

# Pentachlorobenzene sequestration in sediment by carbon rich amendment

Marko Grgić<sup>1</sup>, Jelena Beljin<sup>1</sup>, Snežana Maletić<sup>1</sup>, Marijana Kragulj Isakovski<sup>1</sup>, Jelena Tričković<sup>1</sup>, Tijana Zeremski<sup>2</sup>, Srđan Rončević<sup>1</sup>

<sup>1</sup>University of Novi Sad Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovica 3, 21000 Novi Sad

<sup>2</sup>Institute of Field and Vegetable Crops, Maksima Gorkog 30, 21000 Novi Sad

## Abstract

Organic pollutants in sediments are a worldwide problem because sediments act as sinks for hydrophobic, toxic, persistent and bioaccumulative hazardous compounds such as pentachlorobenzene (PeCB). PeCB can be involved in adsorption, desorption and transformation processes and can be made available to benthic organisms through the sediment–water interface. In order to reduce the risk, this study investigates effects of the dose and contact time between sediment and carbon-rich amendments (activated carbon (AC), biochar (BC) and hummus (HC)) on the effectiveness of detoxification. Four doses of carbon-rich amendments (0.5-10 %) and four equilibration contact times (14 - 180 days) were investigated. The present research highlights the need for further examination and process optimization of different carbon-rich materials used for contaminant removal. Results have shown that the smallest dose (0.5 %) of investigated sorbents was sufficient to reduce the bioavailable fraction of PeCB below 5 %, and the ageing process after 14 days for AC and 30 days for HM and BC negligibly influenced the bioavailable fraction.

**Keywords:** sequestration, bioavailability, sediment, remediation, pentachlorobenzene

Available online at the Journal website: <http://www.ache.org.rs/HI/>

TECHNICAL PAPER

UDC:552.5:504:631.6

*Hem. Ind.* **73** (1) 63-71 (2019)

## 1. INTRODUCTION

Hydrophobic contaminants, such as persistent organic pollutants (POPs), have the ability to associate with fine-grained, organic-rich, sediment material. This association results in contamination of water/sediment system and if conditions in these systems are changed, POPs can be released and become available for uptake by benthic organisms. The term bioavailability represents the amount of a chemical pollutant available for biotransformation and toxicity. This concept is difficult to simplify and numerous scientists tried to define and redefine it [1-7]. Conventional environmental dredging techniques are invasive, expensive and often ineffective, so the management and clean-up of contaminated sediment is a challenging problem [8]. On the other hand, in situ techniques have the ability to isolate contaminants and reduce their maximal flux thus delaying their release to the open water. Active in situ techniques, based on binding, and not eliminating the bioavailable and mobile fraction of organic pollutants (like pentachlorobenzene), currently attract a great interest in the area of sediment quality [8-10].

Pentachlorobenzene (PeCB) has been proposed for inclusion in the Stockholm Convention and in the POPs protocol of the long-range transport of atmospheric pollutants (LRTAP) Convention of the United Nations Economic Community for Europe (UNECE). It was used as a representative chlorinated aromatic because it is frequently detected in sediments [11].

In some earlier studies, researchers observed that POPs may be associated with coal-derived and char particles, in which the compounds are strongly bound and therefore less bioavailable [8]. Addition of carbonaceous materials (such as activated carbons (AC) or biochars (BC)) or hummus (HM) and compost have been shown to significantly reduce pollutant concentrations and risks by binding organic chemicals present in the system sediment/water [12-15]. It is already proven that AC has a great potential for POPs removal. Carbon-rich materials like biochar and hummus have received increased attention in this respect during the past few decades. However, studies are mostly at a lab scale,

Correspondence: Jelena Beljin; University of Novi Sad Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovica 3, 21000 Novi Sad; Fax: +38121/454065

e-mail: [jelena.beljin@dh.uns.ac.rs](mailto:jelena.beljin@dh.uns.ac.rs)

Paper received: 14 November 2018

Paper accepted: 28 January 2019

<https://doi.org/10.2298/HEMIND1811140001G>



focusing on sorption of one or two targeted organic pollutants, while in different natural water/sediment systems coexist organic and inorganic pollutants and there is a competition among them for sorption sites on carbon-rich materials surfaces. Though BC has shown potentials for POPs removal from sediments, its production cost is still the main constraint for field application. Making it cost-effective is a key factor for biochar application in ex situ remediation.

This study is aimed to develop sustainable remediation strategies for sediments contaminated with POPs and to further investigate impacts of different sorbent addition. The more specific objectives of this study were: 1) to review characteristics of activated carbon, biochar and hummus to better understand their efficiency in organic sorption, (2) to investigate effects on sediment geochemistry by amending sediment with hummus, biochar and activated carbon in order to stabilize and sequester the contaminants; 3) to investigate the long-term effects of applied sediment amendments on PeCB bioavailability and 4) to identify problems and suggest directions for future research. Changes in bioavailability of PeCB were measured by using XAD4 Amberlate uptake.

## 2. MATERIALS AND METHODS

### 2. 1. Chemicals

Following chemicals were used in the experiment: amberlite XAD4 resin (Fluka, France), silica gel (Fluka, Switzerland), calcium-chloride (Sigma, Germany), potassium-carbonate (Merck, Germany) and mercury (II)-chloride (Centrochem, Serbia). Organic solvents: acetone (Honeywell, Germany), hexane (Panreac, Germany), pentachlorobenzene (Sigma, Germany) pentane and dichloromethane (Prochem, Germany) were at least of analytical grade. Carbon-rich amendments used in this study were active carbon (Norit, USA), biochar (Maxigrill, Serbia) and humus (Savacoop, Serbia).

### 2. 2. Sediment preparation

Sediment was collected from Jegrička river site in Autonomous Province of Vojvodina (Republic of Serbia). Sediment was air dried in the dark at room temperature, ground, sieved through a 2 mm sieve, spiked with PeCB and left to age 2 years in dark before the experiment. The final concentration of PeCB in the sediment after the two year period was  $3340 \pm 20.5 \mu\text{g kg}^{-1}$ .

### 2. 3. Methods for analysis and characterization

*Sediment and sorbents characterization.* Methods ISO 11277:2009 (wet sieving method)[16] and ISO 8245:1999 (loss of ignition at 550 °C)[17] were used for determination of the particle size distribution and total organic content in sediment, respectively. The surface carbon content in sediment and all investigated sorbents was analyzed by scanning electron microscope (SEM, Hitachi TM3030, Japan) with an energy-dispersive spectrometer (EDS, Bruker Quantax 70 X-ray detector system, Bruker, Germany), while the multi-point BET specific surface area was determined by nitrogen adsorption at 77 K by AutosorbIQ Surface Area Analyzer (Quantachrome Instruments, USA). Mesopore volumes ( $V_{\text{mes}}$ ) were derived from desorption isotherms using the BJH (Barrett–Joyner–Halenda) model. Micropore volumes of sorbents were calculated by t-test and Horwath-Kawazoe (HK) method.

*The total amount of PeCB.* The total amount of PeCB in the sediment and XAD4 resin were determined according to EPA3550B [18]. Elemental sulfur was removed with copper powder according to the EPA3660B method [19]. The samples were fractionated according to the procedure 3620B [20]. PeCB was analyzed using gas chromatography according to the EPA method 8270C [21].

### 2. 4 Sediment amendment with carbon rich sorbents

Sediment was treated by the amendment with a certain amount of appropriate sorbent (activated carbon (AC), biochar (BC) and hummus (HC)). For this purpose, 1 g of the spiked sediment was placed in 40 mL glass vials and AC, BC or HC were added in the next doses: 0.1; 0.5; 1; 5 and 10 wt% with respect to the carbon content in the sorbents given in Table 1. All experiments were done in triplicates. In order to prevent microbiological degradation of organic compounds during the experiment, 20 mL of a  $300 \text{ mg L}^{-1} \text{ HgCl}_2$  solution was added in the glass vials. Mixtures were thoroughly mixed and left to age for 14, 30, 90 and 180 days in the dark with daily mixing, in order to investigate short-term and the long-term effects of the amended sediments. The efficacy of sorbent amendment, with respect to the dose and aging time, was assessed by the bioavailability test using a desorption experiment with the XAD4 resin.

### 2.5 Desorption experiments

Preparation of the resin [22, 23]: the XAD4 resin was purified by Soxhlet extraction with ultra-pure water; methanol; mixture of hexane/acetone 1:1; methanol and finally ultra-pure water. Each extraction took 6 h. After that, 0.2 g of XAD4 beads and  $\text{CaCl}_2$  anhydrous powder (to achieve the amount of 5 mmol  $\text{CaCl}_2$ ) were added to each prepared

amended sediment mixture in 40 mL glass vials. The vials were shaken horizontally on an oscillator at 180 rpm for 2, 4, 6, 24, 48, 96 and 144 h (25 °C). In order to facilitate separation of the resin, at selected times 0.8 g of K<sub>2</sub>CO<sub>3</sub> powder was added into the vials to increase density of the aqueous phase. The XAD4 beads were refreshed, rinsed 2 times with deionized water, and subjected to ultrasonic extraction 3 times with 10 mL of hexane/acetone (1:1, v/v). The combined extracts were then cleaned and concentrated to 1mL for analysis of PeCB.

A two compartments model was used to describe a two-stage process of desorption of PeCB [24]:

$$\frac{S_t}{S_0} = F_{\text{fast}} e^{-k_{\text{fast}}t} + F_{\text{slow}} e^{-k_{\text{slow}}t}$$

$$F_{\text{fast}} + F_{\text{slow}} = 1$$

where,  $S_t$  and  $S_0$  represent the amount of sediment-sorbed contaminant at time  $t$  and time zero, respectively. The  $F_{\text{fast}}$  and  $F_{\text{slow}}$  are fractions of the chemical compound in the rapid and slow desorbing phases at time zero, and  $k_{\text{fast}}$  and  $k_{\text{slow}}$  are the corresponding desorption rate constants, respectively. It is important to note that these compartments are operationally defined and that in reality desorption rates represent a continuum of values. For desorption modeling, the software Origin Lab (free version, OriginLab Corp., MA) was used.

### 3. RESULTS AND DISCUSSION

#### 3. 1. Sediment and sorbents characterization

The sediment used in this study had 31.6 % of clay, 11.9 % of silt and 15.6 % of coarse sand determined by the wet sieving method ISO 11277:2009. The total pore volume was 0.77 cm<sup>3</sup>g<sup>-1</sup> and pH value 7.26. The obtained TOC and BET specific surface area values were 2.90 % and 20.3 m<sup>2</sup>g<sup>-1</sup> respectively, while SEM analyses showed that the examined sediment had 39.7 wt% O, 7.24 wt% C and 53.06 wt% other compounds (Fig. 1a).

The structural and surface characterization of the investigated sorbent materials (AC, BC and HC) is shown in Table 1. As it can be expected, the highest TOC and carbon surface content values had AC. In addition, BET and porosity decreased from AC (690 m<sup>2</sup>g<sup>-1</sup> and 0.25 cm<sup>3</sup>g<sup>-1</sup>, respectively), HC (2.06 m<sup>2</sup>g<sup>-1</sup> and 0.014 cm<sup>3</sup>g<sup>-1</sup>, respectively) to BC (0.897 m<sup>2</sup>g<sup>-1</sup> and 0.007 cm<sup>3</sup>g<sup>-1</sup>, respectively). Characterization of BC and HC using the t-test method showed absence of micropores, while for AC the micropore volume was 0.18 cm<sup>3</sup>g<sup>-1</sup>. However, the HK method showed the presence of micropores in all investigated sorbent materials (Table 1). Based on the obtained results, AC has a microporous structure, while HC and BC consist mainly of mesopores. Besides that, additional information on the surface chemistry of all investigated sorbents is shown in SEM images in Figure 1 (b,c,d).

Table 1. Physical characterization of investigated sorbents

	AC	BC	HC
TOC, %	83.3	75.4	18.5
Content of O, wt%	10.6	18.4	44.0
Content of C, wt%	83.4	81.0	43.3
Content of other elements, wt%	6.00	0.63	12.7
BET specific surface areas, m <sup>2</sup> g <sup>-1</sup>	690	0.897	2.06
BJH pore volume, cm <sup>3</sup> g <sup>-1</sup>	0.25	0.007	0.014
Micropore volume - t test, cm <sup>3</sup> g <sup>-1</sup>	0.18	0	0
Micropore volume - HK method, cm <sup>3</sup> g <sup>-1</sup>	0.20	0.0003	0.0007
Total pore volume, cm <sup>3</sup> g <sup>-1</sup>	0.52	0.006688	0.01
Average pore radius, nm	1.52	149	13.9

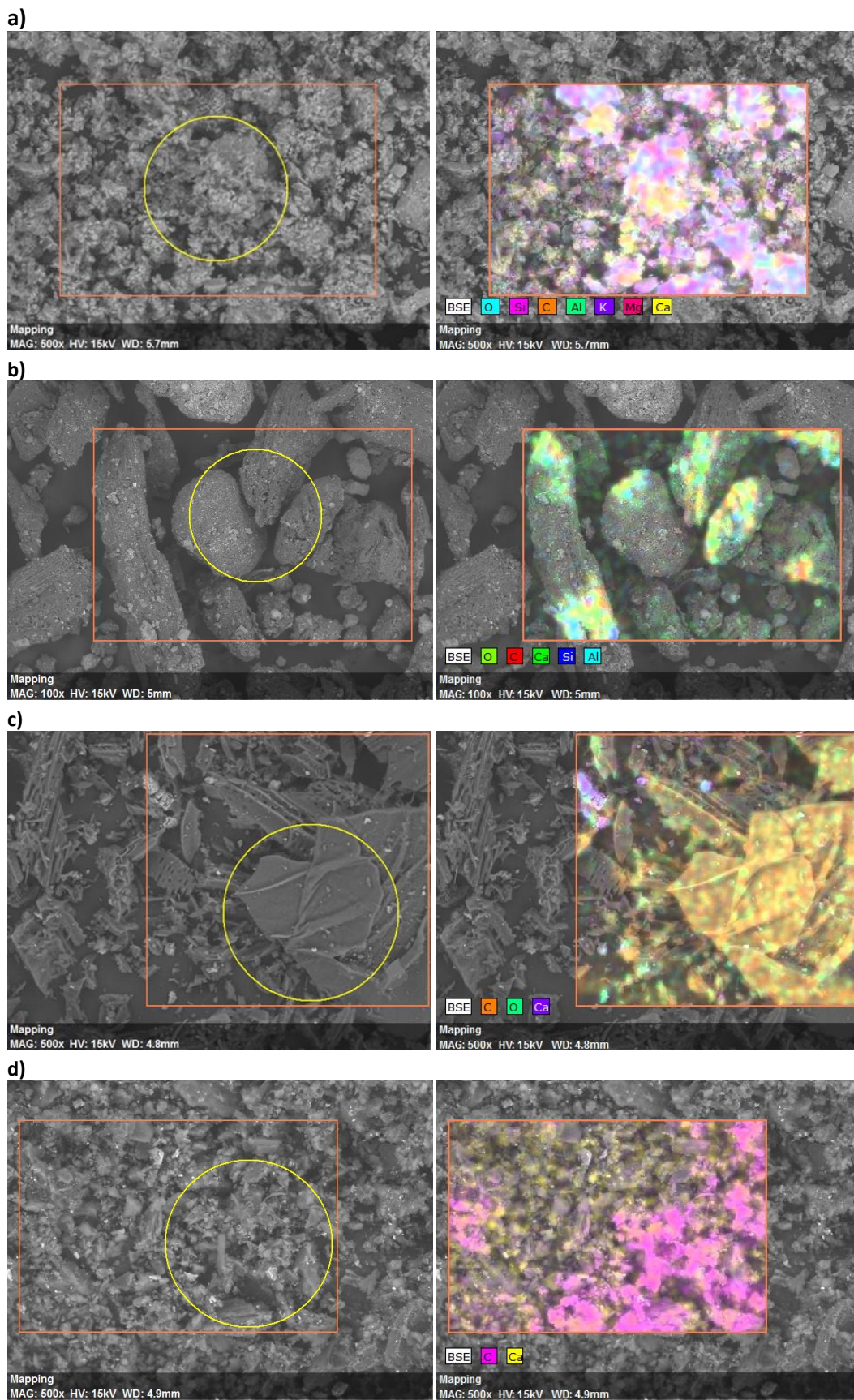


Figure 1. The structural and surface characterization of sediment (a), humus (b), biochar (c) and activated carbon (d) (\*MAG = magnification)

### 3.2. Pentachlorobenzene desorption from the unamended sediment

The total amount of the desorbed PeCB from sediment by XAD4 beads was  $3333 \pm 20.7 \mu\text{g kg}^{-1}$ , which represents 99.8 % of the total PeCB quantity (Fig. 2). The obtained desorption results were modelled according to the two compartments model using the OriginLab software, where  $F_{\text{fast}}$  is generally considered as a readily bioavailable fraction [22-27]. Hua *et al.* [25] reported that the XAD beads have a large sorption capacity for POPs. Obtained results in the present study indicate that, even though the sediment aged for two years, almost all present content of PeCB can be released from the sediment and become bioavailable for uptake through the food chain. As it is stated earlier, it is extremely important to evaluate the available fraction of a pollutant. Estimation of bioavailability is traditionally performed by using biodegradation and accumulation in organism tissues. However, these methods have some limits and the need arises for developing rapid, accurate, compound specific, cheap and environmental-friendly methods such as chemical tests [7]. The desorption test of PeCB in the unamended sediment showed that equilibrium was quickly achieved within 1 day with 38.2 % of PeCB in the fast desorbing domain of organic matter ( $F_{\text{fast}}$ ) (Fig. 2).

### 3.3. Effects of AC, BC and HC amendments on PeCB desorption from sediment

The reduced PeCB availability in AC, BC or HC amended sediments is manifested in the XAD4beads uptake data [28-30]. Addition of all three sorbents individually reduces the ecological risk of PeCB that was present in the examined sediment, which is a crucial issue in the process of remediation [29-32]. Figure 3 shows that the extracted amount of PeCB decreased in all sediment/AC, sediment/BC and sediment/HC treatments after 180 days. At the lowest dose of AC, potentially bioavailable PeCB concentration was  $49.1 \pm 2.45 \mu\text{g kg}^{-1}$ . Increasing the doses from 0.5 wt%, to 1, 5 and 10 wt% the potentially bioavailable amount is reduced to  $36.9 \pm 1.84$ ,  $9.76 \pm 0.49$  and  $2.69 \pm 0.134 \mu\text{g kg}^{-1}$ , respectively. In the sediment/HC treatments, as well as in the BC treatments, increasing the sorbent doses did not lead to the reduction of PeCB uptake by XAD4. The desorbed amount was about  $135 \mu\text{g kg}^{-1}$  for all used doses. Generally, all three sorbents have been shown as good materials for capping the examined pollutant at the concentration 0.5 wt%, although the AC treatment gave the best results with the dose of 10 wt%. Some authors reported that sorption capacity for reduction of HOCs in sediment was determined mainly by the surface area and content of organic carbon [33,34], while others claim that decreasing the surface area does not lead to a decrease in the sorption performance [35-37].

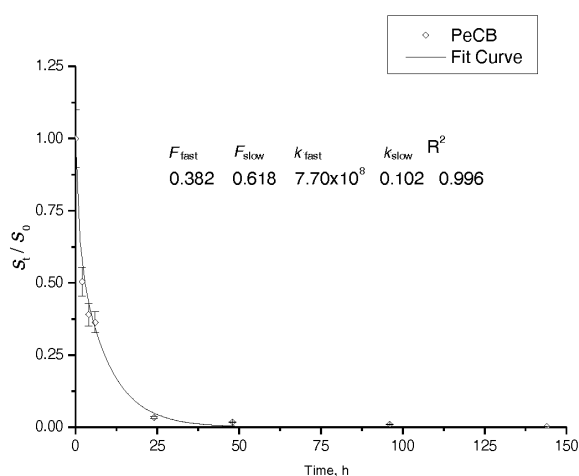


Figure 2. Desorption kinetic modeling by the two-compartment model for the unamended sediment: experimental data (symbols) and model predictions (line) (the units for kinetic rate constants are  $\text{h}^{-1}$ )

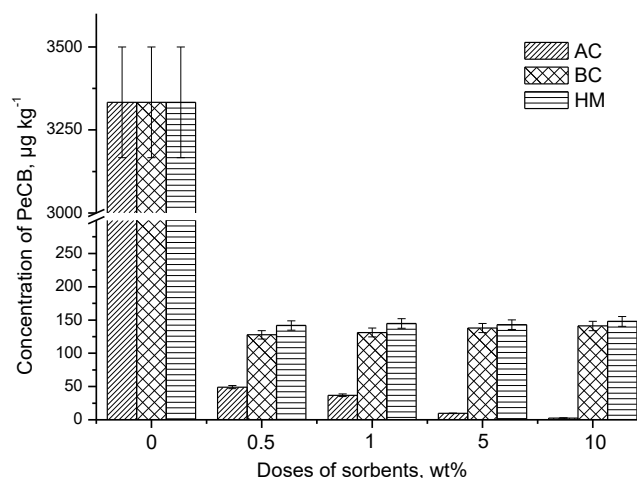


Figure 3. Amounts of PeCB uptaken by XAD4 from sediments without and with sorbent addition

### 3.4. Effects of contact time between sorbents and sediment on potentially bioavailable PeCB fraction

Assuming that aging of the sediment with AC, BC and HM affects the bioavailability, it was expected that the increase in the adsorbent dose and time will result in reduction of the bioavailable fraction (Fig. 4). A good correlation was observed for all three sorbents that were used. Addition of AC in the dose of 0.5 wt%, after 30 days reduced the potentially bioavailable fraction up to almost  $200 \mu\text{g kg}^{-1}$  (compared to the 14 days treatment). After that time, the bioavailable fraction was not further significantly reduced. The same observation can be made for addition of 1 wt% AC. For treatments with 5 and 10 wt% AC it can be concluded that after 14 days the XAD4 uptake is already reduced. After that time, the pollutant stayed sorbed onto AC. Regarding the sediment/BC and sediment/HC treatments, after 30 days the XAD4 uptake was not further reduced so that it can be concluded that the pollutant stayed sorbed (Fig. 4). Some

previous studies have shown that regardless the carbon type, an increase in the contact time between the sorbent and sediment caused a further reduction of the bioavailable fraction, as compared to the untreated sediment [25]. However, in the present study after 14 and/or 30 days in all treatments, sorbents achieved their maximum and prolonging the time did not lead to further sorption or desorption. These results are in agreement with some previous studies [38-42].

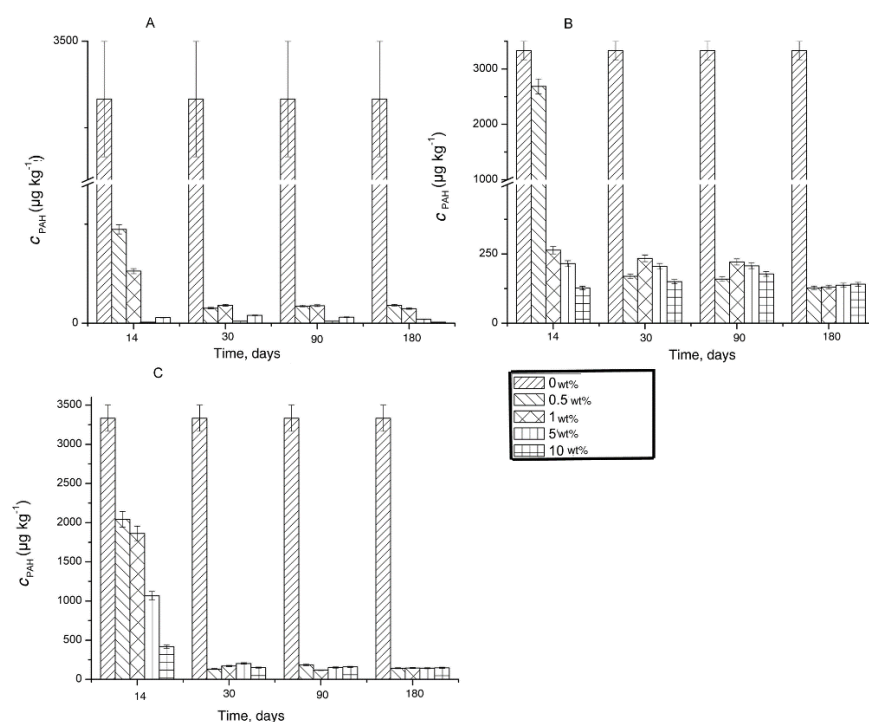


Figure 4. Amounts of PeCB uptaken by XAD4 at different time periods from sediments treated with AC (A), BC (B) and HC (graph C) (0 wt% (without sorbents) was measured only once, in the beginning of the experiment)

The mechanism itself is explained in several research and review papers [13,43-45]. The most probable mechanism of PeCB binding to nanopores of carbonaceous materials is by  $\pi$ - $\pi$  bonds with its graphene surface, which results in an irreversible binding of PeCB to the sorbents and reduction of the extractable fraction. These results are consistent with the mechanism of sorption of highly hydrophobic, persistent organic pollutants with planar structures by soot and soot-like carbon particles [14,45-48].

#### 4. CONCLUSION

The present research highlights the need for further examination and process optimization of different carbon-rich materials used for contaminant removal. The smallest dose (0.5 wt%) of investigated sorbents was sufficient to reduce the bioavailable fraction of PeCB below 5 wt%, and the ageing process after 14 days for AC and 30 days for HM and BC did not affect significantly the bioavailable fraction. By observing the sorbent prices, it can be concluded that satisfactory results can be obtained by BC or HM, which are available in wholesale for acceptable price. Without a doubt the effect of addition of different sorbents to sediments requires further research. However, before direct application, properties and impact of these materials on sediment characteristics and long-term effects on microbial ecology should be investigated. This might be worth proving under field conditions, aiming to evaluate the process efficiency in a real system.

*Acknowledgement:* The authors acknowledge the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, in the frame of projects: Improvement of sediment remediation technologies to protect water (TR37004) and Improving remediation technologies and the development of methods for risk assessment of contaminated sites (III43005).

#### REFERENCES

- [1] Alexander M. Aging, bioavailability and overestimation of risk from environmental pollutants. *Environ Sci Technol.* 2000; 34(20): 4259-4265.
- [2] Bonten LTC, Grotenhuis TC, Rulkens WH. Enhancement of PAH biodegradation in soil by physicochemical pretreatment. *Chemosphere.* 1999; 38(15): 3627-3636.

- [3] Mueller JG, Cerniglia CE, Pritchard PH. Bioremediation of environments contaminated by polycyclic aromatic hydrocarbons. In: Crawford RL, Crawford DL, ed., *Bioremediation: Principles and Applications*, Biotechnology Research Book 6, Cambridge University Press. 1996: 125–194.
- [4] Semple KT, Doick KJ, Wick LY, Harms H. Review microbial interactions with organic contaminants in soil: definitions, processes and measurement. *Environ Pollut.* 2007; 150: 166–176.
- [5] Wu G, Kechavarzi C, Li X, Wu S, Pollard SJT, Sui H, Coulon F. Machine learning models for predicting PAHs bioavailability in compost amended soils. *Chem Eng J.* 2013; 223: 747–754.
- [6] Cachada A, Pereira R, Ferreira da Silva E, Duarte AC. The prediction of PAHs bioavailability in soils using chemical methods: state of the art and future challenges. *Sci Total Environ.* 2014; 472: 463–480.
- [7] Wu G, Li X, Kechavarzi C, Sakrabani R, Sui H, Coulon F. Influence and interactions of multi-factors on the bioavailability of PAHs in compost amended contaminated soils. *Chemosphere.* 2014; 107: 43–50.
- [8] Cho YM, Smithenry DW, Ghosh U, Kennedy AJ, Millward RN, Bridges TS, Luthy RG. Field methods for amending marine sediment with activated carbon and assessing treatment effectiveness. *Mar Environ Res.* 2007; 64: 541–555.
- [9] Chi J, Liu H. Effects of biochars derived from different pyrolysis temperatures on growth of *Vallisneria spiralis* and dissipation of polycyclic aromatic hydrocarbons in sediments. *Ecol Eng.* 2016; 93: 199–206.
- [10] Rakowska MI, Kupryianchuk D, Harmsen J, Grotenhuis T, Koelmans AA. In situ remediation of contaminated sediments using carbonaceous materials. *Environ Toxicol Chem.* 2012; 31: 693–704.
- [11] Bailey RE, van Wijk D, Thomas PC. Review Sources and prevalence of pentachlorobenzene in the environment. *Chemosphere.* 2009, 75: 555–564.
- [12] Fang J, Zhan L, Ok YS, Gao B. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. *J Ind Eng Chem.* 2018; 57: 15–21.
- [13] Kah M, Sigmund G, Xiao F, Hofmann T. Sorption of ionizable and ionic organic compounds to biochar, activated carbon and other carbonaceous materials. *Water Res.* 2017; 124: 673–692.
- [14] Tričković J, Ivančev-Tumbas I, Dalmacija B, Nikolić A, Trifunović S. Pentachlorobenzene sorption onto sediment organic matter. *Org Geochem.* 2007; 38: 1757–1769.
- [15] Vítková M, Dercová K. The application of humic acids as natural sorbents for bioremediation of soils contaminated with pentachlorophenol (PCP) [https://is.stuba.sk/student/prilohy\\_zp.pl?download\\_priloha=20975;lang=sk;studium=64779;zp=22-388;verejny=1](https://is.stuba.sk/student/prilohy_zp.pl?download_priloha=20975;lang=sk;studium=64779;zp=22-388;verejny=1)
- [16] ISO 11277:2009 - Soil quality - Determination of particle size distribution in mineral soil material - Method by sieving and sedimentation. 2009.
- [17] ISO 8245:1999 - Water quality — Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). 1999.
- [18] USEPA, Method 3550B: Ultrasonic Extraction. 1995.
- [19] USEPA, Method 3660B: Sulfur Cleanup. 1996.
- [20] USEPA, Method 3620B: Florisil Cleanup. 1996.
- [21] USEPA, Method 8270C: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). 1996.
- [22] Spasojević JM, Maletić SP, Rončević SD, Radnović DV, Čučak DI, Tričković JS, Dalmacija BD. Using chemical desorption of PAHs from sediment to model biodegradation during bioavailability assessment. *J Hazard Mater.* 2015; 283: 60–69.
- [23] Rončević S, Spasojević J, Maletić S, Jazić JM, Isakovski MK, Agbaba J, Grgić M, Dalmacija B, Assessment of the bioavailability and phytotoxicity of sediment spiked with polycyclic aromatic hydrocarbons. *Environ Sci Pollut Res.* 2016; 23: 3239–3246.
- [24] Cornelissen G, Riegerink H, Ten Hulscher DEM, Vrind BA, Van Noort PCM. A simple Tenax extraction method to determine the availability of sediment-sorbed organic compounds. *Environ Toxicol Chem.* 2001; 20: 706–711.
- [25] Hua S, Gong JL, Zeng GM, Yao FB, Guo M, Ou XM. Remediation of organochlorine pesticides contaminated lake sediment using activated carbon and carbon nanotubes. *Chemosphere.* 2017; 177: 65–76.
- [26] Dubey RK, Tripathi V, Singh N, Abhilash PC. Phytoextraction and dissipation of lindane by *Spinacia oleracea* L. *Ecotoxicol Environ Saf.* 2014; 109: 22–26.
- [27] Schrap SM, Sleijpen GLG, Seinen W, Opperhuizen A. Sorption Kinetics of Chlorinated Hydrophobic Organic Chemicals, Part II Desorption Experiments. *Environ Sci Pollut Res.* 1994; 1(2): 81–92.
- [28] Cornelissen G, Van Noort PCM, Govers HAJ. 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.* 1997; 16: 1351–1357.
- [29] Ghosh U, Luthy RG, Cornelissen G, Werner D, Menzie CA. In-situ sorbent amendments: A new direction in contaminated sediment management. *Environ Sci Technol.* 2011; 45: 1163–1168.
- [30] Birdwell J, Cook RL, Thibodeaux LJ. Desorption kinetics of hydrophobic organic chemicals from sediment to water: A review of data and models. *Environ Toxicol Chem.* 2007; 26(3): 424–434.
- [31] Brennan A, Moreno Jiménez E, Alburquerque JA, Knapp CW, Switzer C. Effects of biochar and activated carbon amendment on maize growth and the uptake and measured availability of polycyclic aromatic hydrocarbons (PAHs) and potentially toxic elements (PTEs). *Environ Pollut.* 2014; 193: 79–87.

- [32] Chai Y, Currie RJ, Davis JW, Wilken M, Martin GD, Fishman VN, Ghosh U. Effectiveness of Activated Carbon and Biochar in Reducing the Availability of Polychlorinated Dibenzo-p-dioxins/ dibenzofurans in Soils. *Environ Sci Technol.* 2012; 46: 1035–1043.
- [33] Josko I, Oleszczuk P, Pranagal J, Lehmann J, Xing B, Cornelissen G. Effect of biochars, activated carbon and multiwalled carbon nanotubes on phytotoxicity of sediment contaminated by inorganic and organic pollutants. *Ecol Eng.* 2013; 60: 50–59.
- [34] Oleszczuk P, Hale SE, Lehmann J, Cornelissen G. Activated carbon and biochar amendments decrease pore-water concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. *Bioresour Technol.* 2012; 111: 84–91.
- [35] Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, Vithanage D, Lee SS, Ok YS. Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere.* 2014; 99: 19–33.
- [36] Rajapaksha AU, Chen SS, Tsang DCW, Zhang M, Vithanage M, Mandal S, Gao B, Bolan NS, Ok YS. Review Engineered/designer biochar for contaminant removal/immobilization from soil and water: Potential and implication of biochar modification. *Chemosphere.* 2016; 148: 276–291.
- [37] Li H, Dong X, da Silva EB, de Oliveira LM, Chen Y, Ma LQ. Review Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. *Chemosphere.* 2017; 178: 466–478.
- [38] Janssen EML, Oen AMP, Luoma SN, Luthy RG. Assessment of field-related influences on polychlorinated biphenyl exposures and sorbent amendment using polychaete bioassays and passive sampler measurements. *Environ Toxicol Chem.* 2011; 30: 173–180.
- [39] Jonker MTO, Hoenderboom AM, Koelmans AA. Effects of sedimentary sootlike materials on bioaccumulation and sorption of polychlorinated biphenyls. *Environ Toxicol Chem.* 2004; 23: 2563–2570.
- [40] Millward RN, Bridges TS, Ghosh U, Zimmerman JR, Luthy RG. Addition of activated carbon to sediments to reduce PCB bioaccumulation by a polychaete (*Neanthes arenaceodentata*) and an amphipod (*Leptocheirus plumulosus*). *Environ Sci Technol.* 2005; 39: 2880–2887.
- [41] McLeod PB, Luoma SN, Luthy RG. Biodynamic modeling of PCB uptake by *Macomabalthica* and *Corbicula fluminea* from sediment amended with activated carbon. *Environ Sci Technol.* 2008; 42: 484–490.
- [42] Sun XL, Ghosh U. PCB bioavailability control in *Lumbricus variegatus* through different modes of activated carbon addition to sediments. *Environ Sci Technol.* 2007; 41: 4774–4780.
- [43] Cornelissen G, Gustafsson O, Bucheli TD, Jonker MTO, Koelmans AA, Van Noort PCM. Extensive Sorption of Organic Compounds to Black Carbon, Coal, and Kerogen in Sediments and Soils: Mechanisms and Consequences for Distribution, Bioaccumulation, and Biodegradation. *Environ Sci Technol.* 2005; 39: 6881–6895.
- [44] Dongqiang Z, Pignatello J. Characterization of Aromatic Compound Sorptive Interactions with Black Carbon (Charcoal) Assisted by Graphite as a Model. *Environ Sci Technol.* 2005; 39: 2333–2041.
- [45] Vasilyeva GK, Strijakova ER, Nikolaeva SN, Lebedev AT, Shea PJ. Dynamics of PCB removal and detoxification in historically contaminated soils amended with activated carbon. *Environ Pollut.* 2010; 158: 770–777.
- [46] Bucheli TD, Gustafsson O. Soot sorption of non-ortho and ortho substituted PCB. *Chemosphere.* 2003; 53: 515–522.
- [47] Zhu D, Pignatello JJ. Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. *Environ Sci Technol.* 2005; 39: 2033–2041.
- [48] Burgess RM, Ryba SA, Cantwell MG, Gundersen GL, Tyen R. Interaction of planar and nonplanar organic contaminants with coal fly ash: effects of polar and nonpolar solvent solutions. *Environ Toxicol Chem.* 2006; 25: 2028–2037.



**SAŽETAK****Sekvestracija pentahlorbenzena u sedimentu primenom sorbenata bogatih ugljenikom**

Marko Grgić<sup>1</sup>, Jelena Beljin<sup>1</sup>, Snezana Maletić<sup>1</sup>, Marijana Kragulj Isakovski<sup>1</sup>, Jelena Tričković<sup>1</sup>, Tijana Zeremski<sup>2</sup>, Srđan Rončević<sup>1</sup>

<sup>1</sup>Univerzitet u Novom Sadu, Prirodno-matematički fakultet, Departman za hemiju, biohemiju i zaštitu životne sredine, Trg Dositeja Obradovića 3, 21000 Novi Sad

<sup>2</sup>Institut za ratarstvo i povrtarstvo, Maksima Gorkog 30, 21000 Novi Sad

(Stručni rad)

Prisustvo organskih polunatanata, kao što je pentahlorbenzen (PeCB) predstavlja problem širom sveta. Sediment se ponaša kao rezervoar za hidrofobne, toksične, perzistentne i bioakumulativne organske komponente. PeCB može da podleže procesima sorpcije, desorpcije, kao i transformacionim procesima, te može postati biodostupan vodenim organizmima. U cilju smanjenja rizika, ova studija imala je za cilj procenu efikasnosti doze i kontaktnog vremena između sedimenta i nekoliko sorbenata bogatih ugljenikom (aktivni ugalj (AC), biougalj (BC) i humus (HM)) na proces detoksifikacije sedimenta. Ispitivane su četiri doze sorbenata (0.5-10 %) i četiri vremena (14-180 dana). Dobijeni rezultati su pokazali da je pri najmanjoj dozi od 0.5 % za sve upotrebljene sorbente biodostupna frakcija smanjena ispod 5 % i da se procesom starenja nakon 14 dana za AC i 30 dana za HM i BC biodostupna količina PeCB ne povećava.

*Ključne reči:* starenje, biodostupnost, sediment, remedijacija, pentahlorbenzen