Journal of Hazardous Materials Advances 20 (2025) 100918

Contents lists available at ScienceDirect

Journal of Hazardous Materials Advances

journal homepage: www.elsevier.com/locate/hazadv

Evaluating the role of biochar in the transport behavior of chlorinated phenols in alluvial soil systems

Tamara Apostolović [a,†], Marijana Kragulj Isakovski [a,†], Marko Šolić [a], Jelena Beljin [a], Lutz Weihermüller [b], Snežana Maletić [a,*]

[a] University of Novi Sad, Faculty of Sciences, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia
[b] Institute of Bio- and Geosciences - IBG-3, Agrosphere Institute, Forschungszentrum Jülich GmbH, Jülich, Germany

ARTICLE INFO

Keywords:
Biochar
Chlorinated phenols
Soil transport
Retention mechanisms

ABSTRACT

This study investigates the influence of soil properties and biochar amendments on the transport behavior of chlorinated phenols (CPs) in alluvial soil systems. The primary focus was to evaluate the adsorption mechanisms governing CP mobility and retention, with particular attention to how the physicochemical properties of the native and biochar-amended soils interact with the molecular characteristics of CPs, such as hydrophobicity, molecular weight, and ionization potential. Therefore, column experiments with an alluvial soil and biochar amended soil were conducted to evaluate the transport of four types of CPs. The advection-dispersion equation (ADE) was used to calculate the retardation factor (R_d). The primary retention mechanisms identified in alluvial soils were hydrophobic, polar, and electron-donor-acceptor interactions, rather than charge-based attractions, though exceptions, such as for pentachlorophenol, were noted. The chemical properties of CPs, including acid dissociation constant (pK_a), molecular weight, and hydrophobicity, played a crucial role in their transport behavior. The addition of biochar significantly enhanced CP retention, increasing breakthrough times by a factor of 12 to 40 and yielding R_d values between 42 and 155. A strong correlation was found between retention and molecular polarizability. Furthermore, addition of biochar into the soil modified the type of interaction from hydrophobic to polar impact on CPs retention during the transport. These findings underscore the potential for mitigating organic pollutant leaching by biochar amendment, highlighting that effectiveness depends on both the physical-chemical properties of the soil/amendment and the physicochemical characteristics of the pollutants. The research emphasizes biochar's role in environmental remediation, particularly in controlling the migration of organic pollutants and protecting ground- and surface water quality. Additionally, the study evaluates biochar's structural and functional properties, underscoring its potential to immobilize hydrophobic and slightly polar contaminants.

Introduction

The increasing demand for clean drinking water, fueled by population growth and industrial expansion, underscores the urgent need for sustainable and cost-effective water treatment solutions. While advanced technologies such as adsorption, ion exchange, membrane filtration, and advanced oxidation processes are highly efficient, their adoption is often limited in developing regions due to the high costs associated with infrastructure and maintenance. In this context, River Bank Filtration (RBF) systems have emerged as a viable alternative. RBF leverages natural processes to enhance surface water quality by using soil and aquifer materials as natural filters, reducing the reliance on complex treatment systems (Kumar et al., 2018; Majeed et al., 2024).

At the core of RBF's effectiveness is the process of geosorption, where pollutants are retained by geosorbents - a mix of mineral and organic components within the soils. The composition of these geosorbents plays a critical role in determining their pollutant retention capacity. The organic fraction of geosorbents primarily interacts with nonpolar pollutants like chlorinated phenols (CPs) through hydrophobic interactions. When the organic carbon content exceeds 0.2 %, it becomes the dominant factor in pollutant retention (Ehlers and Loibner, 2006). In contrast, the mineral fraction, consisting of oxides, hydroxides, and clay

---

* Corresponding author.
E-mail address: snezana.maletic@dh.uns.ac.rs (S. Maletić).
† Tamara Apostolović and Marijana Kragulj Isakovski contributed to this paper equally and share first authorship.

https://doi.org/10.1016/j.hazadv.2025.100918
Received 22 August 2025; Received in revised form 15 October 2025; Accepted 16 October 2025

minerals, predominantly retains polar or ionized pollutants via electrostatic and surface charge interactions, particularly when organic carbon levels are below 0.1 % (Otter et al., 2019; Worch, 2012).

CPs are a group of priority pollutants characterized by their toxicity, persistence, and resistance to biodegradation. These compounds are widely introduced into the environment through industrial effluents and the breakdown of pesticides such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,6-trichlorophenoxyacetic acid (2,4,6-T), which degrade into 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP). Other CPs, including 2-chlorophenol (2-CP) and pentachlorophenol (PCP), are commonly used as pesticides, herbicides, and fungicides. Once introduced into the environment, these pollutants can accumulate in surface and groundwater systems, posing significant risks to both aquatic ecosystems and human health (Cavender and O'Donohue, 2012).

The fate and transport of CPs during RBF vary based on their molecular structure. Polar CPs (e.g., with fewer chlorine atoms) are highly soluble, making them more mobile and prone to leaching into groundwater. In contrast, nonpolar CPs (e.g., with four or more chlorine atoms) tend to sorb onto soil particles, and therefore, reducing their mobility (Patil et al., 2024). This differentiation is crucial for predicting the behavior of CPs in RBF systems and for designing effective pollution mitigation strategies (Afridi et al., 2024). Despite RBF's potential, the persistence of CPs in water bodies remains a global concern. Studies have detected CPs in major water sources, such as the Danube River, with concentrations ranging from 1.64 to 155 ng/L, and in drinking water supplies across Canada, Finland, and Germany. In Canada, PCP was found in 20 % of tested drinking water samples, highlighting the widespread presence and environmental risk posed by CPs (Apostolović et al., 2020; Czaplicka, 2004; WHO, 2017).

To improve the pollutant removal efficiency of RBF, researchers are exploring the use of biochar as a soil amendment. Biochar, a carbon-rich material derived from biomass, has shown significant promise in enhancing the sorption capacity of soils due to its large surface area, high porosity, and diverse functional groups. It not only increases the retention of both polar and nonpolar pollutants but also helps in carbon sequestration and improves soil health by retaining nutrients and enhancing soil structure (Isakovski et al., 2024; Wang et al., 2024). Additionally, biochar introduces new adsorption mechanisms, including π-π interactions and van der Waals forces, which can significantly reduce the bioavailability of contaminants, and therefore, mitigating their toxic impacts on ecosystems (Isakovski et al., 2020; Muoghalu et al., 2023).

There has been a substantial progress in recent years in the field of tailoring biochar with the aim to enhance removal of chlorinated and other organic pollutants from water. Modified biochars (by metal oxides or magnetic particles doping, co-doping strategies or surface activation) have shown high potential in water purification, the removal efficiency for various contaminants in aqueus systems reaching up to 95 % (Trivedi et al., 2025). In addition, funtionalization of biochar and biochar composite materials (such as biochar-clay, biochar with π-conjugated structures) is highly effective in treating chlorinated organic pollutants in soil and water purification processes (Song et al., 2024). At the same time, while the positive effect of RBF on the quality of groundwater is not questionable, research show that there are uncertainties in organic micropollutant removal, especially regarding the transport of compounds governed by heterogeneous travel times and interations with soil and water (Kondor et al., 2024). More recently, strategies coupling RBF with biofilm-regulated nanofiltration as an additional barrier have been proposed, resulting in enhanced performance in selectively removing natural organic matter and trace organic compounds (Li et al., 2025). Despite significant advances in this field, research linking biochar structural properties (surface area, functional groups) and soil properties to the transport and retardation behaviour of chlorinated phenols in river alluvial soil is scarce, leaving a knowladge gap addressed in this study.

The primary aim of this study is to investigate the impact of soil properties and biochar amendments on the retardation and transport behavior of chlorinated phenols in alluvial soil systems. Specifically, the study focuses on elucidating the underlying adsorption mechanisms and exploring how these interactions influence CPs mobility and retention. By examining the physicochemical properties of the native and biochar-amended soils, the research aims to understand how soil and biochar properties interact with the molecular characteristics of CPs, including hydrophobicity, molecular weight, and ionization potential, to modulate their transport dynamics.

This research addresses a critical knowledge gap by providing a mechanistic understanding of how biochar amendments alter the sorption processes of CPs in soils. One of the study's key innovations is the use of Principal Component Analysis (PCA) biplot analysis to investigate the complex interactions between soil/biochar properties and CP characteristics.

Furthermore, the study systematically evaluates biochar's structural and functional properties, providing valuable insights into its optimization for immobilizing both hydrophobic and slightly polar contaminants. By demonstrating biochar's potential to enhance the efficacy of riverbank filtration and other remediation strategies, the research highlights its role in sustainable soil management and pollutant mitigation. The comprehensive analysis fills existing gaps in understanding how biochar's properties—such as surface area, porosity, and functional groups - can be tailored to improve the retention of diverse organic contaminants in various soil matrices, offering new strategies for effective environmental remediation.

Materials and methods

Selected organochlorine phenols

Four chlorinated phenols - 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and pentachlorophenol (PCP)—demonstrate distinct environmental behaviors due to variations in hydrophobicity, molecular size, and chlorine atom content (Table 1). As chlorine substitution increases, the n-octanol-water partition coefficient ($\log K_{\mathrm{OW}}$) rises, enhancing the compounds' affinity for solid matrices like soils, sediments, and biological tissues.

The dissociation behavior of these phenols listed in Table 1 depends on the solution pH relative to their dissociation constant. Under the experimental conditions with a constant pH of 6.9, those phenols (4-CP, 2,4-DCP, and 2,4,6-TCP) with pK_a values of 7.42 to 8.85 predominantly exist in their associated (non-ionized) forms, while PCP ($pK_a = 4.74$) is primarily dissociated. This differential ionization affects their mobility and interaction with the environment. The increasing chlorine substitution also amplifies the electron-accepting nature of these compounds by reducing electron density on the aromatic ring, which diminishes their electron-donating properties. Consequently, higher chlorination enhances interactions with electron-deficient substances, impacting persistence and bioaccumulation. PCP, in particular, is recognized as a priority hazardous substance due to its toxicity and carcinogenic potential. Regulatory measures, such as the EU's environmental quality standards (EQS) (2013/39/EU), set strict limits for PCP concentrations in surface waters (AA-EQS: 0.4 μg/L; MAC-EQS: 1 μg/L) to mitigate risks. Recent research corroborates these findings, emphasizing the compounds' environmental persistence and highlighting advanced remediation methods like bioremediation and photolysis (2000/60/EC).

Soil and biochar samples

A sampling of the alluvial soil of the Danube River was conducted at the "Petrovaradinska ada" drinking water source near Novi Sad (45.261437 N, 19.866364 E). The sampling was carried out following the ISO 10381-2:2002 and ISO 18512:2007 methods. For the sampling, an impact drilling set for heterogeneous soils manufactured by Eijkelkamp Agrisearch Equipment (Giesbeek, Netherlands) was used.

Table 1
Physico-chemical properties of chlorinated phenols taken from Apostolović et al. (2020).

Compounds	*MW*	logK_{OW}	S_w	pK_a	A_i	B_i	S_i	*p*
4-CP	129	2.40	27.1	8.85	0.67	0.23	0.72	0.230
2,4-DCP	163	3.20	4.50	7.68	0.78	0.19	0.84	0.140
2,4,6-TCP	197	3.69	0.800	7.42	0.82	0.08	1.01	0.030
PCP	266	5.01	0.014	4.74	0.97	0.00	0.88	0.0002

MW (g/mol) – molecular weight, logKOW - n-octanol/water partition coefficient, Sw (g/L) – solubility in water, pKa - acid dissociation constant, Ai – electron-acceptor character of molecule, Bi – electron-donor character of molecule, Si – polarizability, p (mmHg) – vapor density. 4-CP = 4-chlorophenol, 2,4-DCP = 2,4-dichlorophenol, 2,4,6-TCP = 2,4,6-trichlorophenol, and PCP = pentachlorophenol.

The sampling procedure involved extracting a vertical core/profile of the alluvial soil from a depth of 0–230 cm.

The first upper layer of the soil, from 0 to 50 cm, was discarded because it was determined that the characteristics of the surface layer are subject to significant changes due to external factors, primarily anthropogenic activities such as recreational use and natural processes like flooding, sedimentation, and riverbank erosion, and therefore, cannot be considered a representative sample. The remaining vertical profile, from 50 to 230 cm, was divided into layers of 20–30 cm thickness. In this way, six layers of alluvial soil were obtained, with their respective depths listed in Table S1 in the Supplementary materials.

The biochar used in the work is a commercially available product of the company Basna d.o.o. from Serbia and the methods used for the certification as well as the reported characteristics of this product are listed in Table 2.

Characterization of the soil layers and biochar

The characterization of alluvial Danube soil samples included saturated hydraulic conductivity (K_s), cation exchange capacity (CEC), organic matter (OM) content, total organic carbon (TOC) content, specific surface area (SSA), pore diameter and pore volume (PV), point of zero charge (pH$_{pzc}$), and elemental analysis. Particle size distribution (texture) was measured according to ISO 11277:2009, using a threshold of 63 μm as the lower limit for the sand fraction. Saturated hydraulic conductivity was assessed using EPA Method 9100 (US EPA, 1986a). CEC was determined following EPA Method 9080 (US EPA, 1986b) by sieving the sample (2 mm) and saturating binding sites with ammonium ions. OM was analyzed gravimetrically according to SRPS EN 12879:2007. TOC was measured with a TOC analyzer (liquiTOCII, Elementar, Germany) following ISO 10694:1995. SSA and pore volume (PV) were evaluated using nitrogen adsorption-desorption analysis (AutosorbTM iQ, Quantachrome Instruments, USA) at 77 K. SSA was calculated using the multi-point BET method, and mesopore volume with the Barrett-Joyner-Halenda (BJH) model. Micropore volume was derived using the V-t Method. pH$_{pzc}$ (point of zero charge) was determined using the salt addition method (Shah et al., 2015) by preparing soil suspensions in 0.1 M $NaNO_3$ and adjusting pH between 4 and 13. The pH$_{pzc}$ was identified as the initial pH where $\Delta pH = 0$ after 24 h. Elemental analysis (C, H, N, S) was performed using a Vario EL III CHNS analyzer with oxygen content calculated by difference.

Table 2
Methods and values obtained for biochar certification.

Parameter	Method	Unit	Undried	Dried
Specific surface area (BET)	DIN 66,137/DIN ISO 9277	m^2/g	/	341
Density	DIN 66,137/DIN ISO 9277	g/cm^3	/	1.7
Moisture	DIN 51,718:2002–06	% (w/w)	10.1	/
Ash content (550 °C)	DIN 51,719:1997–07	% (w/w)	5.8	6.4
C (total)	DIN 51,732:2014–07	% (w/w)	80.8	89.8
C (inorganic)	DIN 51,726:2004–06	% (w/w)	0.4	0.5
C (organic)	Calculated	% (w/w)	80.4	89.3
H	DIN 51,732:2014–07	% (w/w)	0.8	0.9
N (total)	DIN 51,732:2014–07	% (w/w)	0.36	0.40
S (total)	DIN 51,724–3:2012–07	% (w/w)	<0.03	<0.03
O	DIN 51,733:2016–04	% (w/w)	4.1	4.5
H/C_{org} molar ratio)	Calculated	/	0.12	0.12
O/C_{org} molar ratio)	Calculated	/	0.038	0.038
pH (in $CaCl_2$)	DIN ISO 10,390:2005–12	/	9.1	/

Parameters for biochar characterization are provided in Table 2, based on the corresponding certification and specified analytical methods.

In addition to the parameters from the certificate, the biochar characterization also included the determination of pH$_{pzc}$ (following the procedure described in the previous section) and the characterization of surface functional groups using Fourier-transform infrared spectroscopy (FTIR) (Nexus 670, Thermo Nicolet, USA).

Column experiments

Column experiments were conducted using stainless steel columns 20 cm in length and 4 cm in diameter. A specified mass of dried 2 mm sieved alluvial soil was added to the column from the top. Deionized water was simultaneously introduced from the bottom using a peristaltic pump (MasterflexR, Cole-Parmer Instrument Company, USA) to ensure homogeneous packing without trapping air bubbles and to avoid soil layering (Worch, 2012). The flow rate for saturation was set between 0.138 L/h and 0.576 L/h, with the flow directed from the bottom upwards, allowing 24 h for complete soil saturation (Apostolović et al., 2020; Isakovski et al., 2020 and 2024). These flow rates were determined based on the objective of the column experiments, which was to simulate bank filtration under conditions as close as possible to field conditions. The flow through each column was adjusted to reflect the hydraulic conductivity of the tested alluvial soil layer, as determined during the characterization of these layers. This approach resulted in significant variations in flow rates across individual layers.

After 24 h, a solution of non-sorbing thiourea in a synthetic matrix (4 mg/L) was passed through the column. This solution was used as a conservative tracer to assess the homogeneity of column packing and water flow through the soil columns. By using thiourea, which does not interact with the soil or its constituents, the movement of water can be tracked, and uniform saturation across the column can be confirmed. The tracer experiment was conducted at the same flow rate to maintain consistent conditions throughout the saturation and tracer application phases. By tracking the passage of thiourea, it is possible to evaluate whether the water is moving homogeneously through the soil columns or if there are preferential flow paths or heterogeneities. Drainage samples were collected at regular intervals to measure thiourea concentration using a UV spectrophotometer (UV/VIS, model UV-1800 Shimadzu, Japan) at 235 nm, until concentrations at the column outlet matched the initial concentration (steady-state flow conditions). Afterward, a solution of chlorinated phenols with the biocide NaN_3 (400 mg/L) was injected, with initial concentrations of 50 μg/L. pH was continuously measured at the outlet and was recorded as 6.9. The flow rate was directed from the bottom to the top and was consistent with the tracer experiments, ranging from 0.138 L/h to 0.576 L/h, depending on the layer. Drainage samples were collected at specific time intervals, and eluate concentrations were analyzed by GC after appropriate sample preparation, which included derivatization with acetic anhydride and hexane extraction. The analysis was conducted using a gas chromatograph with a mass spectrometer detector (Agilent 7890A/5975C, USA), as detailed in the Supplementary Materials.

The experiments were repeated in the same manner as for the native soils to investigate the transport of chlorinated phenols through columns containing alluvial soil enriched with 0.5 % (m/m) biochar. These experiments were performed for all six layers.

Solute transport modelling

The mathematical transport model employed relies on the analytical solution of the advection-dispersion equation (ADE), which accounts for both sorption and biodegradation using a first-order decay. The analytical solution of the ADE is represented in the following Eqs. (1–4) (Worch, 2006):

$$c(z,t) = \frac{c_0}{2} exp\left(\frac{v_c z}{2D^*}\right)\left\{ exp\left[-\frac{z\ F}{2\ D^*}\right] erfc\left[\frac{z - F\ t}{2\sqrt{D^*\ t}}\right] + exp\left[\frac{z\ F}{2\ D^*}\right] erfc\left[\frac{z + F\ t}{2\sqrt{D^*\ t}}\right]\right\} \tag{1}$$

The following parameters, *F*, v_c, and D^*, are included in Eq. (1):

$$F = \sqrt{v_c^2 + 4\ \frac{\lambda}{R_d} D^*} \tag{2}$$

$$v_c = \frac{v_w}{R_d} \tag{3}$$

$$D^* = \frac{D_{ax}}{R_d} \tag{4}$$

where $c(z,t)$ represents the concentration at position z and time t, v_c is the velocity of the transported substance, z is the spatial position, t is time, λ is the biodegradation rate, R_d is the retardation factor, v_w is the pore water velocity, and D_{ax} is the dispersion coefficient in the axial (longitudinal) direction.

Using this transport model, three key parameters were derived from each experimental breakthrough curve: R_d, λ, and α_{eff}. The retardation factor (R_d) determines the temporal position of the breakthrough curve and reflects the sorption behavior of the substances. When biodegradation occurs, the outlet concentration does not reach the initial input concentration. Under the specified process conditions, the plateau concentration level is governed by the biodegradation rate (λ). The effective dispersivity (α_{eff}) influences the steepness of the breakthrough curve. The raw data used for parameter estimation via the ADE is publicly available and can be accessed through the provided DOI 10.5281/zenodo.14135465.

Statistical analysis

The One-Way Analysis of Variance (ANOVA) was used to determine whether there were any significant differences between the replicates of the column experiments. For this analysis, all experiments were conducted in triplicates to ensure sufficient data for statistical comparison. The null hypothesis in the ANOVA test stated that there were no significant differences between the mean values of the replicates.

The statistical analysis was performed using Microsoft Excel with the Data Analysis Toolpak. After entering the data from the triplicate experiments, the One-Way ANOVA was applied to assess the variation between the replicate groups. A significance level of $p > 0.05$ was used, meaning that if the p-value exceeded 0.05, the null hypothesis could not be rejected, indicating no significant differences between the replicates.

Pearson's correlation and Principal Component Analysis (PCA) were performed using PAST 3.22 (Hammer et al., 2001) to explore the relationships between the physicochemical properties of the soils and chlorinated phenols and their retardation coefficients in unamended and biochar-amended alluvial soils. In order to evaluate the linear relationships between the observed retardation coefficients and the molecular properties of the studied compounds (MW, $\log K_{OW}$, Sw, pKa, Ai, Bi, Si, p), the Pearson's correlation was performed on three observations. PCA incorporated 25 variables, including soil properties (%OM, %Clay, TOC, CEC, K_s, SSA, TPV, pore radius, pH_{PZC}, %C, %H, %O, H/C, O/C, soil bulk density) and chlorinated phenols characteristics (MW, $\log K_{OW}$, Sw, pKa, Ai, Bi, Si, p), as well as the retardation coefficients obtained for all four chlorinated phenols, R_d (no BC) and R_d (with BC) derived from both experimental setups (unamended and amended soils, respectively). For the analysis, the R_d values obtained from the mean breakthrough curves of triplicate experiments were used. The primary objective of the PCA was to reduce the dimensionality of the data while retaining as much variance as possible, enabling the identification of key factors influencing chlorinated phenols retention mechanisms in soils amended with biochar. The resulting PCA biplot served as a visual tool to understand the relationships between the various physicochemical properties and their impact on CP retention.

Results and discussion

Detailed characterization of soil layers and biochar

The characterization of soil layers revealed a predominance of medium sand (0.2–0.8 mm, 70–93 %) across all layers, with fine sand particles (0.063–0.2 mm) comprising 5.5–18.2 % (Fig. 1). Layer 6 had the highest fine particle concentration, while coarse sand (<4 %) was more prevalent below 130 cm depth. Silt and clay contents were minor, with clay content ranging from 0.85 to 2.4 %, peaking in layer 6. These results confirm that the Danube alluvial soils are predominantly sandy, consistent with findings from studies by Sakan et al. (2010) and Kachova (2020). The K_s $2.90 \cdot 10^{-3}$ to $1.31 \cdot 10^{-2}$ cm/s matches values typically found in sandy soils, facilitating high water movement (Schoeneberger et al., 2012; Zhang and Schaap, 2019). The surface layers (up to 150 cm) generally had lower clay content (under 2.5 %), except for layer 6, where clay content was higher at 2.4 %.

Clay content and soil texture have a significant impact on the cation exchange capacity, as finer particles with greater surface areas enhance the soil's ability to retain cations. Across the sampled soil layers, CEC values ranged from 0.003 to 1.52 meq/100 g soil, with deeper layers showing higher CEC due to increased clay content (Table S2 in Supplementary Materials). Literature suggests that sandy soils typically have CEC values below 8 meq/100 g soil, while clay-rich soils often exceed 20 meq/100 g soil (Hendershot et al., 2007) pointing out that the sediments use here are in the low range of reported CEC values.

The bulk density of the soils was relatively homogeneous, ranging from 1.70 to 1.81 g/cm^3 (Table S2 in Supplementary Materials). Organic matter was uniformly low across all layers, remaining below 1 %, while TOC ranged from 0.06 % to 0.23 % (Table 3), increasing with depth.

The specific surface areas and pore volumes indicated a mesoporous soil, with pore diameters between 64.1 Å and 78.8 Å. SSA values ranged from 0.76 to 2.14 m^2/g (Table 3), with deeper layers exhibiting higher SSA due to increased clay and TOC content.

The point of zero charge of layers varied from 8.34 to 9.32 (Table S2 in Supplementary Materials), decreasing with depth. At pH values below the pH_{pzc}, soil particles are positively charged, attracting anions, while at higher pH, they carry a negative charge, favoring cation adsorption.

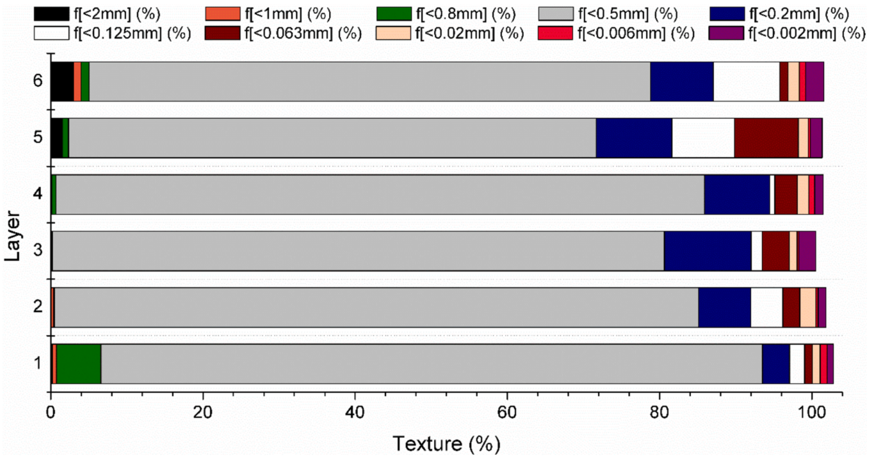

Fig. 1. Texture of the investigated soil layers.

Table 3
Physico-chemical characteristics of investigated soil layers.

Layer	Basic soil properties		Physical properties				Chemical properties, elemental analysis (%)						
	OM (%)	TOC (%)	SSA (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	*Av.* pore diameter (Å)	C	H	S	N	O	H/C	O/C
1	0.81	0.09	0.89	0.003	n.d.	71.0	1.19	0.10	<0.02	<0.02	1.46	1.05	0.93
2	0.52	0.06	0.87	0.003	n.d.	75.4	0.74	0.08	<0.02	<0.02	0.93	1.35	0.94
3	0.29	0.08	0.76	0.003	n.d.	71.7	1.79	0.13	<0.02	<0.02	1.79	0.87	0.75
4	0.69	0.06	1.59	0.004	n.d.	78.8	1.61	0.13	<0.02	<0.02	3.36	0.99	1.56
5	0.53	0.13	2.14	0.006	n.d.	76.1	1.84	0.16	<0.02	<0.02	1.28	1.02	0.52
6	0.72	0.23	2.09	0.005	n.d.	64.5	1.79	0.14	<0.02	<0.02	0.79	0.94	0.59

OM – organic matter, TOC – total organic carbon, SSA – specific surface area.

Under the experimental conditions (pH ~7), the surface exhibited a slight positive charge (Kosmulski, 2011; Worch, 2012).

Elemental analysis of the soils showed carbon content ranging from 0.74 % to 1.84 % (Table 3), with higher levels in deeper layers, which is in line with higher OM or TOC contents at deeper layers. Hydrogen content varied between 0.08 % and 0.16 %, while nitrogen and sulfur levels remained below 0.02 %. Oxygen content was calculated based on CHNS data and ranged from 0.79 % to 3.36 % (Table 3). The H/C molar ratio (below 1.5) indicated a high degree of unsaturation and a predominantly aromatic structure of the sediments, while the O/C ratio was higher in surface layers (0.75 to 1.56) compared to deeper ones (0.52 to 0.59), reflecting the greater abundance of oxygen-containing functional groups near the surface (Table 3).

Biochar characterization revealed a high specific surface area (341 m^2/g) and low H/C and O/C ratios. The biochar’s high pH_{pzc} (10.8) suggests a positively charged surface at pH 7, enhancing its interaction with soil species (Fig. 2a). The calculated H/C and O/C ratios were 0.12 and 0.038, respectively, indicating a highly unsaturated, aromatic structure with minimal polar oxygen functional groups, similar to the findings of Park et al. (2019) for biochars produced from lignocellulosic biomass at high pyrolysis temperatures. These low H/C and O/C ratios suggest extensive carbonization and a high degree of aromaticity, which are characteristics of biochars optimized for adsorption applications.

FTIR analysis was conducted to identify the functional groups present on the surface of the biochar. The FTIR spectrum of the biochar is given in Fig. 2b FTIR analysis confirmed the presence of functional

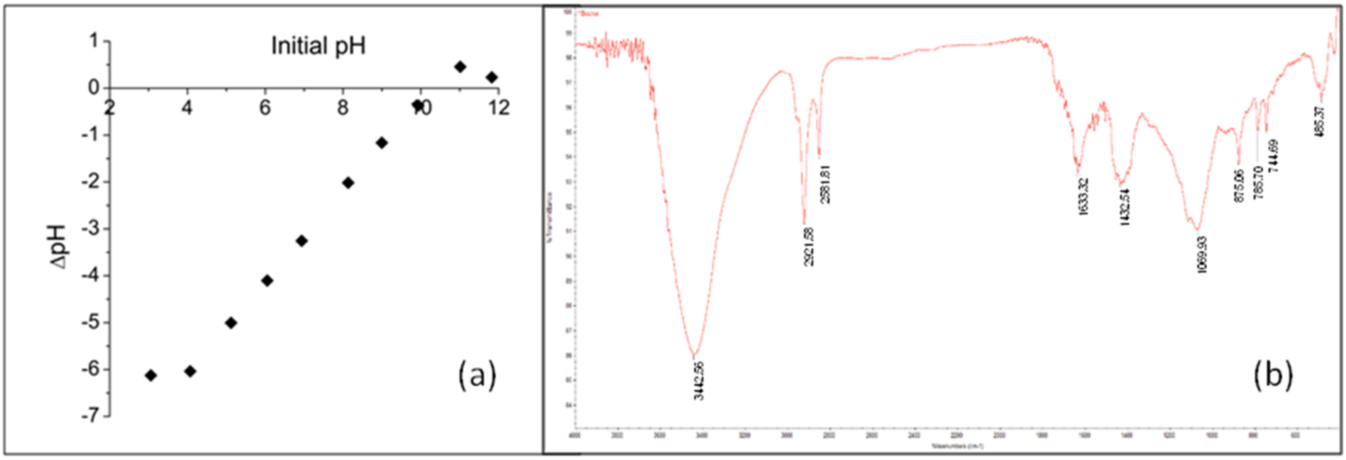

Fig. 2. Characterization of biochar: (a) point of zero charge, (b) FTIR spectrum.

groups like hydroxyls and aromatics, supporting strong adsorption properties (Machado et al., 2020).

A prominent band at approximately 3442 cm^{-1} corresponds to the O—H stretching vibration of hydroxyl groups (Machado et al., 2020). Bands observed at 2921 cm^{-1} and 2851 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of methylene groups, typical of aliphatic and cyclic hydrocarbons without strain.

The band at 1633 cm^{-1} is indicative of $C = C$ stretching vibrations within aromatic rings, signifying a strong aromatic structure within the biochar (Machado et al., 2020). This aromatic nature is further supported by bands at 1432 cm^{-1} and 875 cm^{-1}, corresponding to aromatic $C = C$ structures and aromatic C—H out-of-plane bending, respectively (Peng et al., 2016). Additionally, a band at 1069 cm^{-1} is assigned to C—O stretching vibrations in carboxyl groups and possibly the vibrational oscillation of hydroxyl groups (Machado et al., 2020).

The biochar's experimentally determined point of zero charge was 10.8, as shown in Fig. 2a. This high pH$_{pzc}$ indicates that, under the experimental conditions (pH ~7), the biochar surface carries a positive charge. This charge behavior is relevant to interactions with associated species in the soil environment, impacting biochar's adsorptive properties.

Transport of chlorinated phenols through alluvial soil layers

For each experiment, transport experiments of a non-sorbing - and with respect to the short travel times - stable (conservative) tracer (thiourea), were conducted to assess the homogeneity of column packing within the columns and to test homogeneity between replicates. After, the same columns were used for the transport experiments of the CPs. The flow rate for the CP experiments matched that of the tracer experiments, varying between 0.138 L/h and 0.576 L/h depending on the layer. The specific flow rates (*Q*) for each experiment are detailed in Table 4 and Table 5. Figures S1 and S2 in Supplementary Materials present the mean breakthrough curves from the triplicates of all CPs through the alluvial soil columns with and without the presence of biochar, respectively. Homogeneity between replicates was fulfilled as the results of a one-way ANOVA indicates no significant differences between the replicates ($p > 0.05$). The transport parameters are summarized in Table 4.

The breakthrough curves for thiourea across all six soil layers exhibit a symmetrical, sigmoidal shape. This behavior is characteristic of a non-sorbing substance and indicates the absence of physical non-equilibrium transport processes in the porous medium as suggested by Rahman et al. (2003). Likewise, Jellali et al. (2010) associated symmetrical breakthrough curves for non-sorbing substances with a lack of heterogeneous packing, reinforcing the notion that column homogeneity (within a single column) was achieved in this study.

In examining the transport and retention behavior of thiourea and CPs across the different soil layers, notable variations emerged in both **pore water velocities** (the rate at which water carrying the solute moves through the soil) and **retardation coefficients (R_d).** These variations were influenced by soil composition and the applied flow rates (Q) given in Table 4.

It is important to clarify that the flow rates were specifically adjusted for different soil layers based on their hydraulic conductivity, as determined during the characterization process. Consequently, pore water velocities and solute transport behaviors inherently depended on these varying flow rates. Surface layers with high sand and low clay content, along with the deeper layer 6 (which exhibited similar permeability to the surface layers), were tested at elevated flow rates (ranging from 0.204 to 0.576 L/h for layers at depths of 50–150 cm and 0.138 L/h for the 200–230 cm layer). This adjustment in flow rates was made to **account for** the lower sorption capacities of these layers, which tend to have higher saturated hydraulic conductivity.

Although not all experiments were conducted under identical flow rate conditions, this intentional variation was introduced to simulate the

Table 4

Transport parameters for the investigated CPs through a column filled with alluvial soil.

Layer, depth (cm)	Compound	Q (L/h)	V_w (m/h)	R_d (-)	α (-)	λ (-)	ρ (g/cm^3)	ε (-)	K_d (L/kg)
1	Tracer	0.576	1.32	/	0.002	0	1.74	0.347	/
	4-CP	0.576	1.32	2.13	0.018	0	1.74	0.347	0.147
	2,4-DCP	0.576	1.32	1.98	0.018	0	1.74	0.347	0.128
	2,4,6-TCP	0.576	1.32	1.92	0.018	0	1.74	0.347	0.120
	PCP	0.576	1.32	6.15	0.018	0	1.74	0.347	0.671
2	Tracer	0.564	1.28	/	0.001	0	1.73	0.350	/
	4-CP	0.564	1.28	1.00	0.009	0	1.73	0.350	/
	2,4-DCP	0.564	1.28	1.00	0.009	0	1.73	0.350	/
	2,4,6-TCP	0.564	1.28	1.00	0.009	0	1.73	0.350	/
	PCP	0.564	1.28	4.35	0.038	0	1.73	0.350	0.440
3	Tracer	0.378	0.938	/	0.002	0	1.81	0.321	/
	4-CP	0.378	0.938	1.27	0.007	0	1.81	0.321	0.033
	2,4-DCP	0.378	0.938	1.55	0.007	0	1.81	0.321	0.066
	2,4,6-TCP	0.378	0.938	1,13	0.007	0	1.81	0.321	0.016
	PCP	0.378	0.938	5.25	0.031	0	1.81	0.321	0.512
4	Tracer	0.546	1.27	/	0.002	0	1.75	0.343	/
	4-CP	0.546	1.27	1.10	0.008	0	1.75	0.343	0.013
	2,4-DCP	0.546	1.27	1.15	0.008	0	1.75	0.343	0.019
	2,4,6-TCP	0.546	1.27	1.00	0.008	0	1.75	0.343	/
	PCP	0.546	1.27	1.53	0.008	0	1.75	0.343	0.068
5	Tracer	0.204	0.446	/	0.003	0	1.70	0.364	/
	4-CP	0.204	0.446	1.65	0.016	0	1.70	0.364	0.089
	2,4-DCP	0.204	0.446	1.95	0.016	0	1.70	0.364	0.130
	2,4,6-TCP	0.204	0.446	1.50	0.016	0	1.70	0.364	0.068
	PCP	0.204	0.446	4.28	0.016	0	1.70	0.364	0.448
6	Tracer	0.138	0.316	/	0.003	0	1.72	0.348	/
	4-CP	0.138	0.316	1.90	0.015	0	2.65	0.348	0.118
	2,4-DCP	0.138	0.316	2.20	0.015	0	2.65	0.348	0.157
	2,4,6-TCP	0.138	0.316	1.55	0.015	0	2.65	0.348	0.072
	PCP	0.138	0.316	5.00	0.015	0	2.65	0.348	0.524

Q (L/h) - flow rate, Vw (m/h) - pore water velocity, Rd - retardation coefficient, α - dispersivity, λ - biodegradation rate, ρ (g/cm3) - bulk density, ε - porosity, Kd - sorption distribution coefficients.

Table 5

Transport parameters of chlorinated phenols through layers of alluvial soil with the addition of biochar.

Soil layer	Compound	Q (L/h)	V_w (m/h)	R_d (-)	α (-)	λ (-)	P (g/cm^3)	ε (-)	K_d (L/kg)
1	Tracer	0.570	1.47	1.00	0.003	0	1.84	0.309	
	4-CP	0.570	1.47	135	0.045	0	1.84	0.309	15.5
	2,4-DCP	0.570	1.47	115	0.045	0	1.84	0.309	13.2
	2,4,6-TCP	0.570	1.47	55.0	0.045	0	1.84	0.309	6.25
	PCP	0.570	1.47	85.0	0.065	0	1.84	0.309	9.73
2	Tracer	0.558	1.33	1.00	0.006	0	1.78	0.333	
	4-CP	0.558	1.33	142	0.035	0	1.78	0.333	17.6
	2,4-DCP	0.558	1.33	98.0	0.055	0	1.78	0.333	12.1
	2,4,6-TCP	0.558	1.33	52.0	0.055	0	1.78	0.333	6.38
	PCP	0.558	1.33	94.0	0.055	0	1.78	0.333	11.6
3	Tracer	0.372	0.874	1.00	0.004	0	1.76	0.339	
	4-CP	0.372	0.874	115	0.075	0	1.76	0.339	14.5
	2,4-DCP	0.372	0.874	82.0	0.075	0	1.76	0.339	10.3
	2,4,6-TCP	0.372	0.874	72.0	0.075	0	1.76	0.339	9.02
	PCP	0.372	0.874	108	0.055	0	1.76	0.339	13.6
4	Tracer	0.552	1.42	1.00	0.004	0	1.84	0.310	
	4-CP	0.552	1.42	120	0.045	0	1.84	0.310	13.9
	2,4-DCP	0.552	1.42	92.0	0.045	0	1.84	0.310	10.6
	2,4,6-TCP	0.552	1.42	45.0	0.075	0	1.84	0.310	5.13
	PCP	0.552	1.42	80.0	0.075	0	1.84	0.310	9.20
5	Tracer	0.210	0.444	1.00	0.014	0	1.67	0.376	
	4-CP	0.210	0.444	102	0.055	0	1.67	0.376	14.2
	2,4-DCP	0.210	0.444	83.0	0.055	0	1.67	0.376	11.6
	2,4,6-TCP	0.210	0.444	78.0	0.055	0	1.67	0.376	10.9
	PCP	0.210	0.444	92.0	0.055	0	1.67	0.376	12.8
6	Tracer	0.138	0.261	1.00	0.009	0	1.72	0.421	
	4-CP	0.138	0.261	155	0.035	0	1.72	0.421	24.4
	2,4-DCP	0.138	0.261	108	0.055	0	1.72	0.421	17.0
	2,4,6-TCP	0.138	0.261	56.0	0.095	0	1.72	0.421	8.73
	PCP	0.138	0.261	74.0	0.095	0	1.72	0.421	11.6

Q (L/h) - flow rate, Vw (m/h) - pore water velocity, Rd - retardation coefficient, α - dispersivity, λ - biodegradation rate, ρ (g/cm3) - bulk density, ε - porosity, Kd - sorption distribution coefficients.

natural variability in water movement through soil layers with different hydraulic properties. As a result, breakthrough curves (BTCs) are expressed in **pore volumes** for each corresponding flow condition. For example, the breakthrough for thiourea ranged from 2.1 to 2.4 pore volumes for the unamended alluvial soils (Figure S3a in Supplementary Material), and 2.2 to 2.8 pore volumes for the biochar-amended alluvial soils (Figure S3b in Supplementary Material). The slightly higher retardation of the tracer compound in the biochar-enriched soil layers is reflective of the changes in the soil porosity after biochar addition and the subsequent increase in tortuosity resulting in the observed retardation.

Across all layers, 4-CP, 2,4-DCP, and 2,4,6-TCP exhibited transport patterns similar to thiourea, with relatively low R_d values, indicating limited retention. However, it is important to note that the R_d values for these compounds varied between layers, reflecting some variability in their retention. For instance, in layer six, 4-CP showed an R_d value of 1.9, and in layer five it was 1.65 - both notably higher than the R_d values for thiourea. This suggests that, although these compounds generally exhibit low retention, some interaction with the soil matrix may have occurred, possibly due to weak binding forces, but to a lesser degree compared to more sorptive compounds. These variations in R_d could also be influenced by the differences in flow rates and the sorptive capacities of the individual soil layers.

In contrast, in layers like layer 2, the more polar compounds 4-CP, 2,4-DCP, and 2,4,6-TCP demonstrated transport behavior comparable to the non-sorptive tracer thiourea, with R_d values close to 1. This suggests minimal interaction with the soil particles, likely due to the low organic and clay content in these layers, which limits the soil's binding capacity. Although higher flow rates were applied to more permeable layers, the transport behavior of chlorinated phenols could still be accurately predicted, as it depends on a multifactorial combination of flow rate, sorption, and soil properties.

To further clarify the driving mechanisms for the sorption of CPs in the studied alluvial soil, retardation factors were correlated with CP properties, as presented in Fig. 3. The correlation analysis reveals distinct relationships between R_d and various molecular properties, as shown in the plot. The color of the circles indicates the direction of the correlation, with blue representing a positive correlation and red indicating a negative correlation. Additionally, the size and intensity of the color reflect the strength of the correlation, with larger and darker

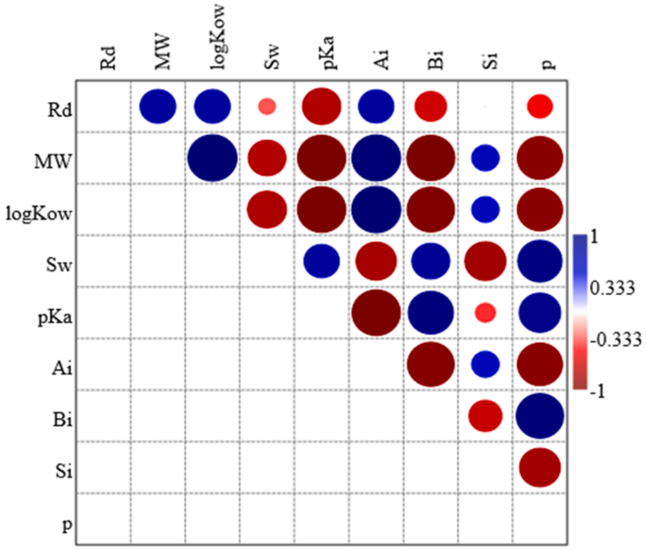

Fig. 3. Correlation between the retardation factor Rd for CPs in the alluvial soil and their physico-chemical properties (MW - molecular weight, KOW - n-octanol/water partition coefficient, Sw - solubility in water, pKa - acid dissociation constant, Ai - electron-acceptor character of molecule, Bi - electron-donor character of molecule, Si - polarizability, p - vapor density).

circles representing stronger correlations.

The obtained R_d values were correlated with soil properties using Pearson's correlation to assess how much influence individual soil characteristics have on CP retardation in the alluvial sediment. The R_d values showed no correlation with the physico-chemical characteristics of the soils with results showing no statistical significance ($p > 0.05$) and R^2 values ranging from 0.01 to 0.29, (Figure S4 in Supplementary material) indicating that the retardation of CPs in the alluvial soil layers was not significantly influenced by the differences in soil properties.

Among CP properties, the acid dissociation constant pK_a exhibited the strongest correlation with R_d values across all soil layers ($R^2 = -0.81$) as shown in Fig. 3. CPs with lower pK_a values, higher molecular weights (MW), higher hydrophobicity (expressed as $\log K_{OW}$), and higher electron acceptor properties (Ai) were more effectively retained, indicating a positive relationship between R_d and these three CP characteristics. This suggests that hydrophobic partitioning and electron-donor acceptor interactions predominantly drive CP retention in the soil studied, as more hydrophobic and heavier CPs are less likely to be transported through the soil layers.

Electrostatic interactions appear to play a secondary role in CP retention as at the experimental pH of 6.9, most CPs exist in their non-dissociated form, reducing the impact of electrostatic attraction to soil particles. However, the soil surface is positively charged due to protonated iron and silicon oxides, with a point of zero charge ranging from 8.34 to 9.32 (Table S2 in Supplementary Materials). This charge facilitates the adsorption of PCP, where electrostatic attraction could enhance its retention, especially given that $pH_{pzc} >$ experimental $pH > pK_a$. This mechanism aligns with findings reported by Song et al. (2021), who emphasized surface charge heterogeneity as a key factor impacting the transport and retention of ionizable organic compounds in porous media. Overall, CP retention in alluvial soil is driven by hydrophobic and electron-donor acceptor interactions, with limited influence from charge-based attraction, except in specific cases like PCP. The same conclusions were observed by Sigmund et al. (2022) who highlighted that sorption and mobility of charged organic compounds depends on the pH of the environment that affects the charge density of soil, which in turn influences the sorption of ionized organic compounds.

Effect of Biochar-Amended Soil on the Transport of CPs

Breakthrough curves for the different soil layers with and without biochar (AS and AS+BC, respectively) are shown in Figures S1 and S2, respectively, in the Supplementary Materials, and clearly demonstrate the effect of biochar amendment on CPs transport. Incorporating biochar into the soil significantly slowed down the transport of CPs, preventing their fast movement through the soil layers. The BTCs from the biochar-amended soils exhibited much longer travel times compared to those from the native soil across all layers, highlighting biochar's effectiveness in enhancing pollutant retention. Thus, the study investigated the impact of a 0.5 % biochar addition to the different alluvial soil layers on the retention and transport of the CPs. The mean values from triplicate measurements for transport parameters of CPs in biochar-enriched alluvial soil are presented in Table 5.

The impact of biochar on transport is directly reflected in the transport parameters. The sorption distribution coefficients (K_d) for biochar-amended soils ranged from 5.13 to 24.4 L/kg, far exceeding those for soils without biochar, where K_d values were up to a thousand times lower (Table 4). This significant increase in sorption capacity underscores biochar's role as an effective measure against CP migration through the soil, even under similar flow conditions. Consequently, the transport experiments with biochar were much longer, with travel times extended by factors of 12–40 (72–400 h) compared to the native soil (Figures S1 and S2 in Supplementary Material, Tables 4 and 5).

Many studies have reported similar findings, indicating that biochar amendments significantly affect the transport and retention of pollutants in soil (Gámiz et al., 2019; Isakovski et al., 2024; Masud et al., 2023; Twagirayezu et al., 2024), reinforcing the potential of biochar as an effective soil amendment for mitigating mobility of contaminants.

The observed retention patterns in biochar-amended soils suggest an interplay between the structural and chemical properties of the pollutants and the sorptive characteristics of biochar-enriched soils. Specifically, the relationship between the retardation factors and the physico-chemical properties of the compounds (Fig. 4) underscores the influence of molecular characteristics, such as polarity and hydrophobicity, on their interaction with the amended soil. Thus, retardation factors are further correlated with the structural and electronic properties of the CPs. The observed relationship between the retardation coefficient and the physico-chemical properties of CPs highlights how specific molecular features influence their retention in biochar-enriched soils.

In terms of negative correlations, R_d shows a strong negative relation with *Si* (polarizability), highlighted by a large, deep red circle, suggesting that more polarizable molecules tend to have lower retention, likely due to reduced interactions with the stationary phase. The weak negative correlation between R_d and molecular weight is reflected by a smaller red circle, indicating that larger molecules tend to exhibit lower retention in hydrophobic environments. Key factors such as polarizability, molecular weight, and electron-donor properties govern this interaction shown in Fig. 4. Analysis revealed a strong correlation between CP polarizability and R_d, with R^2 values ranging from 0.63 to larger 0.99 (Fig. 4), except for the third layer, where R^2 dropped to 0.41. CPs with higher polarizability demonstrate strong π-π electron-donor-acceptor (interactions with biochar's highly aromatic π-conjugated system ($H/C = 0.12$), enhancing retention. For instance, 4-CP shows the highest R_d values (102–155), attributed to its single chlorine substitution, which maintains higher electron density and fosters strong π-π interactions. Conversely, CPs with increased chlorine substitutions, like PCP and 2,4,6-TCP, exhibit moderate R_d values due to reduced electron density, making their π-systems more electron-accepting. Additionally, conclusions are supported by electron-donor acceptor properties showing a positive correlation with R_d (large blue circles), indicating that molecules with stronger electron-donating abilities (high Bi such as 4-CP of 0.230) tend to have higher retention. This suggests that electron-donor molecules may interact more strongly with the surface of biochar-amended alluvial soil, potentially through favorable π–π electron donor-acceptor (EDA) interactions. These interactions are particularly enhanced if the stationary phase, such as biochar, contains π-acceptor moieties that can interact with the electron-rich phenolic rings of CPs.

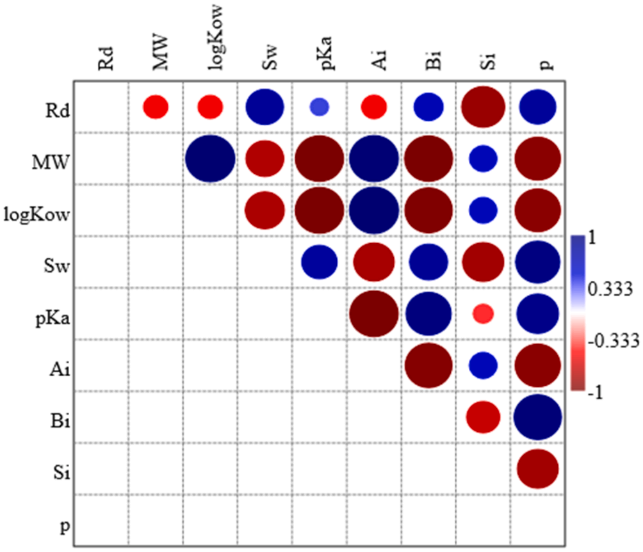

Fig. 4. Correlations between the retardation factor Rd and physico-chemical properties of CPs in the biochar-enriched soil column (MW - molecular weight, KOW - n-octanol/water partition coefficient, Sw - solubility in water, pKa - acid dissociation constant, Ai - electron-acceptor character of molecule, Bi - electron-donor character of molecule, Si - polarizability, p - vapor density).

The influence of such interactions has been extensively investigated by Xiao and Pignatello (2015), who demonstrated that the strength of EDA interactions depends on the difference in quadrupole moments between the donor and acceptor molecules. These quadrupole moments are influenced by ring substituents that either donate or withdraw electron density, particularly through the π system, as well as the polarizability of the donor's π cloud, which directly affects the sorption behavior of aromatic compounds. Furthermore, Wu et al. (2018) observed that a reduction in sorption from single-ring to multi-ring aromatic compounds could be attributed to π-electron delocalization, which affects the formation and strength of EDA interactions. Together, these findings support the conclusion that EDA interactions, governed by molecular electronic properties, play a critical role in the enhanced retention of CPs in biochar-enriched soils. These interactions highlight the ability of biochar to act as an effective sorbent for substituted aromatic pollutants.

For positive correlations, R_d shows a positive relationship with water solubility (S_w), represented by a large, deep blue circle, suggesting that retention increases with increasing solubility. This finding also supports the previous conclusion that more polar phenols, such as mono- and dichlorophenols with higher solubility, exhibit longer retention in biochar-enriched soil columns. Generally, water solubility and R_d are inversely related because highly water-soluble compounds tend to remain in the aqueous phase and interact less with the solid phase. However, in biochar-enriched soils, the polarity and structural properties of biochar may facilitate specific interactions (e.g. π–π interactions) with polar compounds, such as mono- and dichlorophenols, despite their higher solubility. Wu et al. (2018) highlighted that the size and shape of aromatic compounds can significantly influence their sorption behavior. Large molecules with strong π-donor or π-acceptor properties are expected to strongly interact with electron-deficient or electron-rich regions on surfaces. However, due to size exclusion at pore throats, these molecules are unable to penetrate the small pores of porous sorbents. Consequently, accurately predicting the sorption of aromatic compounds is challenging due to the multiplicity and complexity of influencing factors, warranting further investigation. Additionally, pK_a exhibits a weak positive correlation with R_d, as shown by a smaller blue circle.

Beyond the π-π electron-donor acceptor (EDA) interactions, the positive surface charge of biochar under the experimental pH conditions (pH_{pzc}~10) promotes the attraction of CPs, leading to stronger sorption and retention. This effect is particularly relevant for mono-, di-, and trichlorinated phenols, which remain largely non-dissociated at the experimental pH of ~7. Although non-ionized CPs are neutral, their functional groups are influenced by the electron-withdrawing effects of chlorine atoms and the hydroxyl group, which alter the molecule's dipole moment. These molecular dipoles can, in turn, induce dipoles on the positively charged biochar surface, resulting in dipole-induced dipole interactions. As discussed by Wu et al. (2018), biochar's surface charge, which is pH dependent, plays a significant role in its interaction with contaminants. Similarly, Sumaraj and Padhey (2017) and Sajjadi et al. (2019) highlight that surface charges, including those generated by functional group dissociation, strongly influence sorption behavior. For neutral CPs, the positive surface charge of biochar is therefore expected to enhance retention through dipole-induced dipole interactions. In addition, the electrostatic properties of the biochar, commonly expressed through zeta potential, are a key factor in the sorption of charged organic compounds such as CPs. Although zeta potential was not directly measured, the biochar's high pH_{pzc} indicates that its surface area exhibits a positive zeta potential under the near-neutral experimental conditions. This, as a result, contributes to the enhanced retention of the partially ionized CP molecules, due to their interaction with the positively charged biochar surface, complementing π–π electron donor-acceptor and dipole-dipole interactions.

In the case of PCP, relevant mechanisms for retardation are electrostatic interactions between positively charged surfaces of the soil/biochar mixture and negatively charged PCP. The combination of π-π EDA and electrostatic interactions bonds supports PCP retention within the biochar-amended soil. In summary, CP retention efficacy depends on the balance of chlorine content, polarizability, and formation of polar interactions with 4-CP showing the highest retention due to its single chlorine substitution and consequent stronger electron-donating capacity. Therefore, adsorption of organic compounds on carbon-based materials such as biochar is driven by multiple mechanisms (Isakovski et al., 2024; Moreno-Castilla, 2004; Sadegh et al., 2024; Sajjadi et al., 2019; Sumaraj and Padhye, 2017; Wu et al., 2018; Zhang et al., 2011). Additionally, Zhong et al. (2023) investigated CP adsorption on biochar and concluded that the interactions between the CPs and the biochar are mainly attributed to the chemical structure of the CPs.

Overview of retention mechanisms of CPs in alluvial and biochar-amended soils and insights from biplot analysis

A PCA was performed to elucidate the interplay of soil properties, biochar amendments, and CP characteristics on retardation, a critical factor in contaminant transport. The PCA biplot (Fig. 5) provides a visual representation of these interactions, highlighting how soil amendments like biochar can modulate CP retention mechanisms through distinct physicochemical pathways. The analysis included R_d values obtained for all four CPs. The explanatory power of PC1 and PC2 together is 64.2 %, as they collectively account for 33.3 % and 30.9 % of the total variance, respectively.

In the unamended alluvial soil, R_d exhibits strong positive correlations with several molecular parameters of CPs, including molecular weight (1), hydrophobicity (2), electron-acceptor properties (5), and polarizability (7). These correlations indicate that hydrophobic interactions dominate the retention process. For example, larger and more hydrophobic CPs such as PCP demonstrate higher R_d values than smaller and more polar molecules like 4-CP or 2,4-DCP. This trend underscores the pivotal role of molecular size and hydrophobicity in CP retention, as corroborated by finding reported in Endo and Matsuzawa (2024), who highlighted that molecular size was the most significant factor influencing sorption for both PFAS (Per- and polyfluoroalkyl substances) and a wide range of nonfluorinated surfactants. Furthermore, π-π electron donor-acceptor interactions significantly contribute to retention. The positive correlation between R_d and A_i (5) suggests that CPs with high electron-acceptor potential, such as 2,4,6-TCP and PCP, form π-π interactions with aromatic domains in soil organic matter. The presence of rigid, glassy aromatic moieties in SOM, as reflected by a hydrogen-to-carbon (H/C) ratio close to 1, aligns with the dual-domain model of SOM. This model posits that condensed aromatic domains interact more strongly with organic contaminants than expanded aliphatic regions (Ćwieląg-Piasecka, 2023).

Conversely, R_d shows negative correlations with water solubility (3), electron-donor properties (6), acid dissociation constant (4), and vapor density (8). These findings indicate that highly soluble and polar CPs, such as mono- and dichlorophenols, exhibit lower retention. The trend in solubility and electron-donor properties follows the order: mono-CPs > di-CPs > tri-CPs > penta-CPs, the trend in solubility and electron-donor properties follows the order: mono-CPs > di-CPs > tri-CPs > penta-CPs suggesting that the higher values are obtained for hydrophobic PCP. The negative correlation between R_d and pK_a suggests that ionized CPs, present under experimental conditions where soil pH exceeds the pK_a of the compounds, are retained more strongly through electrostatic interactions. As pK_a increases, the proportion of ionized species decreases, resulting in lower retention. This aligns with observations that ionic interactions play a crucial role in ionized CP transport dynamics. Soriano-Meseguer et al. (2021) further support this hypothesis by investigating the retention of partially ionized acid-base compounds in reversed-phase liquid chromatography. They concluded that both hydrophobic and ionic interactions significantly influence retention, with the balance between these forces depending on the compound's molecular structure and the surrounding conditions. Their

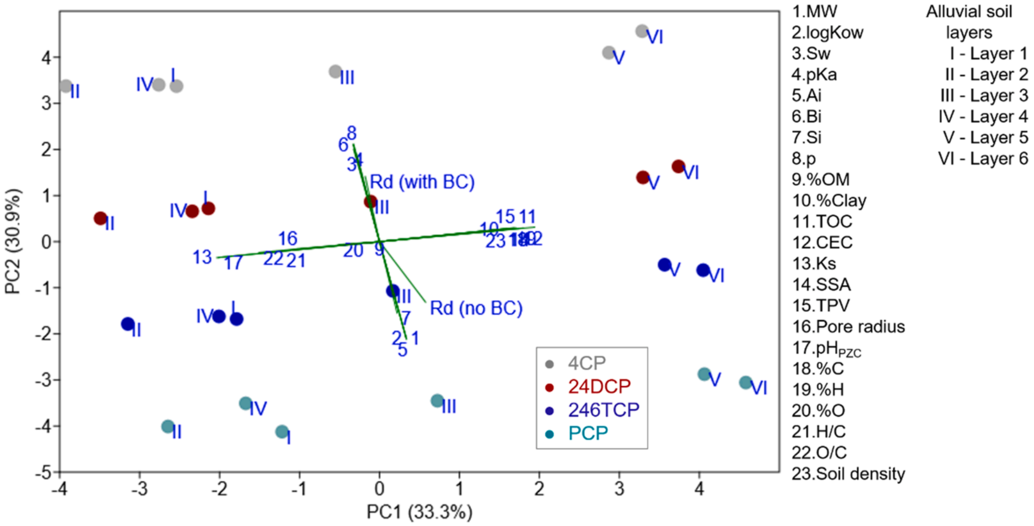

Fig. 5. PCA biplot of the chlorinated phenols molecular properties (MW (g/mol) – molecular weight, logKow - n-octanol/water partition coefficient, Sw (g/L) – solubility in water, pKa - acid dissociation constant, Ai – electron-acceptor character of molecule, Bi – electron-donor character of molecule, Si – polarizability, p (mmHg) – vapor density), and soil properties (%OM – organic matter content, %Clay – clay content, TOC – total organic carbon, CEC – cation exchange capacity, Ks – saturated hydraulic conductivity, SSA – specific surface area, TPV – total pore volume, pHpzc – point of zero charge, %C – carbon content, %H – hydrogen content, %O – oxygen content, H/C ratio, O/C ratio, soil bulk density) affecting the retardation coefficient in alluvial soil (no BC) and biochar-amended soil (with BC).

findings highlight how variations in pH, ionic strength, and compound properties collectively shape retention behavior, emphasizing the dynamic interplay between these factors.

The introduction of biochar significantly alters the retention dynamics of CPs. In biochar-amended soil, R_d demonstrates strong positive correlations with S_W (3), Bi (6), pK_a (4), and p (8), indicating a shift toward more polar interactions. This suggests that biochar enhances the retention of polar CPs, such as 4-CP, by introducing abundant electron-acceptor sites facilitating the formation of dipole-induced dipole interactions, as evidenced by the positive correlation between R_d and pK_a. This finding is consistent with research, which indicates that biochar exhibits a sorption affinity for CPs and related compounds as polar organic substances and concludes that pH significantly influences the adsorption capacity of these compounds (e.g., Choi et al., 2024).

Negative correlations between R_d and MW (1), logK_{OW} (2), Ai (5), and Si (7) further support the influence of polar interaction in biochar-amended soils highlight a reduced influence of hydrophobic interactions. This shift favors the retention of smaller, more polar CPs over larger, hydrophobic molecules such as pentachlorophenol. The diminished role of hydrophobicity, coupled with the enhanced importance of π-π electron donor-acceptor interactions, demonstrates biochar's ability to modulate retention mechanisms. Polar interactions, including electrostatic attraction and π-π EDA interactions, arise from variations in electron density and charge distribution. These mechanisms enhance the retention of polar and semi-polar compounds, particularly under conditions that promote deprotonation and increase surface charge heterogeneity. Additionally, surface charge heterogeneity introduces a variety of adsorption sites, including those that can engage in hydrogen bonding and π-π interactions. This diversity in binding sites allows the biochar to effectively capture and retain a broader range of polar and semi-polar compounds, enhancing its ability to immobilize such contaminants in the soil. By leveraging these polar interactions, biochar enhances soil's capacity to immobilize contaminants, proving to be an effective amendment for reducing the mobility of polar organic pollutants as already stated by Carlini et al. (2023). Additionally, Miao et al. (2017) investigated the adsorption of polar groups and aromatic molecules on biochar, highlighting the role of polar interactions. These groups facilitate hydrogen bonding and electrostatic attraction, enhancing retention as pH increases and deprotonation occurs. The study also concluded that π-π electron donor-acceptor interactions dominate the adsorption process.

Although, no direct correlations were found between R_d and soil physicochemical properties in unamended soils, slight positive correlations were observed with specific surface area, total pore volume, and bulk density. These findings suggest that pore trapping and surface interactions contribute indirectly to CP retention. Increased surface area and pore volume provide more sites for chemical interactions, thereby enhancing retention of hydrophobic organic contaminants as also stated by Ma et al. (2020).

In order to better understand the mechanism of CPs transport through alluvial soil, the observed transport behaviors were compared to literature findings for other soil types. In general, the transport behavior observed in the Danube alluvial soil is notably different from those found in soils with finer texture or rich in Fe. This can primarily be linked to the significant variations in organic carbon content, mineral composition and hydraulic properties of the observed soils. As reported, all layers of the investigated alluvial soil were characterized by high content of sand and low content of clay and organic matter; as a result low SSA and limited sorption capacities were observed. Reflecting these observations, and the highly permeable nature of the sandy soil, the low retardation coefficients were obtained (1–6.15), indicating weak CP-soil interactions and fast advective transport. These findings are consistent with those reported in sandy aquifer materials and sediments with low organic matter content, in which hydrophobic and electron donor-acceptor interactions are dominant over electrostatic binding (Yadav et al., 2023; Kondor et al., 2024). However, significantly higher retardation coefficients can be observed for Fe-rich soils with high clay content (Zhang et al., 2024; Zhou et al., 2023). This can be explained by the presence of reactive metal oxides and surface functional groups which can facilitate redox-driven transformation of CPs, and enhance soprtion. The absence of such mineral phases in the Danube alluvial soil likely contributes to its comparatively low sorption capacity. Moreover, CP mobility is controlled by soil organic carbon and redox potential (Emenike et al., 2024), further explaining the very low retention of CPs in the unamended alluvial soil, as both parameters were low. The significant increase in both retardation coefficients and sorption distribution coefficients (Table 5) after the addition of biochar into the alluvial soil, highlights the key role of sorbent surface chemistry in regulating organic compounds transport through soil. As observed, biochar amendment into the alluvial soil compensated for the naturally low sorption capacity, introducing high surface area, and an abundance of π structures and positively charged sites. This enhanced the retention of both polar and moderately hydrophobic CPs by facilitating π-π electron donor-acceptor and dipole-dipole interactions. The results confirm that the main limiting factors for CPs transport through soil are the physicochemical properties of the soil, particularly soil organic carbon content, the presence of Fe/Al oxides and their abundance, and texture. Further, the results indicate that amending coarse-textured alluvial soils with biochar can shift retention mechanisms towards those typical of more reactive, fine-textured mineral soils.

The overall results highlight biochar's potential as a soil amendment for environmental remediation by shifting retention mechanisms from hydrophobic to polar interactions. Additionally, biochar enhances soil's capacity to immobilize a broader spectrum of contaminants. This increased versatility makes biochar an effective tool for managing pollution in diverse environmental settings.

Conclusion

The column experiments performed in this study evaluated the transport of chlorinated phenols through soil, both with and without biochar addition. In high-permeability layers, breakthrough curves for all four compounds appeared within 10 h, underscoring the rapid transport of CPs in these environments. The study identified the primary retention mechanisms of CPs in alluvial soils as hydrophobic, polar interactions, and electron-donor acceptor interactions, rather than charge-based attractions - though exceptions like pentachlorophenol were noted. The chemical properties of CPs, particularly pK_a, molecular weight, and hydrophobicity, were critical in influencing their transport in the soil. The addition of biochar significantly enhanced CP retention, increasing breakthrough times by 12 to 40 times and yielding retardation values R_d between 42 and 155. A strong correlation was observed between retention and molecular polarizability. The research provides valuable insights into the use of biochar in environmental remediation, particularly for controlling the migration of organic pollutants and mitigating contamination of subsurface water systems. Biochar's ability to enhance retention mechanisms makes it a valuable tool in controlling the transport of organic pollutants and protecting subsurface water quality.

These findings reinforce the potential of riverbank filtration as a sustainable and cost-effective pre-treatment strategy for drinking water, particularly when biochar is used as a soil amendment. The study highlights that the success of such systems hinges on a nuanced understanding of both the physical-chemical properties of the soil and the chemical characteristics of the contaminants.

Funding

This research was supported by the Science Fund of the Republic of Serbia, #6769, Natural based efficient solution for remediation and revitalization of contaminated locations using energy crops – ReNBES.

Data availability

The datasets used or analyzed during the current study are available from the corresponding author upon reasonable request. Additionally, the datasets are hosted in the Zenodo repository, doi:10.5281/zenodo.14135465.

CRediT authorship contribution statement

Tamara Apostolović: Writing – review & editing, Visualization, Formal analysis. **Marijana Kragulj Isakovski:** Writing – original draft, Methodology, Conceptualization. **Marko Šolić:** Methodology, Data curation. **Jelena Beljin:** Methodology, Conceptualization. **Lutz Weihermüller:** Writing – review & editing, Conceptualization. **Snežana Maletić:** Supervision, Project administration, Funding acquisition.

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.

Acknowledgements

This research was supported by the Science Fund of the Republic of Serbia, #6769, Natural based efficient solution for remediation and revitalization of contaminated locations using energy crops – ReNBES. The authors express their gratitude to Dr. Jelena Tričković for her valuable contribution as a supervisor to this research.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2025.100918.

References

Afridi, M.N., Zafar, Z., Khan, I.A., Ali, I., Bacha, A.-U.-R., Maitlo, H.A., Qasim, M., Nawaz, M., Qi, F., Sillanpää, M., Lee, K.H., Asif, M.B., 2024. Advances in MXene-based technologies for the remediation of toxic phenols: a comprehensive review. Adv. Colloid. Interface Sci. 332, 103250. https://doi.org/10.1016/j.cis.2024.103250.

Apostolović, T., Tričković, J., Kragulj Isakovski, M., Jović, B., Maletić, S., Tubić, A., Agbaba, J., 2020. Investigation of chlorinated phenols sorption mechanisms on different layers of the Danube alluvial sediment. J. Environ. Sci. 98, 134–142. https://doi.org/10.1016/j.jes.2020.05.028.

Carlini, C., Chaudhuri, S., Mann, O., Tomsik, D., Hüffer, T., Greggio, N., Marazza, D., Hofmann, T., Sigmund, G., 2023. Benchmarking biochar with activated carbon for immobilizing leachable PAH and heterocyclic PAH in contaminated soils. Environ. Pollut. 325, 121417. https://doi.org/10.1016/j.envpol.2023.121417.

Cavender, F.L., O'donohue, J., 2012. Phenol and phenolics. In: Bingham, E., Cohrssen, B. (Eds.), Patty's Toxicology, 6th edn. John Wiley & Sons, pp. 243–350.

Choi, J., Kim, M., Choi, J., Jang, M., Hyun, S., 2024. Sorption behavior of three aromatic acids (benzoic acid, 1-naphthoic acid and 9-anthroic acid) on biochar: cosolvent effect in different liquid phases. Chemosphere 349, 140898. https://doi.org/10.1016/j.chemosphere.2023.140898.

Ćwieląg-Piasecka, I., 2023. Soil organic matter composition and pH as factors affecting retention of carbaryl, carbofuran and metolachlor in Soil. Molecules 28 (14), 5552. https://doi.org/10.3390/molecules28145552.

Czaplicka, M., 2004. Sources and transformations of chlorophenols in the natural environment. Sci. Total. Environ. 322 (1–3), 21–39. https://doi.org/10.1016/j.scitotenv.2003.09.015.

Ehlers, G.A.C., Loibner, A.P., 2006. Linking organic pollutant (bio)availability with geosorbent properties and biomimetic methodology: a review of geosorbent characterisation and (bio)availability prediction. Environ. Pollut. 141 (3), 494–512. https://doi.org/10.1016/j.envpol.2005.08.063.

Emenike, C.U., He, Q., Koushika, K., 2024. Pentachlorophenol and its effect on different environmental matrices: the need for an alternative wood preservative. Sustain. Earth Rev. 7, 22. https://doi.org/10.1186/s42055-024-00090-x.

Endo, S., Matsuzawa, S., 2024. Hydrophobic sorption properties of an extended series of anionic per- and polyfluoroalkyl substances characterized by C18 chromatographic retention measurement. Environ. Sci. Technol. 58 (17), 7628–7635. https://doi.org/10.1021/acs.est.4c02707.

Gámiz, B., Velarde, P., Spokas, K.A., Celis, R., Cox, L., 2019. Changes in sorption and bioavailability of herbicides in soil amended with fresh and aged biochar. Geoderma 337, 341–349. https://doi.org/10.1016/j.geoderma.2018.09.033.

Hammer, Ø., Harper, D.A.T., Ryan, P.D., 2001. Past: paleontological statistics software Package for education and data analysis. Palaeontol. Electron. 4 (1), 9.

Hendershot, W.H., Lalande, H., Duquette, M., 2007. Soil chemical analyses: ion exchange and exchangeable cations. In: Carter, M.R., Gregorich, E.G. (Eds.), Soil Sampling and Methods of Analysis, 2nd edn. CRC Press, pp. 197–206.

Isakovski, M.K., Jevrosimov, I., Tamindžija, D., Apostolović, T., Knicker, H., de la Rosa, J.M., Rončević, S., Maletić, S., 2024. Enhanced retention of hydrophobic pesticides in subsurface soils using organic amendments. J. Hazard. Mater. 480, 135738. https://doi.org/10.1016/j.jhazmat.2024.135738.

Isakovski, M.K., Maletić, S., Tamindžija, D., Apostolović, T., Petrović, J., Tričković, J., Agbaba, J., 2020. Impact of hydrochar and biochar amendments on sorption and biodegradation of organophosphorus pesticides during transport through Danube alluvial sediment. J. Environ. Manage 274, 111156. https://doi.org/10.1016/j.jenvman.2020.111156.

ISO 10381-2:2002 (2002) Soil quality - sampling - part 2: guidance on sampling techniques.

ISO 10694:1995 (1995) Soil quality - determination of organic and total carbon after dry combustion (Elementary Analysis).
ISO 11277:2009 (2009) Soil quality - determination of particle size distribution in mineral Soil material - method by sieving and sedimentation.
ISO 18512:2007 (2007) Soil quality - guidance on long and short term storage of Soil samples.
Jellali, S., Diamantopoulos, E., Kallali, H., Bennaceur, S., Anane, M., Jedidi, N., 2010. Dynamic sorption of ammonium by sandy soil in fixed bed columns: evaluation of equilibrium and non-equilibrium transport processes. J. Environ. Manage 91 (4), 897–905. https://doi.org/10.1016/j.jenvman.2009.11.006.
Kachova, V.G., 2020. Characteristics of alluvial soils from Aydemir and Vetren Islands of Lower Danube. Ecol. Balk 12 (2), 121–129.
Kondor, A.C., Vancsik, A.V., Bauer, L., Szabó, L., Szalai, Z., Jakab, G., Maász, G., Pedrosa, M., Sampaio, M.J., Lado Ribeiro, A.R., 2024. Efficiency of the bank filtration for removing organic priority substances and contaminants of emerging concern: a critical review. Environ. Pollut. 340, 122795. https://doi.org/10.1016/j.envpol.2023.122795.
Kosmulski, M., 2011. The pH-dependent surface charging and points of zero charge. V. Update. J. Colloid. Interface Sci. 353 (1), 1–15. https://doi.org/10.1016/j.jcis.2010.08.023.
Kumar, P., Mehrotra, I., Gupta, A., Kumari, S., 2018. Riverbank filtration: a sustainable process to attenuate contaminants during drinking water production. J. Sustain. Dev. Energy Water Environ. Syst. 6 (1), 150–161. https://doi.org/10.13044/j.sdewes.d5.0176.
Li, N., Liu, Y., Wan, H., Long, L., Xing, J., Shao, S., Liu, G., van der Meer, Wgj, 2025. Nature-inspired water purification: integrating riverbank filtration and biofilm-regulating nanofiltration. Water. Res. 285, 124077. https://doi.org/10.1016/j.watres.2025.124077.
Ma, L., Li, K., Wang, C., Liu, B., Peng, H., Mei, Y., Ning, P., 2020. Enhanced adsorption of hydrophobic organic contaminants by high surface area porous graphene. Environ. Sci. Pollut. Res. 27 (7), 7309–7317. https://doi.org/10.1007/s11356-019-07439-2.
Machado, L.M.M., Lütke, S.F., Perondi, D., Godinho, M., Oliveira, M.L.S., Collazzo, G.C., Dotto, G.L., 2020. Treatment of effluents containing 2-chlorophenol by adsorption onto chemically and physically activated biochars. J. Environ. Chem. Eng. 8 (6), 104473. https://doi.org/10.1016/j.jece.2020.104473.
Majeed SA al-din, Mohammed, Saleh, L.A., Jaber, N.H., 2024. Evaluation of riverbank filtration to improve groundwater quality (Euphrates River, Karbala, Iraq). Water Sci. 38 (1), 438–447. https://doi.org/10.1080/23570008.2024.2381151.
Al Masud, M.A., Shin, W.S., Sarker, A., Septian, A., Das, K., Deepo, D.M., Iqbal, M.A., Islam, A.R.M.T., Malafaia, G., 2023. A critical review of sustainable application of biochar for green remediation: Research uncertainty and future directions. Sci. Total Environ. 904, 166813. https://doi.org/10.1016/j.scitotenv.2023.166813.
Miao, Q., Bi, E., Li, B., 2017. Roles of polar groups and aromatic structures of biochar in 1-methyl-3-octylimidazolium chloride ionic liquid adsorption: pH effect and thermodynamics study. Environ. Sci. Pollut. Res. 24, 22265–22274. https://doi.org/10.1007/s11356-017-9886-4.
Moreno-Castilla, C., 2004. Adsorption of organic molecules from aqueous solutions on carbon materials. Carbon. N. Y. 42 (1), 83–94. https://doi.org/10.1016/j.carbon.2003.09.022.
Muoghalu, C.C., Owusu, P.A., Lebu, S., Nakagiri, A., Semiyaga, S., Iorhemen, O.T., Manga, M., 2023. Biochar as a novel technology for treatment of onsite domestic wastewater: a critical review. Front. Environ. Sci. 11, 1095920. https://doi.org/10.3389/fenvs.2023.1095920.
Otter, P., Malakar, P., Sandhu, C., Grischek, T., Sharma, S.K., Kimothi, P.C., Nüske, G., Wagner, M., Goldmaier, A., Benz, F., 2019. Combination of River bank filtration and solar-driven electro-chlorination assuring safe drinking water supply for river bound communities in India. Water. (Basel) 11 (1), 122. https://doi.org/10.3390/w11010122.
Park, J.H., Choi, S.-H., Bong, Y.-S., 2019. Geographical origin authentication of onions using stable isotope ratio and compositions of C, H, O, N, and S. Food Control 101, 121–125. https://doi.org/10.1016/j.foodcont.2019.02.023.
Patil, P., Jeppu, G., Vallabha, M.S., Girish, C.R., 2024. Enhanced adsorption of phenolic compounds using biomass-derived high surface area activated carbon: isotherms, kinetics and thermodynamics. Environ. Sci. Pollut. Res. 31, 67442–67460. https://doi.org/10.1007/s11356-024-32971-1.
Peng, P., Lang, Y.-H., Wang, X.-M., 2016. Adsorption behavior and mechanism of pentachlorophenol on reed biochars: pH effect, pyrolysis temperature, hydrochloric acid treatment and isotherms. Ecol. Eng. 90, 225–233. https://doi.org/10.1016/j.ecoleng.2016.01.039.
Rahman, M., Amiri, F., Worch, E., 2003. Application of the mass transfer model for describing nonequilibrium transport of HOCs through natural geosorbents. Water Res. 37 (19), 4673–4684. https://doi.org/10.1016/S0043-1354(03)00430-5.
Sadegh, F., Sadegh, N., Wongniramaikul, W., Apiratikul, R., Choodum, A., 2024. Adsorption of volatile organic compounds on biochar: a review. Process. Saf. Environ. Prot. 182, 559–578. https://doi.org/10.1016/j.psep.2023.11.071.
Sajjadi, B., Zubatiuk, T., Leszczynska, D., Leszczynski, J., Chen, W.Y., 2019. Chemical activation of biochar for energy and environmental applications: a comprehensive review. Rev. Chem. Eng. 35 (7), 777–815. https://doi.org/10.1515/revce-2017-0113.
Sakan, S.M., Dordević, D.S., Manojlović, D.D., 2010. Trace elements as tracers of environmental pollution in the canal sediments (alluvial formation of the Danube River, Serbia). Environ. Monit. Assess. 167 (1–4), 219–233. https://doi.org/10.1007/s10661-009-1044-0.
Schoeneberger P.J., Wysocki D.A., Benham E.C., Soil Survey Staff (2012) Field Book for describing and sampling soils, version 3.0. Natural Resources Conservation Service, National Soil Survey Center, Lincoln, Nebraska (NE).
Shah, I., Adnan, R., Ngah, W.S.W., Mohamed, N., 2015. Iron impregnated activated carbon as an efficient adsorbent for the removal of methylene blue: regeneration and kinetics studies. PLoS One 10 (4), e0122603. https://doi.org/10.1371/journal.pone.0122603.
Sigmund, G., Arp, H.P.H., Aumeier, B.M., Bucheli, T.D., Chefetz, B., Chen, W., Droge, S.T.J., Endo, S., Escher, B.I., Hale, S.E., Hofmann, T., Pignatello, J., Reemtsma, T., Schmidt, T.C., Schönsee, C.D., Scheringer, M., 2022. Sorption and mobility of charged organic compounds: how to confront and overcome limitations in their assessment. Environ. Sci. Technol. 56 (8), 4702–4710. https://doi.org/10.1021/acs.est.2c00570.
Song, Q., Kong, F., Liu, B.F., Song, X., Ren, H.Y., 2024. Biochar-based composites for removing chlorinated organic pollutants: applications, mechanisms, and perspectives. Environ. Sci. Ecotechnol. 21, 100420. https://doi.org/10.1016/j.ese.2024.100420.
Song, S., Peng, W., Li, H., 2021. Surface chemistry of mineral adsorbents. In: Song, S., Li, B. (Eds.), Adsorption At Natural Minerals/Water Interfaces. Engineering Materials. Springer Nature Switzerland AG, pp. 55–91.
Soriano-Meseguer, S., Fuguet, E., Abraham, M.H., Port, A., Rosés, M., 2021. Linear free energy relationship models for the retention of partially ionized acid-base compounds in reversed-phase liquid chromatography. J. Chromatogr. A 1635, 461720. https://doi.org/10.1016/j.chroma.2020.461720.
SRPS EN 12879:2007 (2007) Characterization of sludges - determination of the loss on ignition of dry mass.
Sumaraj, Padhye LP, 2017. Influence of surface chemistry of carbon materials on their interactions with inorganic nitrogen contaminants in soil and water. Chemosphere 184, 532–547. https://doi.org/10.1016/j.chemosphere.2017.06.021.
Trivedi, Y., Sharma, M., Mishra, R.K., Sharma, A., Joshi, J., Gupta, A.B., Achintya, B., Shah, K., Vuppaladadiyamd, A.K., 2025. Biochar potential for pollutant removal during wastewater treatment: a comprehensive review of separation mechanisms, technological integration, and process analysis. Desalination 600, 118509. https://doi.org/10.1016/j.desal.2024.118509.
Twagirayezu, G., Cheng, H., Wu, Y., Lu, H., Huang, S., Fang, X., Irumva, O., 2024. Insights into the influences of biochar on the fate and transport of pesticides in the soil environment: a critical review. Biochar 6 (9). https://doi.org/10.1007/s42773-024-00301-w.
US E.P.A. (1986a) Method 9100: saturated hydraulic conductivity, saturated leachate conductivity, and intrinsic permeability.
US E.P.A. (1986b) Method 9080: cation-exchange capacity of soils (ammonium acetate).
Wang, Y., Chen, L., Zhu, Y., Fang, W., Tan, Y., He, Z., Liao, H., 2024. Research status, trends, and mechanisms of biochar adsorption for wastewater treatment: a scientometric review. Environ. Sci. Eur. 36 (25). https://doi.org/10.1186/s12302-024-00859-z.
WHO, 2017. Guidelines For Drinking-Water quality: Fourth Edition Incorporating the First Addendum. World Health Organization, Geneva, 2017. Licence: CC BY-NC-SA 3.0 IGO.
Worch E. (2006) Program TransMod (Version 2.2) Program documentation.
Worch, E., 2012. Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling, 1st edn. De Gruyter, Berlin, Boston.
Wu, L., Li, B., Liu, M., 2018. Influence of aromatic structure and substitution of carboxyl groups of aromatic acids on their sorption to biochars. Chemosphere 210, 239–246. https://doi.org/10.1016/j.chemosphere.2018.07.003.
Xiao, F., Pignatello, J.J., 2015. $\pi^{+}-\pi$ interactions between (Hetero)aromatic amine cations and the graphitic surfaces of pyrogenic carbonaceous materials. Environ. Sci. Technol. 49 (2), 906–914. https://doi.org/10.1021/es5043029.
Yadav, S., Kumar, S., Haritash, A.K., 2023. A comprehensive review of chlorophenols: fate, toxicology and its treatment. J. Environ. Manage 342, 118254. https://doi.org/10.1016/j.jenvman.2023.118254.
Zhang, G., Zhang, Q., Sun, K., Liu, X., Zheng, W., Zhao, Y., 2011. Sorption of simazine to corn straw biochars prepared at different pyrolytic temperatures. Environ. Pollut. 159 (10), 2594–2601. https://doi.org/10.1016/j.envpol.2011.06.012.
Zhang, J., Xu, X., Liang, J., Huang, W., Zhao, L., Qiu, H., Cao, X., 2024. Natural attenuation of 2,4-dichlorophenol in Fe-rich soil during redox oscillations: anoxic−oxic coupling mechanism. Environ. Sci. Technol. 58, 13467–13477. https://doi.org/10.1021/acs.est.4c03244.
Zhang, Y., Schaap, M.G., 2019. Estimation of saturated hydraulic conductivity with pedotransfer functions: a review. J. Hydrol. 575 (May), 1011–1030. https://doi.org/10.1016/j.jhydrol.2019.05.058.
Zhong, J., Li, W., Xie, Y., Yang, Y., Ding, L., 2023. Interaction between chlorophenols in the adsorption process on corn straw biochar. Desalin. Water Treat. 290, 104–112. https://doi.org/10.5004/dwt.2023.29376.
Zhou, L., Fang, Y., Chi, T., Zou, H., Fan, X., Zeng, Y., Chen, H., Wu, H., 2023. Biochar as an electron shuttle loaded with Fe/Ni bimetallic nanoparticles for efficient removal of 2,4-dichlorophenols: performance, degradation pathway and mechanism. J. Water. Process. Eng. 55, 104187. https://doi.org/10.1016/j.jwpe.2023.104187.

Further reading

Commission, European, 2000. Directive 2000/60/EC of the European Parliament and the Council of 23 October 2000 establishing a framework for community action in the field of Water policy. Off. J. Eur. Communities 1–72, L327.
European Commission, 2013. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending directives 2000/60/EC and 2008/105/EC as regards Priority substances in the field of Water policy. Off. J. EU 1–17 L226.