Oleszczuk, P., 2021. The dark side of black gold: ecotoxicological aspects of biochar and biochar-amended soils. J. Hazard. Mater. 403, 123833.

Grgić, M.G., Beljin, J.M., Maletić, S.P., Kragulj-Isakovski, M.M., Tricković, J.S., Zeremski, T.M., Rončević, S.D., 2019. Pentachlorobenzene sequestration in sediment by carbon rich amendment (Article). Hem. Ind 73 (1), 63–71.

Guo, M., Song, W., Tain, J., 2020. Biochar facilitated soil remediation: mechanisms and efficacy variations. Front. Environ. Sci. 8, 521512. doi:10.3389/fenvs.2020.521512.

ISO 11277:2009, 2009. Soil quality — Determination of particle size distribution in mineral soil material — Method by sieving and sedimentation

ISO 5667-12:2017.Water quality — Sampling — Part 12: guidance on sampling of bottom sediments from rivers, lakes and estuarine areas

Kanaly, R.A., Harayama, S., 2000. Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. J. Bacteriol. 182 (8), 2059–2067.

Lamichhane, S., Bal Krishna, K.C., Sarukkalige, R., 2016. Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: a review. Chemosphere 148, 336–353.

Leng, L., Huang, H., Li, H., Li, J., Zhou, W., 2019. Biochar stability assessment methods: a review. Sci. Total Environ. 647, 210–222.

Li, F., Chen, J., Hu, X., He, F., Bean, E., Tsang, D.C.W., Ok, S.Y., Gao, B., 2020. Applications of carbonaceous adsorbents in the remediation of polycyclic aromatic hydrocarbon–contaminated sediments: a review. J. Clean. Prod. 255, 120263.

Mahmud, A., Camps-Arbestain, M., Hedley, M., 2018. Investigating the influence of biochar particle size and depth of placement on nitrous oxide (N2O) emissions from simulated urine patches. Agriculture 8 (11), 175.

Maletić, S.P., Beljin, J.M., Roncević, S.D., Grgić, M.G., Dalmacija, B.D., 2019. State of the art and future challenges for polycyclic aromatic hydrocarbons are sediments: sources, fate, bioavailability and remediation techniques (Review). J. Hazard. Mater. 365, 467–482.

Maletić, S., Beljin, J., Tamindžija, D., Grgić, M., Molnar Jazić, J., Kragulj Isakovski, M., Rončević, S., 2021. Bioremediation perspective of historically contaminated sediment with polycyclic aromatic hydrocarbons. Int. J. Sediment Res. 36 (4), 479–488.

Maletić, S., Kragulj Isakovski, M., Sigmund, G., Hofmann, T., Hüffer, T., Beljin, J., Rončević, S., 2022. Comparing biochar and hydrochar for reducing the risk of organic contaminants in polluted river sediments used for growing energy crops. Sci. Total Environ. 843, 157122. doi:10.1016/j.scitotenv.2022.157122.

Molnar Jazić, J., Kragulj Isakovski, M., Maletić, S., Tubić, A., Apostolović, T., Beljin, J., Agbaba, J., 2021. Assessing method performance for polycyclic aromatic hydrocarbons analysis in sediment using GC-MS: method validation and principal component analysis for quality control. Int. J. Environ. Anal. Chem. doi:10.1080/03067319.2021.1993841.

Ni, N., Wang, F., Song, Y., Bian, Y., Shi, R., Yang, X., Gu, C., Jiang, X., 2018. Mechanisms of biochar reducing the bioaccumulation of PAHs in rice from soil: degradation stimulation vs immobilization. Chemosphere 196, 288–296.

Nichols, E.G., Gregory, S.T., Musella, J.S., 2008. The impact of vegetation on sedimentary organic matter composition and PAH desorption. Environ. Pollut. 156, 928–935.

Paszkiewicz, M., Sikorska, C., Leszczynska, D., Stepnowski, P., 2018. Helical multiwalled carbon nanotubes as an efficient material for the dispersive solidphase extraction of low and high molecular weight polycyclic aromatic hydrocarbons from water samples: theoretical study. Water Air Soil Pollut. 229 (8), 253.

Poot, A., Jonker, M.T.O., Gillissen, F., Koelmans, A.A., 2014. Explaining PAH desorption from sediments using Rock Eval analysis. Environ. Pollut. 193, 247–253.

Qiao, K., Tian, W., Bai, J., Dong, J., Zhao, J., Gong, X., Liu, S., 2018. Preparation of biochar from Enteromorpha prolifera and its use for the removal of polycyclic aromatic hydrocarbons (PAHs) from aqueous solution. Ecotoxicol. Environ. Saf. 149, 80–87.

Rončević, S., Spasojević, J., Maletić, S., Jazić, J.M., Isakovski, M.K., Agbaba, J., Grgić, M., Dalmacija, B., 2016. Assessment of the bioavailability and phytotoxicity of sediment spiked with polycyclic aromatic hydrocarbons. Environ. Sci. Pollut. Res. 23, 3239–3246.

Sauvé, S., Manna, S., Turmel, M.C., Roy, A.G., Courchesne, F., 2003. Solid-solution partitioning of Cd, Cu, Ni, Pb, and Zn in the organic horizons of a forest soil. Environ. Sci. Technol. 37, 5191–5196.

Scott, H.E.M., Aherne, J., Metcalfe, C.D., 2012. Fate and Transport of polycyclic aromatic hydrocarbons in upland irish headwater lake catchments. Sci. World J. 2012Article ID 828343.

Serbian Environmental protection agency, 2011. The official report about environmental State 2009. Serbian Environmental Protection Agency, 20.

Silvani, L., Di Palma, P.R., Riccardi, C., Eek, E., Hale, S.E., Viotti, P., Petrangeli Papini, M., 2017. Use of biochar as alternative sorbent for the active capping of oil contaminated sediments. J. Environ. Chem. Eng. 5, 5241–5249.

Spasojević, J., Maletić, S., Rončević, S., Grgić, M., Krčmar, D., Varga, N., Dalmacija, B., 2018. The role of organic matter and clay content in sediments for bioavailability of pyrene. Water Sci. Technol. 77 (1–2), 439–447.

Spasojević, J.M., Maletić, S.P., Rončević, S.D., Radnović, D.V., Čučak, D.I., Tričković, J.S., Dalmacija, B.D., 2015. Using chemical desorption of PAHs from sediment to model biodegradation during bioavailability assessment. J. Hazard. Mater. 283, 60–69.

Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O:c molar ratios. Carbon Manag. 1 (2), 289–303.

SRPS EN 12879:2007, 2007. Characterization of sludges - Determination of the loss on ignition of dry mass

Wang, C., Wang, Y., Herath, H.M.S.K., 2017. Polycyclic aromatic hydrocarbons (PAHs) in biochar – Their formation, occurrence and analysis: a review. Org. Geochem. 114, 1–11.

Xiong, B., Zhang, Y., Hou, Y., Arp, H.P.H., Reid, B.J., Cai, C., 2017. Enhanced biodegradation of PAHs in historically contaminated soil by M. gilvum inoculated biochar. Chemosphere 182, 316–324.

Yang, X., Chen, Z., Wu, Q., Xu, M., 2018. Enhanced phenanthrene degradation in river sediments using a combination of biochar and nitrate. Sci. Total Environ. 619–620, 600–605.

Yang, X., Ng, W., Wong, B.S.E., Baeg, G.H., Wang, C.H., Ok, Y.S., 2019. Characterization and ecotoxicological investigation of biochar produced via slow pyrolysis: effect of feedstock composition and pyrolysis conditions. J. Hazard. Mater. 365, 178–185.

Yang, W., Qu, T., Flury, M., Zhang, X., Gabriel, S., Shang, J., Li, B., 2021. PAHs sorption to biochar colloids changes their mobility over time. J. Hydrol. 603 (A), 126839. doi:10.1016/j.jhydrol.2021.126839.

Yang, Y., Ye, S., Zhang, C., Zeng, G., Tan, X., Song, B., Zhang, P., Yang, H., Li, M., Chen, Q., 2021. Application of biochar for the remediation of polluted sediments. J. Hazard. Mater. 404, 124052.

Yin, L., Hu, Q.K., Mondal, S., Xu, J.Q., Ouyang, G.F., 2019. Peanut shell-derived biochar materials for effective solid-phase microextraction of polycyclic aromatic hydrocarbons in environmental. Talanta 202, 90–95.

Zhang, C., Zeng, G., Huang, D., Lai, C., Chen, M., Cheng, M., Tang, W., Tang, L., Dong, H., Huang, B., Tan, X., Wang, R., 2019. Biochar for environmental management: mitigating greenhouse gas emissions, contaminant treatment, and potential negative impacts. Chem. Eng. J. 373, 902–922.

Zhang, X., Gao, B., Creamer, A.E., Cao, C., Li, Y., 2017. Adsorption of VOCs onto engineered carbon materials: a review. J. Hazard Mater. 338, 102–123.

Zhu, D., Pignatello, J., 2005. Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. Environ. Sci. Technol. 9 (7), 2033–2041. doi:10.1021/es0491376.