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Optymalizacja procesu kompostowania osadów ściekowych przy zastosowaniu biowęgli i biowęgli projektowanych w celu otrzymania kompostów o zredukowanym ryzyku środowiskowym i podwyższonych właściwościach nawozowych

(Optimizing sewage sludge composting with customized biochars for improved fertilizer quality and lower environmental risk)

Rozprawa doktorska przygotowywana pod kierunkiem naukowym
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Spis treści

Wykaz stosowanych skrótów

BC	biowęgiel (ang. *biochar*)
BCR	procedura sekwencyjnej ekstrakcji (ang. *The Community Bureau of Reference*)
C_{free}	zawartość biodostępnej frakcji zanieczyszczeń (ang. *freely dissolved concentration*)
C_{tot}	całkowita zawartość zanieczyszczeń (ang. *solvent extractable concentration*)
DOC	rozpuszczalny węgiel organiczny (ang. *dissolved organic carbon*)
EPA	Agencja Ochrony Środowiska (ang. *The Environmental Protection Agency*)
FT-IR	spektroskopia w podczerwieni z transformatą Fouriera
F1, F2, F3, F4	frakcje metali oznaczane przy pomocy procedury BCR, odpowiednio frakcja: F1 – wymienna i związana z węglanami, F2 – związana z tlenkami żelaza i manganu (ulegająca redukcji), F3 – związana z materią organiczną i siarczkami (ulegająca utlenianiu) oraz F4 – niedostępna (rezydualna)
GC-MS	chromatografia gazowa sprzężona ze spektrometrem mas (ang. *gas chromatography - mass spectrometry*)
ICP-OES	optyczna spektrometria emisyjna ze wzbudzeniem w plazmie indukcyjnie sprzężonej (ang. *Inductively Coupled Plasma Optical Emission Spectrometry*)
JCR	ang. *Journal Citation Reports*
MNiSW	Ministerstwo Nauki i Szkolnictwa Wyższego
POM	polioksymetylen
PTE	pierwiastki potencjalnie toksyczne (ang. *potentially toxic elements*)

SIM	monitorowanie wybranych jonów (ang. *selected ion monitoring)*
SL-BC	biowęgle pochodzące z osadu ściekowego (ang. *sewage sludge-derived biochars*)
SL500	biowęgiel otrzymany z osadu ściekowego w 500 °C
SL700	biowęgiel otrzymany z osadu ściekowego w 700 °C
TOC	całkowity węgiel organiczny (ang. *total organic carbon*)
WL-BC	biowęgle pochodzące z wierzby (ang. *willow-derived biochars*)
WL500	biowęgiel otrzymany z wierzby w 500 °C
WL700	biowęgiel otrzymany z wierzby w 700 °C
WWA	wielopierścieniowe węglowodory aromatyczne (ang. *polycyclic aromatic hydrocarbons*, PAHs)

1. Wykaz artykułów naukowych będących przedmiotem rozprawy

[D1] **Rombel A.,** Krasucka P., Oleszczuk P.
Sustainable biochar-based soil fertilizers and amendments as a new trend in biochar research
Science of the Total Environment, 2021, 816: 151588
doi.org/10.1016/J.SCITOTENV.2021.151588 **IF**: 8,2 **Punkty MNiSW**: 200

[D2] **Rombel A.**, Różyło K., Oleszczuk P.
The high dose of biochar reduces polycyclic aromatic hydrocarbons losses during co-composting of sewage sludge and wheat straw
Journal of Environmental Management, 2024, 351: 119628
doi.org/10.1016/J.JENVMAN.2023.119628 **IF**: 8,0 **Punkty MNiSW**: 200

[D3] **Rombel A**., Raczkiewicz M., Oleszczuk P.
Reducing metal mobility and associated ecological and human health risks in sewage sludge compost via biochar addition
Biomass Conversion and Biorefinery, **artykuł wysłany do czasopisma**

[D4] **Rombel A.,** Różyło K., Ok Y.S., Oleszczuk P.
Influence of biochar characteristics on polycyclic aromatic hydrocarbons content during co-composting of sewage sludge
Bioresource Technology, 2025, 423: 132220
doi.org/10.1016/J.BIORTECH.2025.132220 **IF**: 9,7 **Punkty MNiSW**: 140

[D5] **Rombel A.**, Raczkiewicz M., Pan B., Oleszczuk P.
Stage-dependent effects of willow- and sewage sludge-derived biochar on compost ecotoxicity across multiple trophic levels
Journal of Environmental Chemical Engineering, 2026, 14: 121924
doi.org/10.1016/j.jece.2026.121924 **IF:** 7,2 **Punkty MNiSW**: 100

Sumaryczny *impact factor* (IF): 33,1

Sumaryczna liczba punktów MNiSW: 640

2. Streszczenie w języku polskim

Rozprawa doktorska pt. „*Optymalizacja procesu kompostowania osadów ściekowych przy zastosowaniu biowęgli i biowęgli projektowanych w celu otrzymania kompostów o zredukowanym ryzyku środowiskowym i podwyższonych właściwościach nawozowych*” składa się z cyklu pięciu powiązanych tematycznie artykułów naukowych, w których cztery zostały opublikowane w recenzowanych czasopismach naukowych znajdujących się na liście *Journal Citation Reports* (JCR), a piąty został wysłany do czasopisma. **Wstęp** do zagadnień badawczych poruszanych w rozprawie doktorskiej stanowi praca przeglądowa [D1]. W Publikacji [D1] przedstawiono wpływ różnych rodzajów nawozów otrzymywanych na bazie biowęgla (BC) na właściwości gleby oraz wielkość plonu. Podkreślono charakter typu „multi-win” stosowania BC, jako istotnego i efektywnego składnika nawozu. **Badania własne** stanowiące przedmiot rozprawy doktorskiej obejmowały dwa główne etapy. **Pierwszy etap badań** miał na celu określenie optymalnej dawki BC (1% lub 5%) dodanego do osadu ściekowego i słomy pszenicy, w kontekście obniżenia poziomu i dostępności wielopierścieniowych węglowodorów aromatycznych (WWA), przekształcania pierwiastków potencjalnie toksycznych (PTE) do form mniej dostępnych oraz dokonanie oceny wpływu na organizmy żywe. Dodatek BC na poziomie 1% okazał się bardziej efektywny pod kątem obniżenia zawartości WWA w finalnym kompoście (Publikacja [D2]). W związku z tym ta dawka BC została wybrana do realizacji dalszych badań (Publikacje [D4, D5]). W przypadku PTE, wpływ dawki BC na ich transformację do form mniej dostępnych zależał przede wszystkim od rodzaju PTE (dla Ni bardziej efektywna była dawka 1% BC, podczas gdy dla Cu i Zn – dawka 5% BC). Biorąc pod uwagę wpływ na organizmy żywe (bakterie, rośliny i bezkręgowce), zaobserwowano, że wyższa dawka BC wpływała bardziej korzystnie (obniżenie toksyczności oraz większa stymulacja) na organizmy testowe w porównaniu do niższej (Publikacja [D3]). **W drugim**

etapie badań określono wpływ warunków (temperatura pirolizy oraz surowiec) otrzymywania BC dodanego do kompostowania osadu ściekowego na poziom i dostępność WWA oraz różne organizmy testowe. Wykazano, że BC otrzymane w niższej temperaturze pirolizy (500 °C) bardziej efektywnie obniżyły poziom i dostępność WWA w kompoście niż BC otrzymane w 700 °C (Publikacja [D4]). Badania pokazały również, że zarówno surowiec użyty do produkcji BC, jak i temperatura pirolizy miały wpływ na ekotoksyczność kompostu z BC (Publikacja [D5]). Zaobserwowano, że efekt w istotnym stopniu zależał od rodzaju organizmu. Stwierdzono pozytywny wpływ wszystkich BC na ekotoksyczność kompostu w stosunku do bakterii. W przypadku roślin wyraźnie lepszy wpływ zaobserwowano dla wariantów z BC z osadu ściekowego. Wybór surowca do otrzymania BC był również kluczowy dla bezkręgowców. BC otrzymane z wierzby wykazały dużo korzystniejszy wpływ na bezkręgowce niż te z osadu ściekowego (Publikacja [D5]). Uzyskane w ramach badań wyniki pokazały, że dodanie BC podczas kompostowania osadu ściekowego, jest interesującym i praktycznym kierunkiem utylizacji tego odpadu. Poprzez zmniejszenie mobilności i biodostępności PTE oraz WWA, jak również obniżenie ekotoksyczności na wielu poziomach troficznych, kompostowanie z dodatkiem BC minimalizuje ryzyko zanieczyszczenia gleby i wód gruntowych oraz ogranicza ich pośredni i bezpośredni, negatywny wpływ na organizmy żywe. Kluczowe jednak są właściwości BC (determinowane przez warunki otrzymywania) oraz jego dawka, które wpływają na efektywność wiązania zanieczyszczeń oraz ekotoksyczność kompostu. Wykazano, że odpowiedni dobór właściwości BC oraz jego dawki umożliwia uzyskanie zróżnicowanych efektów ukierunkowanych na określone grupy zanieczyszczeń lub organizmów żywych. Jednocześnie zagadnienie to wymaga dalszych badań, które pozwolą na lepsze poznanie mechanizmów tych oddziaływań oraz bardziej precyzyjne dostosowanie parametrów stosowania BC do konkretnych zastosowań środowiskowych.

3. Streszczenie w języku angielskim

The doctoral dissertation, entitled "*Optimizing sewage sludge composting with customized biochars for improved fertilizer quality and lower environmental risk*" consists of a series of five thematically related research papers, four of which have been published in peer-reviewed scientific journals listed on the *Journal Citation Reports* (JCR), and the fifth was submitted to the journal. The review article [D1] provides an **introduction** to the research topics addressed in the doctoral dissertation. Publication [D1] presents the impact of various types of fertilizers obtained based on or with the addition of biochar (BC) on soil properties and crop yield. The multi-win nature of BC use was highlighted as an important and effective fertilizer component. **The research part** of the doctoral dissertation comprised two main stages. **The first stage of the research** aimed to determine the optimal BC dose (1% or 5%) added to sewage sludge and wheat straw composting in the context of reducing the levels and availability of polycyclic aromatic hydrocarbons (PAHs), transforming potentially toxic elements (PTEs) into less available forms, and assessing the impact on living organisms. The lower, 1% BC dose proved more effective in reducing PAH content in the final compost (Publication [D2]). Consequently, this dosage was selected for further research (Publications [D4, D5]). For PTEs, the influence of the BC on their transformation into less available forms depended primarily on the type of PTE (a 1% dose was more effective for Ni, while a 5% dose was more effective for Cu and Zn). Regarding the impact on living organisms (bacteria, plants, and invertebrates), it was observed that a higher BC dose was more beneficial (reduced toxicity and greater stimulation) for the test organisms compared to the lower dose (Publication [D3]). In **the second stage of the research**, the influence of BC production conditions (pyrolysis temperature and feedstock) added to sewage sludge composting on the level and availability of PAHs and various test organisms was determined. It was demonstrated

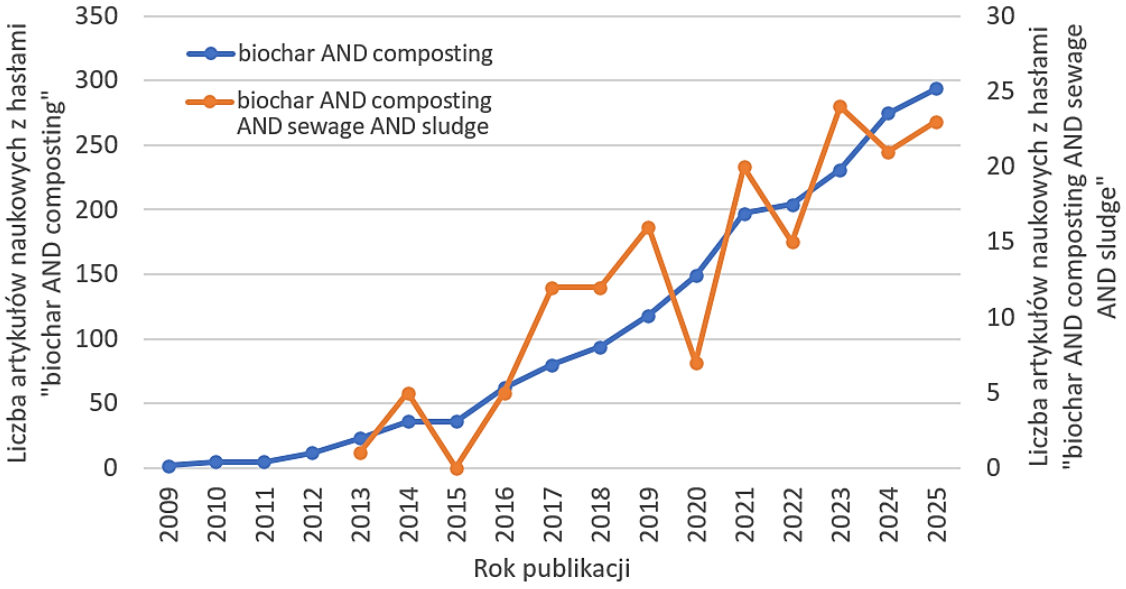
that BC obtained at a lower pyrolysis temperature (500 °C) more effectively reduced the level and availability of PAHs in the compost than BC obtained at 700 °C (Publication [D4]). The research also showed that both the feedstock used for BC production and the pyrolysis temperature influenced the ecotoxicity of the BC-amended compost (Publication [D5]). It was observed that the effect depended significantly on the type of organism. A positive effect of all BCs on the ecotoxicity of the compost towards bacteria was found. For plants, a clearly better effect was observed for variants with sewage sludge-derived BC. The choice of feedstock for BC production was also crucial for invertebrates. BC obtained from willow showed a much more favorable effect on invertebrates than those derived from sewage sludge (Publication [D5]). The results obtained in the study showed that adding BC during sewage sludge composting is an interesting and practical direction for waste utilization. By reducing the mobility and bioavailability of PTEs and PAHs, as well as lowering ecotoxicity across numerous trophic levels, composting with BC minimizes the risk of soil and groundwater contamination and limits their indirect and direct negative impact on living organisms. However, the properties of BC (determined by the production conditions) and its dosage are key factors influencing the efficiency of contaminants binding and the compost's ecotoxicity. It was shown that an appropriate selection of BC properties and its dosage enables diverse effects aimed at specific groups of contaminants or living organisms. At the same time, this issue requires further research to better understand the mechanisms of these interactions and to more precisely adapt BC application parameters to specific environmental applications.

4. Aktualny stan wiedzy

4.1. Strategia „*multi-win*”: kompostowanie odpadów z biowęglem w roli głównej

Biowęgiel (BC, ang. *biochar*) to materiał porowaty otrzymywany w wyniku termicznego rozkładu biomasy w warunkach beztlenowych, który na przestrzeni ostatnich lat zyskał ogromne zainteresowanie w dziedzinie rolnictwa [1]. BC otrzymywany jest z wielu surowców, m.in. pozostałości po uprawach (np. kukurydzy, ryżu, pszenicy) lub innych odpadów zielonych, odpadów spożywczych, leśnych, ogrodowych, obornika, pozostałości z biogazowni czy osadu ściekowego [2]. Warunki zastosowane do otrzymywania BC mogą prowadzić do produkcji celowanych materiałów o pożądanych właściwościach fizykochemicznych [3]. Dotychczasowe badania pokazują, że rodzaj surowca użytego do otrzymania BC oraz temperatura pirolizy są kluczowe w kształtowaniu właściwości BC [3]. Dzięki swojej strukturze aromatycznej, BC często charakteryzują się wysoką hydrofobowością, co pozwala na adsorpcję zanieczyszczeń organicznych (wielopierścieniowych węglowodorów aromatycznych (WWA) czy pestycydów) [4]. BC jako materiał często otrzymywany z frakcji odpadowej, może stanowić bezpieczną metodę zagospodarowania tych odpadów zapewniając sekwestrację węgla i ograniczając emisję gazów cieplarnianych (w wyniku biodegradacji niezagospodarowanej materii organicznej może dochodzić do ich emisji), co wpisuje się w zasady gospodarki o obiegu zamkniętym oraz zrównoważonego rozwoju [1]. BC na przestrzeni ostatnich lat cieszy się ogromnym zainteresowaniem badaczy, głównie jako dodatek do gleb. Od niedawna badany jest również jako dodatek do nawozów, pasz, materiałów budowlanych, odzieży, tekstyliów, kosmetyków, farmaceutyków, kompozytów czy tworzyw sztucznych [2]. Jednym z prężnie rozwijających się nurtów zastosowania BC jest przemysł rolniczy. Badacze ciągle szukają

nowych, lepszych, bezpieczniejszych i bardziej wydajnych sposobów nawożenia gleb celem intensyfikacji plonu oraz zapewnienia odpowiedniej ilości pożywienia dla stale rosnącej populacji ludzi na świecie. Nawozy z dodatkiem BC wydają się pod tym względem szczególnie atrakcyjne. Przegląd różnych rodzajów nawozów na bazie BC został przedstawiony w **Publikacji [D1]**. Często badanym kierunkiem zastosowania BC w rolnictwie jest kompostowanie (**Rys. 1**).



Rys. 1. Liczba opublikowanych artykułów naukowych z hasłami: „biochar AND composting" oraz „biochar AND composting AND sewage AND sludge" w tytule, streszczeniu oraz słowach kluczowych od 2009 roku według bazy SCOPUS (data dostępu: 12.03.2026 r.).

Jednym z odpadów powstających corocznie w dużych ilościach jest osad ściekowy. Szacuje się, że na świecie rocznie produkowanych jest nawet 53 milionów ton osadu ściekowego, w przeliczeniu na suchą masę [5]. Co ciekawe, wraz z przewidywanym wzrostem ludności do 2050 r. mającej osiągnąć 9,7 miliarda, generowanie osadu ściekowego ma ulec zwiększeniu o ponad 50% [6]. Zarządzanie tym zasobem odpadowym stanowi jedno z wyzwań środowiskowych współczesnej gospodarki wodno-ściekowej, zarówno ze względu na jego dużą objętość, jak i obecność szkodliwych składników, takich

jak pierwiastki potencjalnie toksyczne (PTE), WWA, mikroplastiki, pozostałości antybiotyków czy jaja pasożytów [7,8]. Jednakże nie należy zapominać, że osad ściekowy stanowi równocześnie źródło materii organicznej bogatej w azot, fosfor, wapń czy magnez [9]. W konsekwencji, rozwój efektywnych i bezpiecznych metod zagospodarowania osadu ściekowego stał się istotnym kierunkiem badań naukowych oraz tematem debat na poziomie globalnym [10].

Od lat kompostowanie osadu ściekowego jest stosowane jako jedna z form jego zagospodarowania [11]. W wyniku kompostowania następuje przekształcenie odpadu w stabilny materiał organiczny bogaty w składniki odżywcze, który jest wykorzystywany jako polepszacz gleby lub nawóz w rolnictwie i rekultywacji gleb zdegradowanych [12]. W trakcie kompostowania zachodzi intensywna humifikacja i biodegradacja materii organicznej, prowadząca do powstania stabilnych związków humusowych poprawiających strukturę gleby, zdolność retencji wody oraz aktywność mikrobiologiczną [13]. Wysoka temperatura pojawiająca się w fazie termofilnej kompostowania sprzyja higienizacji produktu końcowego, a odpowiednio zaprojektowane kompostowanie może prowadzić do znacznego ograniczenia zawartości niektórych zanieczyszczeń organicznych [14]. Jednocześnie kompostowanie osadu ściekowego wiąże się w pewnymi zagrożeniami środowiskowymi. Osad jako materiał o wysokim ryzyku środowiskowym, mogący zawierać różnorodne toksyny, w przypadku niewłaściwego podejścia do metody zagospodarowania lub przy zbyt wysokich dawkach aplikacyjnych, może przyczyniać się do kumulowania zanieczyszczeń w glebie i ich przenikania do środowiska [15]. Dlatego też kluczowe znaczenie ma odpowiednia kontrola parametrów kompostowania oraz staranne monitorowanie jakości powstałego kompostu, celem zapewnienia bezpieczeństwa środowiskowego po wprowadzeniu do gleby.

Wraz z rozwojem technologii otrzymania BC, piroliza osadu ściekowego stała się również jedną z dróg zagospodarowania tego materiału. Ten sposób przekształcania odpadów umożliwia jednoczesną znaczącą redukcję objętości materiału odpadowego oraz pozyskanie cennego materiału o wielu pożądanych właściwościach, w tym BC [16]. Piroliza prowadzi do rozkładu materii organicznej, co skutkuje stabilizacją węgla organicznego oraz zatężeniem składników mineralnych w powstałym BC [17]. Dodatkowo piroliza umożliwia eliminację lub zmniejszenie poziomu niektórych zanieczyszczeń (jaja pasożytów, patogeny, WWA, pozostałości farmaceutyków) obecnych w osadzie ściekowym, co zwiększa bezpieczeństwo dalszego wykorzystania BC [16]. Oczywiście, produkcja BC z osadu ściekowego jest procesem bardziej skomplikowanym technologicznie, wymagającym bardziej zaawansowanej aparatury, niż kompostowanie. Należy się liczyć z tym, że nie wszystkie zakłady uzdatniania wody będą w stanie pozwolić sobie na wprowadzenie instalacji do produkcji BC, pozostając przy kompostowaniu jako głównej metodzie zagospodarowania osadu ściekowego.

Użycie osadu ściekowego jako substratu do kompostowania z dodatkiem BC (potencjalnie otrzymanego z odpadów, w tym osadu ściekowego) może stanowić rozwiązanie o charakterze „*multi-win*", jako że łączy ze sobą trzy istotne aspekty: (1) recykling i zagospodarowanie odpadów, (2) polepszenie właściwości gleb oraz (3) produkcję bezpiecznych i skutecznych nawozów [11]. Już od roku 2013 w dostępnej literaturze naukowej można zaobserwować rosnący trend zainteresowania społeczności naukowej w temacie dotyczącym kompostowania osadu ściekowego z dodatkiem BC (**Rys. 1**). Osad ściekowy nie jest powszechnym surowcem wybieranym podczas kompostowania, jako że prace naukowe na ten temat stanowią jedynie około 10% wszystkich artykułów dotyczących kompostowania z BC (**Rys. 1**). Dodatek BC do kompostowania wywiera złożony wpływ zarówno na sam proces, jak i właściwości oraz

poziom zanieczyszczeń w kompoście, ale również na właściwości gleby, do której dodano kompost, oraz uzyskany plon [18]. Obecność BC podczas kompostowania zwiększa temperaturę podczas fazy termofilnej, jednocześnie wydłużając tą fazę [19]. Takie warunki sprzyjają efektywnemu usunięciu patogenów [20]. BC powoduje zwiększenie różnorodności bakterii rozkładających materię organiczną oraz wspiera aktywność enzymatyczną, co przekłada się na przyspieszenie i zwiększenie efektywności rozkładu materii organicznej podczas kompostowania, przez co proces przebiega krócej [21]. BC dodany do kompostowanego surowca reguluje pH, zawartość rozpuszczalnego węgla organicznego (DOC), ilość i jakość kwasów humusowych (fulwowych i huminowych), wilgotność oraz napowietrzenie kompostu [22,23]. Co ważne, BC ma zdolność obniżania emisji gazów cieplarnianych podczas kompostowania dzięki swojej dużej powierzchni właściwej, rozwiniętej strukturze porów, wysokiej aromatyczności oraz obecności kwasowych grup funkcyjnych [24]. Umożliwia to adsorpcję związków gazowych i jonów (np. amoniaku, ditlenku węgla, jonów amonowych) na powierzchni BC i/lub w rozbudowanej sieci porów BC [25]. BC, jako materiał bogaty w węgiel, poprawia stosunek węgla do azotu w materiale kompostowym, który jest jednym z najważniejszych parametrów odpowiadających za efektywność kompostowania [22]. BC może poprawiać strukturę kompostu poprzez obniżenie liczby miejsc beztlenowych w pryzmie kompostowej [26]. Jednakże jedną z najważniejszych ról BC w kompostowaniu jest zdolność do wiązania zanieczyszczeń, zarówno organicznych, jak i nieorganicznych (PTE, WWA, pestycydy, uniepalniacze, polichlorowane bifenyle, mikroplastiki, estry kwasu ftalowego) [27]. Wykazano, że obecność BC podczas kompostowania sprzyja degradacji wielu zanieczyszczeń, które w wyniku rozkładu nie stanowią zagrożenia podczas stosowania kompostu do gleby [28]. Silne związanie zanieczyszczeń przez BC ogranicza ich dostępność, przez co obniżeniu ulega ich akumulacja przez rośliny czy organizmy

glebowe [28]. Kompost z BC przyczynia się do spowolnienia kinetyki uwalniania składników odżywczych, co zmniejsza straty cennych substancji, a przez zatrzymanie ich w glebie i stopniowe uwalnianie, ograniczana jest eutrofizacja wód [29]. Wpływ BC dodanego do kompostowania zależy od wielu czynników. Są to m.in.: dawka oraz surowiec i warunki otrzymywania BC, przekładające się na zróżnicowanie jego właściwości [30,31]. Niemniej jednak stosowanie kompostów z dodatkiem BC jest obiecującym rozwiązaniem problemu nadmiernego używania nawozów mineralnych, wywiera realny wpływ na realizację celów zrównoważonego rozwoju oraz promuje produkcję nawozów o kontrolowanym uwalnianiu składników odżywczych.

Pomimo wielu udowodnionych korzyści, zastosowanie BC w kompostowaniu osadu ściekowego pozostaje nadal stosunkowo słabo poznane w porównaniu z jego szerokim wykorzystaniem w kompostowaniu odpadów rolniczych czy obornika [32,33].

Dotychczasowe badania nad kompostowaniem odpadów z dodatkiem BC koncentrowały się przede wszystkim na podstawowych parametrach procesu kompostowania, takich jak dynamika przemian materii organicznej, aktywność mikroorganizmów, emisja gazów cieplarnianych, straty azotu czy stopień humifikacji materii organicznej [19]. W pracach analizowano zdolność BC do immobilizacji PTE oraz zmniejszania ich dostępności dla roślin [34]. Znacznie rzadziej podejmowano badania dotyczące losów zanieczyszczeń organicznych obecnych w osadzie ściekowym, w szczególności WWA [35–37]. Co istotne, w literaturze naukowej istnieją jedynie pojedyncze badania analizujące zmiany zawartości WWA podczas kompostowania osadu ściekowego z BC [38], a jednocześnie brak jest prac oceniających biodostępność tych związków w trakcie procesu kompostowania. To właśnie biodostępna frakcja zanieczyszczeń odzwierciedla ich rzeczywisty wpływ na organizmy żywe oraz ich potencjalne oddziaływania fizykochemiczne i biologiczne w glebie. Pomijanie tego

aspektu w wielu badaniach znacząco ogranicza możliwość rzetelnej oceny bezpieczeństwa środowiskowego kompostów powstających z osadu ściekowego.

Kolejnym niedostatecznie poznanym zagadnieniem jest wpływ właściwości samego BC na efektywność immobilizacji zanieczyszczeń w kompoście. Dotychczas nie przeprowadzono badań kompleksowo analizujących wpływ temperatury pirolizy oraz rodzaju biomasy użytej do otrzymywania BC na zawartość i biodostępność WWA oraz PTE podczas kompostowania osadu ściekowego. Również zależność między dawką BC a stopniem immobilizacji zanieczyszczeń w tym układzie pozostaje w dużej mierze niezbadana.

Istotną luką badawczą pozostaje także ocena ekotoksyczności materiałów powstających w trakcie kompostowania odpadów organicznych z BC. Dotychczasowe prace w tym zakresie najczęściej ograniczają się do testów kiełkowania roślin [39]. Jednakże kompleksowa ocena bezpieczeństwa środowiskowego kompostu powinna obejmować testy w fazie stałej, jak i ciekłej oraz badania z udziałem organizmów reprezentujących różne poziomy troficzne, takich jak bakterie, rośliny czy bezkręgowce glebowe. Jest to szczególnie istotne w przypadku kompostów wytwarzanych z osadu ściekowego, które mogą zawierać liczne zanieczyszczenia oddziałujące synergistycznie lub prowadzące do powstawania potencjalnie toksycznych metabolitów. Co więcej, większość badań dotyczy wyłącznie końcowego produktu kompostowania, pomijając analizę poszczególnych etapów procesu, które mogą być kluczowe dla zrozumienia mechanizmów powstawania lub zmniejszania toksyczności [40].

Wskazuje się również, że wyniki analiz chemicznych nie zawsze korelują z rzeczywistymi efektami biologicznymi. W badaniach Roques i in. [41] materiał o niższej zawartości zanieczyszczeń wykazywał silniejsze działanie toksyczne wobec organizmów

testowych niż materiał bardziej zanieczyszczony. Podkreśla to konieczność prowadzenia badań ekotoksykologicznych z wykorzystaniem różnych organizmów testowych.

W świetle powyższych ograniczeń istnieje wyraźna potrzeba prowadzenia kompleksowych badań obejmujących zarówno wpływ dawki, jak i parametrów otrzymywania BC użytego w kompostowaniu, analizę zawartości i biodostępności zanieczyszczeń organicznych, oraz kompleksową ocenę ekotoksyczności materiałów powstających w trakcie kompostowania osadu ściekowego z BC. Badania takie wypełniają istotną lukę informacyjną w aktualnym stanie wiedzy, dostarczając nowych danych dotyczących mechanizmów immobilizacji i usuwania zanieczyszczeń, wpływu właściwości i dawki BC oraz rzeczywistego oddziaływania powstających kompostów na organizmy reprezentujące różne poziomy troficzne.

4.2. WWA podczas kompostowania osadu ściekowego

WWA stanowią grupę hydrofobowych związków o niskiej rozpuszczalności w wodzie i niewielkiej biodegradowalności w środowisku, co klasyfikuje je jako trwałe zanieczyszczenia organiczne [42]. WWA powstają w wyniku niecałkowitego spalania materiałów organicznych podczas procesów antropogenicznych oraz naturalnych, takich jak spalanie paliw kopalnych czy odpadów, rafinacja ropy naftowej, pożarów lasów i erupcji wulkanów [43]. Agencja Ochrony Środowiska Stanów Zjednoczonych (US EPA) opracowała listę szesnastu priorytetowych WWA, jako substancji uważanych za szczególnie niebezpieczne dla człowieka oraz środowiska, biorąc pod uwagę ich częste występowanie oraz negatywne oddziaływanie na środowisko [44]. WWA wykazują działanie mutagenne, kancerogenne oraz teratogenne, powodują zaburzenia hormonalne i tłumią działanie układu immunologicznego [45].

Jak już wspomniano w podrozdziale 4.1, osad ściekowy może zawierać znaczne ilości różnych zanieczyszczeń organicznych [46], z których WWA stanowią istotną grupę

[47]. Jednym ze sposobów eliminacji WWA z osadu ściekowego przed jego rolniczym wykorzystaniem jest kompostowanie [35], które łączy procesy biologiczne, chemiczne i fizyczne sprzyjające degradacji tych związków.

W wyniku kompostowania uzyskuje się nie tylko obniżenie zawartości WWA [35], ale również polepsza się właściwości osadu ściekowego pod względem jego właściwości nawozowych i stabilności materii organicznej [48]. W różnych badaniach początkowe całkowite stężenie Σ16 WWA w surowcu kompostowym złożonym z osadu ściekowego i różnych dodatków (odpady zielone, żywnościowe, trociny czy słoma) wahało się od 0,21 mg/kg do nawet 82 mg/kg, w zależności od pochodzenia osadu ściekowego [11]. Z drugiej strony, efektywność usuwania WWA podczas kompostowania sięgała od 30% do blisko 93% [11], co udowadnia znakomite działanie kompostowania jako sposobu ponownego wykorzystania ryzykownych odpadów. Mechanizmy ograniczające dostępność WWA podczas kompostowania obejmują przede wszystkim dwa procesy: biodegradację oraz adsorpcję i/lub sekwestrację [11]. Mikroorganizmy odpowiedzialne za biodegradację WWA podczas kompostowania wykorzystują te związki jako źródło węgla lub przekształcają je w procesach metabolicznych [49]. Dodatek kompostu do gleby może w konsekwencji znacząco przyspieszać rozkład WWA obecnych w glebie zanieczyszczonej, dzięki zwiększeniu aktywności mikroorganizmów oraz dostępności składników odżywczych, w które osad ściekowy jest bogaty [50]. W degradacji WWA istotną rolę odgrywają również enzymy oksydacyjne (lakazy, proteazy, oksydazy, polifenolooksydazy), które katalizują reakcje utleniania pierścieni aromatycznych, prowadząc do powstawania związków pośrednich, które następnie mogą ulegać dalszej mineralizacji lub włączeniu do struktur humusowych [49]. Drugą możliwą drogą, która znacząco ogranicza biodostępność WWA podczas kompostowania jest adsorpcja i/lub sekwestracja [51]. WWA, jako związki silnie hydrofobowe, wykazują skłonność do

adsorpcji na materii organicznej, co wpływa na ich niższą mobilność oraz dostępność dla organizmów [52]. Podczas kompostowania dochodzi do intensywnych przemian materii organicznej, prowadzących do powstawania substancji humusowych o dużej powierzchni właściwej oraz licznych grupach funkcyjnych, a struktury te mają zdolność silnego wiązania WWA poprzez oddziaływania hydrofobowe, oddziaływania π-π czy siły van der Waalsa [53]. Procesy te prowadzą do stopniowego włączania WWA w struktury humusowe, co skutkuje ich sekwestracją w matrycy kompostowej [53]. Silne związanie WWA z materią organiczną może zmniejszać toksyczność kompostu po zastosowaniu do gleby, ponieważ związki te stają się trudniej dostępne. Mechanizm adsorpcji jest szczególnie ważny w przypadku związków o wysokiej masie cząsteczkowej, dla których biodegradacja nie zachodzi lub zachodzi jedynie w niewielkim stopniu [54]. Z drugiej jednak strony częściowa adsorpcja WWA w miejscach niedostępnych (ligninoceluloza, holoceluloza) ogranicza mobilność tych związków i pozwala uniknąć „ataku" mikroorganizmów, co skutkuje niskim poziomem nieodwracalnego usuwania WWA (biodegradacji) [55].

Liczba badań obejmujących zmiany WWA podczas kompostowania osadu ściekowego jest ograniczona. W badaniach Poluszyńskiej i in. [35] podczas kompostowania osadu ściekowego wraz z dodatkiem trocin osiągnięto znaczący spadek zawartości Σ16 WWA ze średnio 26,07 do 4,01 mg/kg (efektywność usuwania na poziomie 85%). Średnie zmniejszenie indywidualnych związków sięgało od 74% dla 4-pierścieniowych WWA aż do 100% dla 2-pierścieniowego naftalenu. WWA o niższej masie cząsteczkowej, dzięki słabszym właściwościom hydrofobowym, były mniej związane z cząstkami stałymi, przez co bardziej podatne na biodegradację. Ozaki i in. [36] zbadali surowe osady ściekowe oraz gotowy kompost, otrzymany z mieszanki osadu oraz odpadów żywnościowych i przemysłowych, odnotowując efektywność usuwania Σ16 WWA na poziomie 57%, która była odwrotnie proporcjonalna do ilości pierścieni

aromatycznych w WWA. Autorzy wskazali, że w procesie usuwania WWA podczas kompostowania były zaangażowane zarówno procesy biodegradacji, jak i sekwestracji. W badaniach Guo i in. [56] podczas kompostowania osadu ściekowego z zielonymi odpadami leśnymi zmieszanymi w różnych stosunkach osiągnięto efektywność usuwania WWA na poziomie od 62% do 75%, w zależności od stosunku zmieszanych substratów. Czynnikami wpływającymi na stopień usuwania WWA były głównie temperatura, pH, zawartość całkowitego węgla organicznego (TOC) i azotu oraz stosunek węgla do azotu. Eksperyment Vrábl i in. [37] polegający na kompostowaniu osadu ściekowego wraz z pięcioma innymi materiałami odpadowymi (na bazie drewna, trawy i gleby) udowodnił, że kompostowanie osadu z dodatkiem skrawków drzewnych w największym stopniu obniżyło poziom Σ15 WWA w kompoście, co autorzy połączyli bezpośrednio z najwyższą zawartością kwasów humusowych w tym wariancie kompostu.

Wyniki badań pokazują, że rzadko dochodzi do pełnej eliminacji WWA z osadu ściekowego po kompostowaniu, co w przypadku wielokrotnej aplikacji kompostów otrzymanych na bazie osadu ściekowego może prowadzić do akumulacji tych niebezpiecznych zanieczyszczeń w glebie, bądź pobierania ich przez rośliny i włączenie do łańcucha pokarmowego człowieka.

4.3. Metale nie znikają - jak je unieszkodliwić?

Pierwiastki potencjalnie toksyczne, takie jak rtęć, ołów, kadm, arsen, cynk, nikiel, miedź, stanowią jedną z najgroźniejszych kategorii zanieczyszczeń środowiska, ze względu na swoją wysoką toksyczność oraz trwałość [57]. Nie ulegają one biodegradacji, co sprawia, że przy okresowej lub ciągłej ekspozycji akumulują się w glebach lub osadach dennych, wywierając negatywny wpływ na środowisko. PTE występują naturalnie zarówno w skorupie ziemskiej, jak i w biosferze: skałach, glebie i wodach [58]. Naturalne źródła występowania PTE, obejmujące erozję gleby i wietrzenie skorupy ziemskiej, mają

niewielki wkład w globalne zanieczyszczenie środowiska tymi pierwiastkami [58]. Górnictwo, hutnictwo, produkcja pestycydów, ścieki przemysłowe, ruch uliczny, produkty uboczne spalania z elektrowni oraz przemysł chemiczny i petrochemiczny uważane są natomiast za główne źródła obecności PTE w środowisku w ilościach nadmiarowych, stwarzających zagrożenie dla zdrowia ludzi i jakości środowiska [58]. Niektóre PTE, jak np. żelazo, cynk, miedź czy chrom odgrywają kluczową rolę w procesach biochemicznych organizmów, zarówno u ludzi (jako składniki enzymów i białek), jak i w środowisku (wspierając funkcjonowanie roślin i mikroorganizmów) [57]. Jednakże, zarówno niedobór, jak i nadmiar większości PTE może prowadzić do poważnych zaburzeń. Efekt toksyczny wywołany PTE jest zależny od jego typu, dawki, drogi podania i czasu trwania narażenia oraz formy specjacyjnej obecnej w danej matrycy [59]. Przykładem jest chrom, który na +III stopniu utlenienia jest korzystny dla zdrowia, regulując metabolizm, podczas gdy chrom na +VI stopniu utlenienia może wywoływać wiele niepożądanych efektów zdrowotnych [57,60]. Oczywiście istnieją PTE, takie jak ołów czy rtęć, które nie są potrzebne człowiekowi i stanowią jedynie zagrożenie dla jego organizmu [58]. Toksyczność PTE głównie obejmuje choroby nerek, mózgu, skóry, serca czy wątroby, ale również uszkodzenie DNA i zaburzenia ogólnoustrojowe [57]. W przypadku roślin, PTE zakłócają wzrost już na poziomie komórkowym, pośrednio ograniczając wchłanianie składników odżywczych oraz bezpośrednio zaburzając metabolizm i szlaki enzymatyczne, często prowadząc do obumarcia [61].

PTE stanowią zanieczyszczenie często występujące w osadzie ściekowym. Stosowanie odpadów jako surowców do kompostowania wiąże się bezpośrednio z ryzykiem wprowadzania PTE do środowiska [62]. PTE w znikomym stopniu usuwane są z kompostu (głównie z odciekami), ulegając w nim bardzo często zatężeniu w związku ze stratami masy zachodzącymi podczas tego procesu [63]. W związku z tym najbardziej

rozsądnym kierunkiem minimalizacji ryzyka związanego z obecnością PTE w kompostowanym materiale, jest zmiana ich formy z biodostępnej do trudno- albo niedostępnej [64]. Do określenia udziału metali w poszczególnych frakcjach stosuje się metody, takie jak ekstrakcja sekwencyjna (np. Tessiera czy *The Community Bureau of Reference* (BCR)) [65].

Badania zajmujące się oceną wpływu kompostowania osadu ściekowego na rozkład frakcji PTE podczas kompostowania pojawiają się od wielu lat. Bardziej aktualne opracowania z reguły używają pewnych modyfikacji, w tym dodatków do kompostowania (np. soli nieorganicznych, popiołu z biomasy, zeolitu, wapna [66–68]) lub nowoczesnych systemów kompostowania jak np. kompostowanie pod funkcjonalnym pokryciem membranowym [69]. Badania Xu i in. [70] obejmowały kompostowanie osadu ściekowego wraz z odpadami kuchennymi i łodygami kukurydzy i dowiodły, że choć całkowite stężenie badanych PTE wzrosło podczas kompostowania, to PTE były związane przede wszystkim z frakcjami słabo dostępnymi: ulegającą utlenianiu (F3) oraz rezydualną (F4). Zmiany temperatury w trakcie kompostowania oraz pH materiału kompostowego były dominującymi parametrami wpływającymi na zmiany rozkładu frakcji PTE. Wang i in. [67] wykorzystali dodatek dwóch soli nieorganicznych: diwodorofosforanu (V) potasu oraz siarczanu (VI) żelaza do kompostowania osadu ściekowego i udowodnili, że dodatek soli zmniejszał mobilność Cu, Zn i Pb, sprzyjając tworzeniu stabilniejszych form chemicznych PTE, tym samym ograniczając ich dostępność w środowisku. Dodatek bogatego w składniki odżywcze popiołu z biomasy użyty w kompostowaniu osadu ściekowego w badaniach Dede i in. [66] sprzyjał pasywacji Cr, Cd i Pb, powodując ich przechodzenie do frakcji słabo- lub niedostępnych (F3 i F4). Wykorzystanie techniki kompostowania osadu ściekowego pod funkcjonalnym pokryciem membranowym, zapewniające wysoką kontrolę nad napowietrzaniem oraz wilgotnością materiału w trakcie kompostowania,

w badaniach Cai i in. [69], pozwoliło na znaczące zwiększenie wkładu frakcji F4 dla Cr, Pb i As w kompoście (o 7,5%, 17,6% i 28,2%, odpowiednio) na rzecz obniżenia wkładu łatwiej dostępnych frakcji (F1 i F2).

Atrakcyjnym rozwiązaniem, mającym na celu minimalizację ryzyka wprowadzania PTE do środowiska, jest połączenie kompostowania osadu ściekowego z dodatkiem BC. BC dzięki swoim znakomitym właściwościom adsorpcyjnym oraz zdolności zwiększania aktywności mikrobiologicznej, wspomagającej powstawanie kwasów humusowych w trakcie kompostowania, bezpośrednio przyczynia się do unieruchomienia PTE w matrycy kompostowej [64,71]. Kilka z istniejących na ten temat prac koncentruje się na ocenie BC otrzymanych z różnych surowców na pasywację PTE podczas kompostowania osadu ściekowego [72–74], w innych opracowaniach badano wpływ dodatku BC wraz z innym składnikiem (wapno [75], montmorylonit [76], torf [77]), niewiele artykułów naukowych miało na celu ocenę znaczenia dawki BC [71,78] czy wykorzystania BC modyfikowanego [79]. Guo i in. [72] udowodnili, że do pasywacji różnych rodzajów PTE należy rozważyć zastosowanie określonych typów BC: otrzymany z łusek ryżowych sprawdził się najlepiej dla Zn i Pb, z osadu ściekowego – dla Cr i Hg, a ze skorup kokosa – dla Cu, Ni, As i Cd. Analogicznie, badania Quan i in. [74] dowiodły, że BC otrzymane zarówno ze słomy pszenicy, jak i z obornika kurzego zwiększyły stopień immobilizacji Cd, Cu i Zn w kompoście, jednak BC otrzymany z odpadów roślinnych był bardziej efektywny. W badaniach Zhao i in. [73] ustalono, że zmniejszenie biodostępności Zn i Cu odbywało się bardziej wydajnie w kompostowaniu osadu ściekowego z BC na bazie odpadów roślinnych, a w przypadku Pb i Cd – z BC na bazie odpadów zwierzęcych. Analiza wykonana metodą spektroskopii w podczerwieni z transformatą Fouriera (FT-IR) wykazała, że BC wspomagały humifikację, przy czym „roślinny” BC promował tworzenie grup karboksylowych i polisacharydowych, podczas gdy „zwierzęcy” BC sprzyjał

tworzeniu struktur chinonowych i eterów arylowych [73]. Te powierzchniowe grupy funkcyjne BC prawdopodobnie przyczyniły się do wiązania PTE poprzez chelatowanie, adsorpcję i/lub transport elektronów [73]. Biorąc pod uwagę wpływ dawki BC, Liu i in. [78] udowodnili, że wyższy dodatek BC (15,15% *vs* 8,2%, w przeliczeniu na mokrą masę) w większym stopniu obniżał udział frakcji łatwo dostępnych (F1 i F2), stymulując jednocześnie wzrost wkładu frakcji trudnodostępnych (F3 i F4) badanych PTE. Podczas kompostowania osadu ściekowego i słomy, Liu i in. [71] zbadali wpływ czterech dawek BC (1%, 3%, 5%, 7%). Co ciekawe, najniższa dawka 1% BC wykazała najlepszy efekt na pasywację PTE, jednakże wyniki były zróżnicowane w zależności od badanego PTE.

Mimo, że istnieje wiele badań dotyczących kompostowania matryc organicznych z dodatkiem BC i ich wpływu na zawartość PTE w kompoście [63,80–84], to stosunkowo niewielka ilość z nich koncentrowała się na osadzie ściekowym jako surowcu. Co więcej, większość opracowań badała wpływ surowca z jakiego otrzymany został BC dodany do kompostowania [72–74], a rzadko badana była dawka BC dodanego do tego typu eksperymentów [71,78]. Dodatkowo wnioski co do optymalnej dawki BC są rozbieżne. Ponadto brakuje kompleksowych badań, których celem jest analiza poziomu i/lub dostępność PTE połączona z innymi wskaźnikami bezpieczeństwa ekologicznego, takimi jak wpływ na różnorodne organizmy żywe czy zawartość innych zanieczyszczeń.

4.4. Toksyczność: kompost „oczami” organizmów

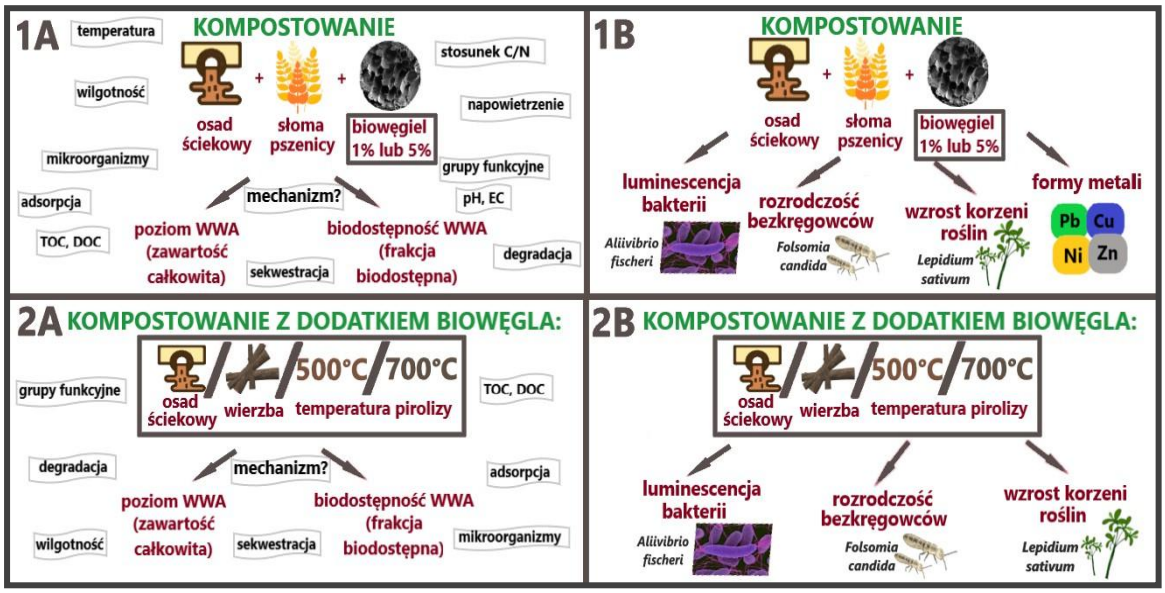
Głównym celem kompostowania osadu ściekowego jest przygotowanie materiału (kompostu) charakteryzującego się pozytywnym wpływem na gleby, wpływającym pozytywnie na zwiększenie plonu. Odbywa się to m.in. przez dostarczenie odpowiedniej ilości składników odżywczych, niezbędnych dla prawidłowego wzrostu i rozwoju roślin [85]. Niemniej jednak parametrem, który powinien być wzięty pod uwagę zaraz obok dostarczenia składników odżywczych, jest bezpieczeństwo środowiskowe [86]. Analiza

chemiczna, choć dostarcza ważnych informacji dotyczących poziomu zanieczyszczeń, nie odzwierciedla w pełni ich potencjalnego wpływu na organizmy żywe [87,88]. Jednym z kluczowych wskaźników jakości kompostu jest ekotoksyczność, która powinna być oceniona względem organizmów reprezentujących różne poziomy troficzne: od mikroorganizmów, przez rośliny, aż po bezkręgowce [88]. Jedynie takie wszechstronne podejście umożliwia ocenę rzeczywistego, wielokierunkowego wpływu kompostu na ekosystem glebowy.

Przegląd aktualnej literatury naukowej ujawnia lukę w kompleksowych badaniach ekotoksyczności kompostów pochodzących z odpadów [88]. Najczęściej badania nad bezpieczeństwem kompostu koncentrują się na wskaźnikach fitotoksyczności, z których głównie wykorzystywany jest wskaźnik kiełkowania (*germination index*, GI), oznaczany w obecności ekstraktów wodnych otrzymanych z kompostów [87,89]. Ograniczenie oceny ekotoksykologicznej jedynie do tego parametru, nie pozwala na poznanie pełnego obrazu potencjalnych skutków ekologicznych. Dlatego niezbędne jest rozszerzenie oceny toksyczności kompostów, szczególnie tych otrzymanych z surowców organicznych o wysokim ryzyku zanieczyszczeń, o wpływ na organizmy reprezentujące różne poziomy troficzne: bakterie czy bezkręgowce. Tego typu badania są nieliczne, a jedynie pojedyncze dotyczą kompostu na bazie osadu ściekowego i BC [90]. W kontekście kompostów otrzymywanych z osadu ściekowego lub innych biomas odpadowych, które oprócz dobrze znanych zanieczyszczeń, takich jak PTE czy WWA, mogą zawierać również liczne związki organiczne o niezidentyfikowanej lub słabo poznanej strukturze, brak wszechstronnej analizy ich toksyczności stanowi istotną lukę w ocenie ryzyka środowiskowego. W szczególności dotyczy to potencjalnego oddziaływania tych związków na organizmy glebowe, rośliny oraz mikroorganizmy, a także możliwości ich kumulacji w środowisku.

5. Cel i zakres badań

Głównym celem badań była optymalizacja procesu kompostowania osadu ściekowego z dodatkiem BC w kontekście minimalizacji ryzyka środowiskowego związanego z otrzymanym kompostem. Badania będące przedmiotem rozprawy doktorskiej były realizowane w dwóch głównych etapach (**Rys. 2**). Celem pierwszego etapu był wybór optymalnej dawki BC dodanego do kompostowania pod kątem: a) obniżenia poziomu i biodostępności WWA w kompoście oraz b) optymalizacji oddziaływania kompostu na organizmy reprezentujące różne poziomy troficzne i powiązanie tego z formami specjacyjnymi PTE podczas różnych faz kompostowania. Drugi etap badań obejmował badanie wpływu warunków otrzymywania BC dodanego do kompostowanego surowca na: a) zawartość i dostępność WWA w kompoście oraz b) ekotoksyczność w stosunku do wybranych organizmów.



Rys. 2. Schemat przedstawiający doświadczenia będące przedmiotem rozprawy doktorskiej.

Hipotezy badawcze postawione w ramach przeprowadzonych badań były następujące:

1. Dawka BC będzie istotnie wpływała na przebieg kompostowania oraz właściwości finalnego produktu (kompostu) w kontekście zawartości zanieczyszczeń i ich form oraz ekotoksyczności (**Publikacja [D2, D3]**).
2. Obecność BC w kompostowanym materiale będzie prowadziła do obniżenia biodostępności zanieczyszczeń, przy czym wyższa dawka BC będzie sprzyjała jednocześnie lepszej ich immobilizacji (**Publikacja [D3]**).
3. Warunki otrzymywania BC (temperatura pirolizy oraz surowiec) będą miały znaczący wpływ na poziom oraz biodostępność WWA w kompoście. Różnice będą głównie wynikały z właściwości fizykochemicznych BC (**Publikacja [D4]**).
4. Dodanie BC do kompostowanego surowca wpłynie na organizmy testowe w zróżnicowany sposób, w zależności od właściwości BC, determinowanych warunkami ich otrzymywania (**Publikacja [D5]**).

6. Metodologia zastosowana w badaniach

6.1. Otrzymanie biowęgli

W celu oceny wpływu dawki, wykorzystano BC otrzymany z przedsiębiorstwa Fluid S.A. (Sędziszów) (surowiec stanowiły zrębki drewna liściasto-iglastego, temperatura pirolizy – 650 ℃) (**Publikacja [D2], [D3]**). W badaniach dotyczących wpływu rodzaju surowca zastosowanego do otrzymania BC i temperatury pirolizy na proces kompostowania (**Publikacje [D4, D5]**), BC otrzymano we własnym zakresie przeprowadzając powolną pirolizę w poziomym rurowym piecu retortowym PRS 168 × 380/90G (Czylok, Polska). Szczegóły dotyczące warunków otrzymania przedstawiono w **Publikacjach [D4, D5]**. BC wykorzystane w tych badaniach otrzymano z wierzby lub osadu ściekowego, w temperaturze 500 °C lub 700 °C. Osad ściekowy otrzymano z oczyszczalni ścieków komunalnych w Zamościu (50°44'9.39" N, 23°14'14.92" E). Przed pirolizą osad ściekowy został wysuszony w temperaturze pokojowej i następnie rozdrobniony do rozmiaru cząstek < 1 mm. Wierzbę (*Salix viminalis L.*) uzyskano z lokalnego przedsiębiorstwa zajmującego się uprawą roślin energetycznych. Po wysuszeniu, łodygi wierzby rozdrobniono w laboratoryjnym młynku nożowym (TESTCHEM, Radlin).

6.2. Kompostowanie osadu ściekowego

Jako materiał wyjściowy do kompostowania użyto osadu ściekowego (pochodzącego z oczyszczalni ścieków komunalnych w Zamościu (50°44'9.39" N, 23°14'14.92" E)) oraz słomy pszenicy (uzyskanej od lokalnego rolnika) zmieszanych w stosunku 1:1 (na podstawie suchej masy). Słoma pszenicy została dodana dla zapewnienia prawidłowego stosunku C/N oraz jako materiał strukturotwórczy (ułatwiający wymianę gazową). W badaniach dotyczących wpływu dawki BC (**Publikacje [D2, D3]**)

zastosowano 1% i 5% dodatek BC z przedsiębiorstwa Fluid S.A. Szczegółowe informacje dotyczące tego BC zostały przedstawione w **Publikacji [D2]**. W dalszych badaniach, dotyczących oceny wpływu surowca i temperatury pirolizy (**Publikacje [D4, D5]**), stosowano 1% dodatek BC otrzymanych zgodnie z procedurą opisaną w podrozdziale 6.1. Wybór dawki BC został podyktowany rezultatami **Publikacji [D2]**.

Osad ściekowy, słomę pszenicy oraz BC dokładnie wymieszano w celu otrzymania mieszaniny jak najbardziej homogenicznej. W celu zapewnienia różnorodności mikrobiologicznej i mikroorganizmów do prawidłowego przebiegu kompostowania, materiał został wzbogacony roztworem preparatu mikrobiologicznego bicompost zawierającego szczepy bakterii rodzaju *Bacillus* sp. (Organika-Agrarius Sp. z o.o., Przemyśl, Polska). Wymieszane substraty umieszczono następnie w bioreaktorach do kompostowania (BKB-100, ROTAMETR, Gliwice) o pojemności 100 L. Bioreaktory (**Rys. 3**) były wyposażone w elektroniczny system pomiaru temperatury oraz regulacji napowietrzenia.

Rys. 3. Fotografie przedstawiające bioreaktory do kompostowania.

Substraty kompostowano przez pięć tygodni, regulując poziom napowietrzenia oraz wilgotności do optymalnych warunków. W trakcie kompostowania oznaczano również stężenie gazów (O_2, CO_2, CO, NO, CH_4 oraz N_2) tworzących się podczas procesu (OPTIMA7, MRU GmbH, Niemcy). Po upływie pięciu tygodni, wstępnie przekompostowany materiał umieszczono w pojemnikach z tworzywa sztucznego i poddano etapowi dojrzewania przez dwa miesiące. Próbki do badań pobrano na początku kompostowania (0 dzień), a następnie po 3, 7, 14, 21, 28, 35, 70 i 98 dniach. Szczegóły dotyczące pobierania próbek oraz ich przygotowania do analiz przedstawiono w poszczególnych publikacjach dołączonych do niniejszego opracowania.

6.3. Oznaczanie całkowitej i biodostępnej zawartości WWA

W celu oznaczenia całkowitej (ekstrahowanej rozpuszczalnikiem organicznym, C_{tot}) zawartości WWA w próbkach uzyskanych z doświadczeń, próbki ekstrahowano techniką przyspieszonej ekstrakcji rozpuszczalnikowej (ASE) przy użyciu systemu Dionex ASE 350 Accelerated Solvent (Massachusetts, USA) [91]. Szczegóły dotyczące ekstrakcji przedstawiono w **Publikacjach [D2, D4]**.

Biodostępną (C_{free}) frakcję WWA oznaczono w oparciu o procedurę zaproponowaną przez Cornelissen i in. [92] oraz Hawthorne i in. [93]. Metoda wykorzystuje podział analitu między fazę stałą (próbka), wodę oraz próbnik pasywny wykonany z polioksymetylenu (POM). Po ustaleniu stanu równowagi (30 dni), oznacza się zawartość analitu zaadsorbowaną na POM, a zawartość C_{free} (zawartość analitu w wodzie) wylicza się z następujących wzorów, na podstawie współczynników podziału (K_{POM_w}) określonych we wcześniejszych badaniach [94]:

$$c_{POM} = \frac{m_{WWA}}{m_{POM}} \qquad \text{Wzór (1)}$$

$$c_{free} = \frac{c_{POM} - c_{POM\_kontrola}}{K_{POM\_w}} \qquad \text{Wzór (2)}$$

gdzie:

c_{POM} – stężenie poszczególnych związków z grupy WWA na pasywnym próbniku POM [ng/kg],

m_{WWA} – masa danego WWA oznaczona za pomocą GC-MS [ng],

m_{POM} – masa użytego próbnika pasywnego [kg],

c_{free} – stężenie biodostępnej frakcji WWA [ng/L],

$c_{POM\_kontrola}$ – stężenie poszczególnych związków z grupy WWA na pasywnym próbniku POM w kontroli [ng/kg],

K_{POM_w} – współczynnik podziału WWA między POM i wodę [L/kg].

Szczegóły dotyczące ekstrakcji przedstawiono w **Publikacjach [D2, D4]**.

Analizę jakościową i ilościową WWA (szesnastu WWA wyróżnionych przez US EPA) wykonano metodą chromatografii gazowej sprzężonej ze spektrometrem mas (GC-MS) (Trace 1300, ThermoFisher Scientific, Waltham, Massachusetts, USA). Do rozdziału poszczególnych WWA wykorzystano kolumnę kapilarną Restek Rxi-5 ms (długość 30 m, średnica wewnętrzna 0,25 mm, grubość filmu 0,25 µm) (Restek, Glastron, Francja). W detektorze MS wykorzystano tryb SIM – monitowania wybranych jonów, połączony z jonizacją elektronową. Szczegóły dotyczące parametrów systemu GC-MS przedstawione zostały w **Publikacji [D2]**.

6.4. Oznaczanie zawartości metali

Oznaczenie pseudocałkowitej zawartości PTE w otrzymanych BC przeprowadzono po mineralizacji próbek (500 mg) w piecu mikrofalowym (Start D, Microwave Digestion System, Milestone, ETHOS EASY, Włochy) w mieszaninie kwasu azotowego (V) i chlorowodorowego (3:1, objętościowo) przez 90 minut w temperaturze 200 °C.

Oznaczenie rozpuszczalnej w wodzie frakcji badanych PTE w kompostowanym materiale oraz kompoście wykonano ekstrahując próbki (1 g) wodą (10 mL) (Milli Q) przez

24 godziny z użyciem wytrząsarki laboratoryjnej (Laboratory shaker, Type 358A, ELPIN+, Katowice, Polska), przy obrotach 10 rpm/min i w temperaturze 22 ± 2 °C. Otrzymany roztwór został odwirowany (5000 rpm przez 15 minut) (Centrifuge MPW-352, Polska) i przesączony przez filtr membranowy o średnicy 0,45 μm (Lab Unlimited, Dublin, Irlandia). Szczegóły przygotowania próbek przedstawiono w **Publikacji [D5]**.

W celu oznaczenia form specjacyjnych PTE w badanym materiale przeprowadzono zmodyfikowaną procedurę ekstrakcji BCR według metody zaproponowanej przez Pueyo i in. [95] (**Publikacja [D3]**). W ramach procedury otrzymano cztery frakcje: wymienną i związaną z węglanami (F1), związaną z tlenkami żelaza i manganu (frakcja ulegająca redukcji) (F2), związaną z materią organiczną i siarczkami (frakcja ulegająca utlenianiu) (F3) oraz niedostępną (frakcja rezydualna) (F4). Szczegółowe informacje na temat procesu ekstrakcji przedstawiono w **Publikacji [D3]**.

Oznaczenie ilościowe i jakościowe PTE w ekstraktach przeprowadzono przy użyciu spektrometru ICP-OES (iCAP 7400 Duo Thermo Scientific, USA). Do otrzymania plazmy oraz rozpylania próbek wykorzystano argon o czystości 99,9999% (AirLiquide, Polska). W celu analizy ilościowej użyto sześciopunktowej krzywej kalibracyjnej przygotowanej dla wszystkich PTE w zakresie od 0,01 do 5 mg/L poprzez rozcieńczenie wielopierwiastkowego roztworu standardu (1 g/L, Merck, Niemcy) ultraczystą wodą (0,08 μS/cm, Hydrolab) zakwaszoną kwasem azotowym (V).

6.5. Badania ekotoksykologiczne

Ocenę ekotoksykologiczną badanych materiałów prowadzono przy użyciu testów ekotoksykologicznych wykorzystując następujące parametry i organizmy testowe: hamowanie luminescencji bakterii *Aliivibrio fischeri* (test Microtox®), hamowanie kiełkowania nasion i wzrostu korzeni rośliny *Lepidium sativum* (test Phytotoxkit®) oraz określenie śmiertelności i reprodukcji bezkręgowców *Folsomia candida* (test

Collembolan). W testach z bakteriami oceniano toksyczność ekstraktów wodnych otrzymanych według metody opisanej w podrozdziale 6.4, natomiast toksyczność frakcji stałej analizowano przy użyciu testów Phytotoxkit® i Collembolan.

Szczegółowe informacje dotyczące przeprowadzania testów zostały przedstawione w **Publikacjach [D3, D5].**

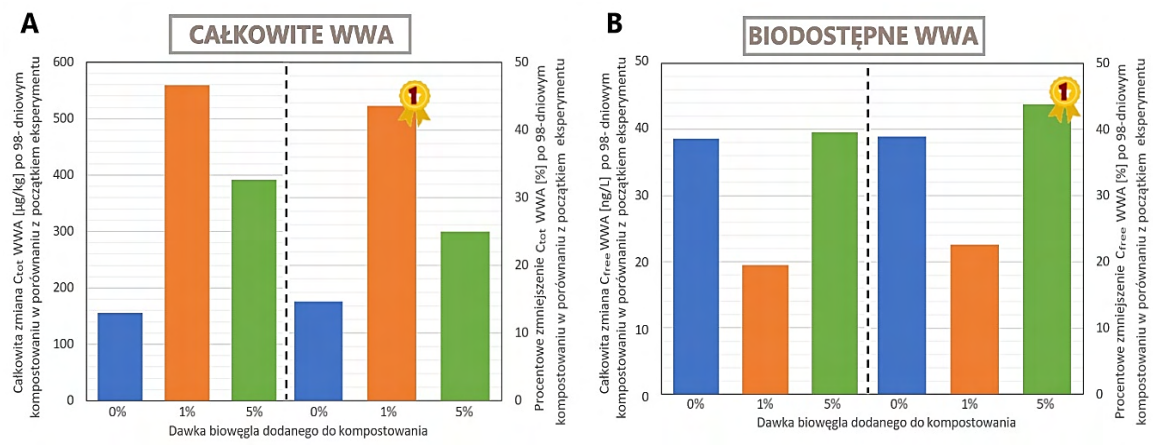
7. Badania własne

7.1. Wpływ dawki biowęgla dodanego do kompostowania osadu ściekowego na zawartość WWA w kompoście (Publikacja [D2])

Celem pracy było określenie wpływu dawki BC na całkowitą zawartość oraz biodostępność WWA podczas kompostowania osadu ściekowego. Oceniono wpływ wybranych właściwości fizykochemicznych materiału kompostowego na straty WWA w celu wyjaśnienia możliwych mechanizmów stojących za tymi zmianami.

Dodatek BC do kompostowanej mieszaniny zwiększył istotnie zawartość Σ16 C_{tot} WWA. W wyniku kompostowania zaobserwowano jednak, że WWA były bardziej efektywnie usuwane w układach z BC niż w kontroli (wariant bez dodatku BC) (15% zmniejszenie Σ16 C_{tot} WWA dla kontroli, 44% i 25% zmniejszenie odpowiednio dla 1% i 5% dodatku BC) (**Rys. 4**). Lepsze obniżenie zawartości WWA w wariantach z BC związane było z korzystniejszymi warunkami do rozwoju mikroorganizmów (odpowiedzialnych za degradację WWA) w układach z BC niż w kontroli. Ponadto obecność BC mogła wpływać na tworzenie pozostałości związanej (unieruchamiającej WWA) podczas mineralizacji materii organicznej w trakcie kompostowania [96]. Odpowiednio dobrana dawka BC (1%) doprowadziła do 20% niższej końcowej całkowitej zawartości WWA w kompoście w porównaniu do kontroli (*[D2], Rys. 3A*). Było to związane ze stworzeniem przez BC sprzyjających warunków do rozwoju mikroorganizmów, poprzez ich adhezję czy kolonizację na porowatej powierzchni BC oraz zapewnienie im ochrony, co prowadziło do wydłużenia przeżywalności mikroorganizmów m.in. odpowiedzialnych za biodegradację WWA [97]. W przypadku dawki 5% sugerowany główny mechanizm obniżenia się C_{tot} WWA związany był z procesami sekwestracji, co w dłuższej perspektywie po wprowadzeniu kompostu do gleby może skutkować wtórnym uwalnianiem WWA do środowiska w wyniku osłabienia oddziaływań kompost-WWA.

Zbyt wysoki dodatek BC poskutkował najwyższym spośród wariantów końcowym poziomem WWA w kompoście, co mogło być konsekwencją wprowadzenia dużej ilości WWA wraz z BC i/lub obniżenia biodostępności WWA w wyniku ich związania przez BC (*[D2], Rys. 3A*). Dzięki analizie współczynnika podziału węgiel organiczny – woda (K_{oc}) udowodniono, że siła wiązania WWA zmieniała się w różnych fazach procesu i jest najwyższa dla 5% dodatku BC (*[D2], Rys. 7*), co potwierdziło hipotezę o większym udziale sekwestracji i/lub adsorpcji niż degradacji WWA dla wariantu z wyższym stężeniem BC. W przeciwieństwie do całkowitego stężenia WWA, największą efektywność w zmniejszaniu biodostępności WWA odnotowano dla 5% dodatku BC (44%), następnie dla kontroli (39%), a najniższą wartością charakteryzował się wariant eksperymentu z 1% dawką BC (23%) (**Rys. 4**).



Rys. 4. Zmiana poziomu (A) oraz biodostępności (B) WWA na przestrzeni kompostowania osadu ściekowego wraz z BC użytym w różnych dawkach.

Mogło to być związane z silnym związaniem WWA przez kompost z wyższym dodatkiem BC (potwierdzono to przez najwyższe wartości K_{oc} dla tego wariantu) i brakiem możliwości ich wypłukiwania, co wpłynęło na obniżenie C_{free} WWA. Analiza korelacji pokazała, że wiodącą rolę w mechanizmie strat WWA (zarówno C_{tot}, jak i C_{free}) odgrywają

zmiany zawartości TOC, DOC oraz zawartości frakcji mineralnej (popiołu) w kompoście (*[D2], Tab. S6*).

Dodatek BC do kompostowania osadu ściekowego wpłynął na obniżenie całkowitej i biodostępnej zawartości WWA, ale efektywność zależała ściśle od zastosowanej dawki BC. Niższa dawka (1%) BC wspierała degradację mikrobiologiczną, podczas gdy wyższa (5%) prowadziła do silnego wiązania WWA z matrycą, co ograniczyło ich mobilność i dostępność, jednocześnie utrudniając ich rozkład. Uwzględniając całościową ocenę korzyści i potencjalnych ograniczeń środowiskowych oraz aspektów praktycznego zastosowania BC, w tym obserwowane zmiany w zawartości WWA, za najbardziej korzystną uznano dawkę 1% BC.

7.2. Wpływ dawki biowęgla dodanego do kompostowania osadu ściekowego na formy metali oraz toksyczność kompostu (Publikacja [D3])

Założeniem badań było oszacowanie, jak zróżnicowana dawka BC, zastosowana do kompostowanego osadu ściekowego i słomy pszenicy, wpłynie na dostępność i mobilność wybranych PTE oraz toksyczność kompostowanego materiału (względem organizmów żywych, reprezentujących trzy poziomy troficzne).

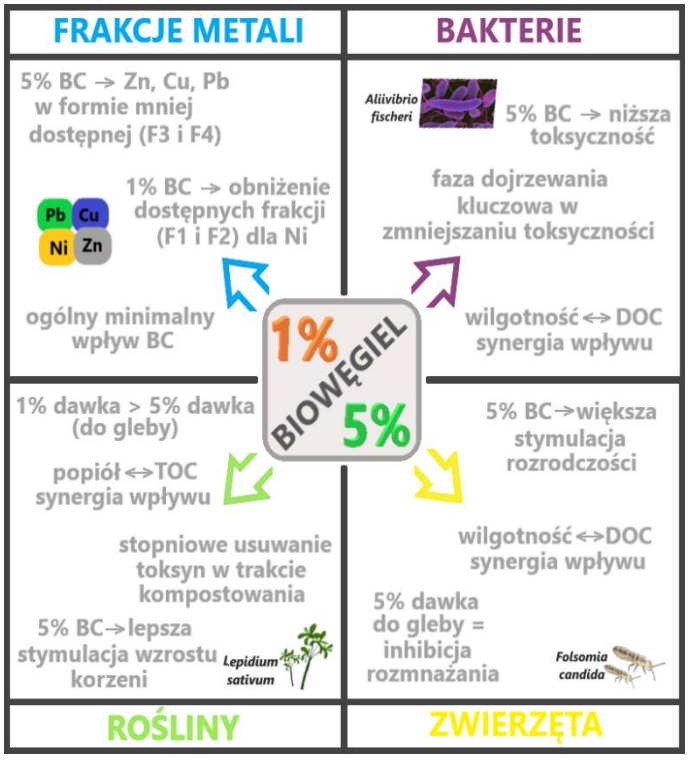
W badaniach oceniano wpływ dawki BC (1% i 5%) na formy specjacyjne Ni, Cu, Zn i Pb podczas kompostowania w odniesieniu do kształtowania się ekotoksyczności badanych materiałów. Dawka BC wpłynęła zarówno na formy specjacyjne PTE, jak i toksyczność materiału na różnych etapach kompostowania (**Rys. 5**).

Przekształcenia poszczególnych form PTE były głównie zależne od właściwości chemicznych danego pierwiastka. Wyższa dawka BC powodowała bardziej zauważalne efekty w dynamice zmian form specjacyjnych PTE. Obserwowano, że przekształcenie Zn, Cu i Pb (obecnych we frakcjach F1 i F2) do mniej dostępnych frakcji F3 i F4 (związanych odpowiednio z materią organiczną i siarczkami oraz ze strukturą mineralną) było pozytywnie skorelowane z dawką BC dodanego do kompostowanego materiału (*[D3], Rys. 2*). W przypadku Ni niższa dawka BC przyczyniła się do bardziej efektywnego obniżenia frakcji F1 i F2 w porównaniu do wariantu kontrolnego (*[D3], Rys. 2*). Korzystny wpływ wywierany przez BC wynikał głównie z rozbudowanej powierzchni BC, obecności grup funkcyjnych oraz zdolności BC do wspierania aktywności mikrobiologicznej podczas kompostowania [98,99].

Biorąc pod uwagę toksyczność badanych materiałów stwierdzono, że wzbogacenie mieszaniny kompostowej w BC skutkowało zwiększonym zahamowaniem luminescencji *A. fischeri* w początkowych fazach kompostowania (*[D3], Rys. 4*), co mogło być związane

ze stopniowym uwalnianiem substancji toksycznych podczas mineralizacji materii organicznej [100]. Podczas fazy dojrzewania, efekty toksyczny kompostowanego materiału uległ jednak obniżeniu do wartości niższej niż na początku eksperymentu, a warianty z BC osiągnęły niższą toksyczność niż eksperyment kontrolny. Zaobserwowano również istotną zależność między dawką BC a obserwowanym efektem (*[D3], Rys. 4*). Obniżenie toksyczności kompostowanego materiału po fazie dojrzewania mogło być związane z zachodzeniem intensywnych procesów humifikacji i stabilizacji podczas tej fazy. Procesy te powodują wprowadzanie zanieczyszczeń w tworzące się struktury humusowe, bogate w grupy funkcyjne, lub też adsorpcję zanieczyszczeń, czego rezultatem jest silne związanie substancji toksycznych, skutkujące obniżeniem toksyczności całego materiału (kompostu) [101].

Wykazano również, że 1% dawka kompostowanego materiału zastosowana do gleby stymulowała wzrost korzeni *L. sativum*. Obserwowany efekt ulegał pogłębieniu w kolejnych fazach kompostowania i był wprost proporcjonalny do dawki BC (w końcowym etapie osiągnięto 42 – 48% stymulację wzrostu korzeni dla wariantów z BC, w zależności od jego dawki w kompostowanym materiale) (*[D3], Rys. 7*). Z jednej strony, obserwowane zwiększanie się pozytywnego efektu BC w miarę upływu kompostowania mogło być związane ze



Rys. 5. Zakres badań wraz z najważniejszymi wnioskami otrzymanymi w Publikacji [D3].

stopniowym usuwaniem czynników odpowiedzialnych za hamowanie wzrostu korzeni. Mogło to się odbywać w wyniku biodegradacji (bezpośrednie usuwanie czynnika toksycznego) lub dzięki silnemu wiązaniu przez składniki kompostowanego materiału i tworzących się form humusowych (pośrednie usunięcie czynnika toksycznego) [102]. Z drugiej strony, poprawiające się właściwości nawozowe kompostu (dostępność składników odżywczych, ustabilizowana materia organiczna) w wyniku kompostowania również mogły mieć pozytywny wpływ na obserwowany efekt. Warianty z BC zastosowane w dawce 5% do gleby przyczyniły się do wyraźnie słabszego efektu stymulującego, w porównaniu z niższą dawką aplikacyjną (*[D3], Rys. 7*).

Wpływ BC na reprodukcję *F. candida* był zróżnicowany w zależności od udziału BC w kompostowanym materiale, jak i od zastosowanej dawki kompostowanego materiału do gleby. Udział BC na poziomie 5% w kompostowanym materiale miał bardziej korzystny wpływ na reprodukcję *F. candida* niż udział 1%, po zastosowaniu kompostowanego materiału do gleby w dawce 1% (*[D3], Rys. 8*). Warianty z dodatkiem BC spowodowały o 38% i 91% wyższą stymulację rozrodczości w porównaniu do gleby bez dodatku BC (po 98 dniach kompostowania, odpowiednio dla 1% i 5% dawki BC) (*[D3], Rys. 8A*). Wyższa (5%) dawka kompostowanego materiału do gleby przyczyniła się do negatywnego wpływu na rozrodczość *F. candida*, niezależnie od terminu kompostowania, przy czym odnotowano gwałtowny wzrost inhibicji reprodukcji na etapie dojrzewania kompostu. Warianty z BC przyczyniły się do nieznacznie niższej inhibicji w porównaniu do gleby bez BC, jednakże wszystkie warianty wywołały > 60% inhibicję reprodukcji *F. candida* w końcowym terminie badań (*[D3], Rys. 8B*).

Zastosowanie wyższej dawki BC (5%) podczas kompostowania w większym stopniu wpływało na zróżnicowanie udziału poszczególnych form specjacyjnych PTE w porównaniu do niższego udziału BC (1%), przy czym efekt ten był determinowany rodzajem pierwiastka. Wyższy udział BC w kompostowanym materiale wywarł również bardziej korzystny wpływ na testowane organizmy, wielokrotnie wskazując na stymulujące działanie. Zaobserwowano jednak, że zastosowanie zbyt wysokiej dawki przekompostowanego materiału do gleby może mieć negatywny wpływ na bezkręgowce oraz rośliny.

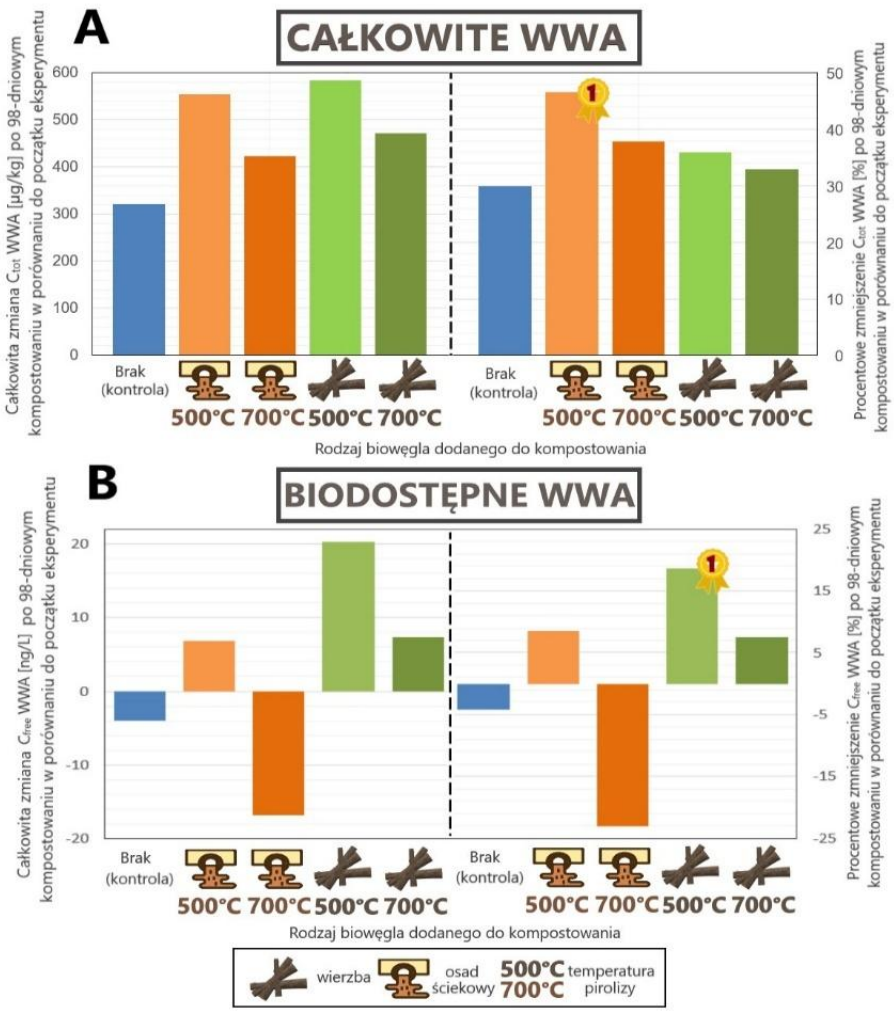
7.3. Wpływ warunków otrzymywania biowęgla na zawartość WWA w kompoście (Publikacja [D4])

Celem pracy było określenie wpływu parametrów otrzymywania BC (rodzaj surowca oraz temperatura pirolizy) na zawartość i biodostępność WWA podczas kompostowania oraz w finalnym kompoście. Szczególny nacisk położono na zrozumienie mechanizmów odpowiedzialnych za biodostępność i trwałość WWA podczas kompostowania.

Dodatek BC zastosowany w dawce 1% wpłynął zarówno na całkowitą zawartość WWA (C_{tot}), jak i ich biodostępną frakcję (C_{free}), przy czym obserwowany efekt zależał przede wszystkim od temperatury pirolizy, a w mniejszym stopniu od rodzaju surowca użytego do produkcji BC. Niskotemperaturowe BC (otrzymane w 500 °C) sprzyjały bardziej efektywnemu obniżaniu zarówno C_{tot}, jak i C_{free} WWA podczas kompostowania w porównaniu z BC otrzymanymi w temperaturze 700 °C (**Rys. 6**). Różnica ta mogła wynikać z gorszych parametrów sorpcyjnych niskotemperaturowych BC (takich jak powierzchnia właściwa, objętość porów, aromatyczność czy hydrofobowość) w porównaniu z BC otrzymanymi w 700 °C (*[D4], Tab. 1*). W konsekwencji w kompostach z dodatkiem BC otrzymanych w 500 °C mechanizm usuwania WWA był prawdopodobnie związany głównie z degradacją mikrobiologiczną, czyli rzeczywistym zanikiem badanych zanieczyszczeń.

Po kompostowaniu z dodatkiem BC wytworzonych z osadu ściekowego (SL-BC) całkowita zawartość WWA była istotnie niższa w porównaniu z wariantem kontrolnym (*[D4], Rys. 2A*). Może to sugerować, że SL-BC sprzyjały degradacji WWA, co potwierdzają niskie wartości log K_{oc} uzyskane dla kompostów zawierających SL-BC, wskazujące na osłabione oddziaływania sorpcyjne między BC a WWA (*[D4], Rys. 6*). Zjawisko to mogło być związane z większą średnicą porów oraz wyższą polarnością SL-BC w porównaniu z BC otrzymanymi z wierzby (WL-BC) (*[D4], Tab. 1*). Większe

pory mogły stwarzać korzystniejsze warunki dla rozwoju mikroorganizmów oraz ułatwiać transfer WWA z powierzchni BC do roztworu, zwiększając tym samym podatność tych związków na degradację [103]. Z kolei wyższa polarność BC mogła osłabiać siłę oddziaływań między WWA a powierzchnią adsorbentu [104], ograniczając jednocześnie ich odwracalną sorpcję i zwiększając dostępność zanieczyszczeń dla mikroorganizmów.



Rys. 6. Zmiana poziomu (A) oraz biodostępności (B) WWA na przestrzeni kompostowania osadu ściekowego wraz z BC otrzymanym w różnych warunkach.

W odniesieniu do C_{free} WWA bardziej efektywny okazał się jednak dodatek BC pochodzących z wierzby, zarówno pod kątem względnej zmiany procentowej, jak i bezwzględnego obniżenia stężenia tych związków, w porównaniu z SL-BC (**Rys. 6**).

Niskie wartości log K_{oc} uzyskane dla SL-BC potwierdzają bowiem większą mobilność zanieczyszczeń oraz słabsze ich wiązanie w matrycy kompostu, co było szczególnie widoczne w przypadku 2- i 6-pierścieniowych WWA (*[D4], Rys. 6*).

Przedstawiona praca wnosi istotny wkład do wiedzy dotyczącej zastosowania BC w kompostowaniu osadu ściekowego, zwłaszcza w kontekście wpływu właściwości BC – zależnych od parametrów jego otrzymania – na przemiany WWA. Szczególnie istotnym aspektem badań była ocena biodostępności WWA, która w wielu wcześniejszych pracach była pomijana [56,105].

Wyniki dowiodły, że efektywność BC w zmniejszaniu C_{tot} WWA w kompoście otrzymanym na bazie osadu ściekowego zależy głównie od surowca, natomiast w przypadku C_{free} WWA – również od temperatury pirolizy. Bardziej efektywnym rozwiązaniem w celu zmniejszenia ryzyka związanego z obecnością WWA w osadzie ściekowym i kompoście jest stosowanie niskotemperaturowych BC. Zdolność BC do obniżania zawartości zanieczyszczeń w kompoście otrzymanym z odpadów stanowi doskonałe podstawy do promowania jego stosowania zarówno w rolnictwie, jak i w zrównoważonej gospodarce odpadami.

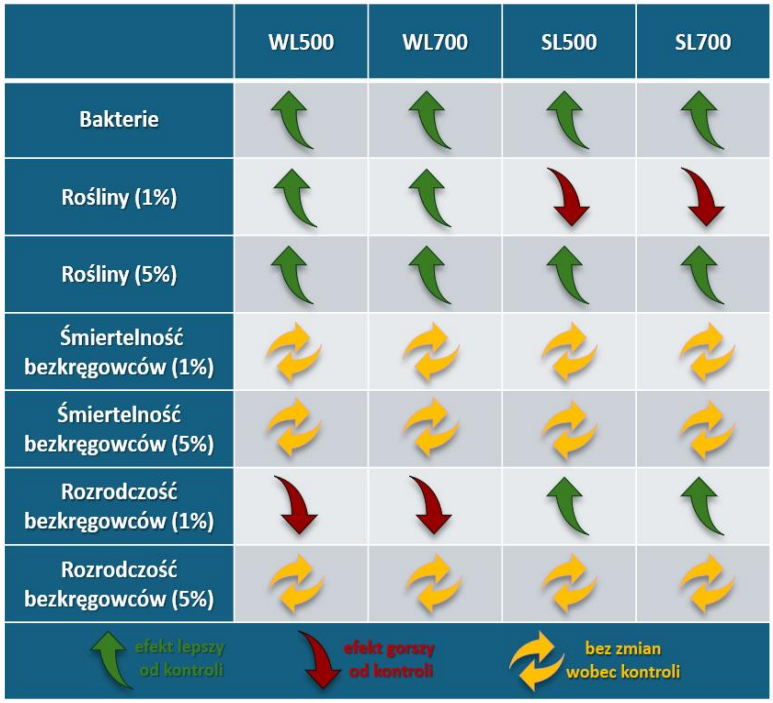
7.4. Wpływ warunków otrzymywania biowęgla na toksyczność kompostu (Publikacja [D5])

Założeniem badań była ocena, jak BC otrzymany z różnych surowców i w różnych temperaturach pirolizy wpływa na toksyczność materiału na różnych etapach kompostowania. Analizę toksyczności przeprowadzono w oparciu o organizmy reprezentujące różne poziomy troficzne: bakterie, rośliny i bezkręgowce.

Uzyskane wyniki wykazały, że dodatek BC do kompostowanego materiału wpłynął na toksyczność względem wszystkich badanych organizmów, a efekt w istotnym stopniu determinowany był warunkami otrzymywania BC (**Rys. 7**).

Dodatek BC wpłynął w zróżnicowany sposób na *A. fischeri* w zależności od fazy kompostowania oraz temperatury otrzymania BC. BC otrzymane w 700 °C generalnie obniżały toksyczność w porównaniu z ich niskotemperaturowymi odpowiednikami oraz kontrolą *([D5], Rys. 1*). Większa efektywność BC otrzymanych w 700 °C niż 500 °C wynikała przede wszystkim z większego pola powierzchni właściwej oraz wyższej hydrofobowości (na podstawie stosunku molowego H/C) dla BC wysokotemperaturowych niż niskotemperaturowych, co przełożyło się na bardziej efektywne wiązanie hydrofobowych zanieczyszczeń, które mogły być odpowiedzialne za obserwowany efekt toksyczny w wariancie kontrolnym [106,107]. Dodatkowo wysokotemperaturowe BC mogły działać jako bufor lub adsorbent dla reaktywnych form tlenu, co zmniejszało stres oksydacyjny i pozwalało *A. fischeri* na bardziej efektywny rozwój [108]. Oceniając toksyczność poszczególnych wariantów w ostatnim etapie badań (po fazie dojrzewania), największe obniżenie hamowania luminescencji spośród wszystkich badanych BC, odnotowano dla BC otrzymanego z osadu ściekowego w temperaturze 700 °C (SL700) *([D5], Rys. 1*). Ten korzystny wynik powiązano z wysoką zawartością frakcji nieorganicznej w SL700, której wpływ mógł oddziaływać na: (1) obniżenie biodostępności toksycznych jonów w wyniku ich adsorpcji oraz (2) uwolnienie mikroskładników (Mg,

Na), które bezpośrednio stymulowały metabolizm bakterii [109]. W przypadku bakterii, zdolność frakcji mineralnej zawartej w SL700 do dostarczania składników odżywczych równoważyła, bądź nawet przewyższyła jej potencjalną toksyczność [110].



Rys. 7. Wpływ dodatku BC na toksyczność względem organizmów, w porównaniu do kompostowania bez BC (efekt w ostatnim dniu eksperymentu, po 98 dniach kompostowania).

Podobnie jak w przypadku wcześniejszych badań z roślinami i bezkręgowcami (**Publikacja [D3]**), również w tym eksperymencie oceniano wpływ kompostowanego materiału na te organizmy w dwóch dawkach (1% i 5%) zastosowanych do gleby. Rezultaty pokazały, że w przypadku 1% dawki kompostowanego materiału zarówno temperatura pirolizy, jak i surowiec do otrzymania BC miały wpływ na wzrost korzeni *L. sativum*. Istotnie lepszy efekt obserwowany był dla BC otrzymanych z osadu ściekowego niż wierzby, przyczyniając się do 32 – 39% stymulacji wzrostu korzeni (po 98 dniach kompostowania) *([D5], Rys. 2*). Komposty z WL-BC po fazie dojrzewania jako jedyne spośród badanych wariantów wykazały działanie neutralne (inhibicja < 20%) *([D5], Rys. 2*). Związane to było z właściwościami BC (zawartość DOC i przewodność

elektryczna) oraz warunkami, które tworzyły (obecność SL-BC w większym stopniu obniżała zawartość rozpuszczalnych w wodzie frakcji Zn, Ni oraz Pb, niż obserwowano to dla WL-BC). Brak stymulującego wpływu WL-BC na wzrost korzeni *L. sativum* przypisano wysokiemu uwalnianiu DOC, który prawdopodobnie zawierał fitotoksyczne kwasy organiczne o niskich masach cząsteczkowych oraz związki fenolowe, które po przeniknięciu do korzeni roślin, wywołały stres oksydacyjny i zakłócały procesy metaboliczne rośliny [111,112]. Dodatkowo komposty z dodatkiem WL-BC charakteryzowały się wyższą zawartością Σ16 C_{tot} WWA niż te z SL-BC. BC otrzymane w 700 °C promowały wzrost w większym stopniu niż ich odpowiedniki niskotemperaturowe *([D5], Rys. 2*). Odmienne wyniki otrzymano przy badaniu wyższej, 5%, dawki dodatku do gleby. Toksyczność względem roślin w tym przypadku w większym stopniu zależała od fazy kompostowania. Początkowo, warianty z BC reprezentowały analogiczne lub gorsze rezultaty w porównaniu do kontroli *([D5], Rys. 2*). W następnych fazach kompostowania, SL-BC wykazały 41 – 51% stymulacji wzrostu korzeni, co mogło być związane z wyższą zawartością składników odżywczych (Na, Mg, K) w SL-BC, w porównaniu do WL-BC *([D5], Rys. 2*).

Przy zastosowaniu 1% dawki kompostu z dodatkiem BC wpływ na śmiertelność i reprodukcję *F. candida* zależał zarówno od etapu kompostowania, jak i rodzaju surowca użytego do produkcji BC. Na początku eksperymentu obecność BC ograniczała śmiertelność oraz obniżała hamowanie reprodukcji, niezależnie od wariantu, w porównaniu z kontrolą (*[D5], Rys. 3*). W późniejszych etapach kompostowania warianty zawierające SL-BC wykazywały jednak silniejsze działanie hamujące wobec *F. candida* niż warianty z WL-BC oraz kontrola, co powiązano z wyższą zawartością frakcji mineralnej oraz PTE w SL-BC (*[D5], Rys. 3*). Dodatkowo warianty z WL-BC charakteryzowały się wyższą zawartością biodostępnego Fe, który odgrywa istotną rolę w stymulacji rozwoju bakterii

i grzybów stanowiących źródło pokarmu dla *F. candida* [113]. Ponadto środowisko bogate w materię organiczną zapewnione przez WL-BC (wysoka zawartość DOC) sprzyjało proliferacji grzybów, co mogło prowadzić do wzbogacenia sieci troficznej *F. candida* i tłumaczyć niższy stopień inhibicji reprodukcji obserwowany w tych wariantach (*[D5], Rys. 3*). Warianty z dodatkiem WL-BC w późniejszych etapach kompostowania (po 14 dniu) wykazywały neutralny wpływ na reprodukcję *F. candida*, prawdopodobnie w wyniku wyższej zawartości rozpuszczalnych związków organicznych.

W przypadku wyższej (5%) dawki kompostowanego materiału obserwowane efekty w stosunku do *F. candida* były bardziej zróżnicowane w porównaniu do dawki 1%. Początkowo obecność BC obniżała śmiertelność organizmów w porównaniu z kontrolą, jednak w dalszych etapach kompostowania odnotowano wyraźne zwiększenie toksyczności (powyżej 60%), niezależnie od rodzaju zastosowanego BC (*[D5], Rys. 3*). Jednocześnie reprodukcja była silnie hamowana (powyżej 60%) we wszystkich wariantach eksperymentalnych.

Uwzględniając ogólną tendencję wariantów wzbogaconych w BC do ograniczania reprodukcji oraz zwiększania śmiertelności *F. candida*, szczególnie przy wyższej dawce dodatku kompostowanego materiału do gleby, można przypuszczać, że obserwowany efekt hamujący był związany z pośrednim wpływem na mikroorganizmy glebowe. Wysokie zasolenie oraz wahania pH wywołane obecnością SL-BC mogły ograniczać rozwój grzybów preferowanych przez *F. candida* [114].

Uzyskane wyniki podkreślają konieczność prowadzenia oceny multitroficznej kompostu przed jego aplikacją do gleby, ponieważ analizy chemiczne oraz badania obejmujące organizmy reprezentujące pojedynczy poziom troficzny mogą być niewystarczające i prowadzić do mylących, rozbieżnych wniosków. Wpływ kompostów wzbogaconych w BC w dużym stopniu zależy od warunków wytwarzania BC, co wskazuje

na potrzebę przeprowadzania badań pilotażowych przed wdrożeniem BC do zastosowań rolniczych na większą skalę. Na podstawie uzyskanych wyników zaproponowano wykorzystanie BC bogatych w frakcję mineralną (otrzymanych z osadu ściekowego) do wspomagania wzrostu roślin oraz procesów fitostabilizacji, natomiast BC bogatych w węgiel organiczny (pochodzących z biomasy), jako skuteczniejszego narzędzia rewitalizacji ekosystemów poprzez stymulację aktywności i liczebności bezkręgowców glebowych.

Wpływ warunków otrzymywania BC był znaczący i oddziaływał na zachowanie wszystkich badanych organizmów. Efekt jednak był zróżnicowany i zależał od badanego organizmu oraz właściwości BC. Podczas gdy rozwój bakterii i roślin najkorzystniej kształtował się przy zastosowaniu BC otrzymanego z osadu ściekowego w temperaturze 700 °C jako dodatku, tak biorąc pod uwagę rozrodczość bezkręgowców, to BC otrzymane z wierzby wykazały bardziej stymulujący efekt. Odpowiednio dobrane warunki otrzymywania BC mogą poprawić jakość kompostu i zmniejszyć jego toksyczność, co przełoży się na „zdrowie" gleby, wyższy plon oraz rozpowszechni praktykę zrównoważonego przetwarzania odpadów.

8. Wnioski

1. Zastosowanie biowęgla jako dodatku do kompostowania osadu ściekowego istotnie wpłynęło na przemiany wielopierścieniowych węglowodorów aromatycznych (WWA). Wyższa dawka biowęgla (5%) ograniczała straty tych związków podczas kompostowania, co wskazuje na wzrost znaczenia procesów sorpcyjnych w obecności większej ilości materiału węglowego **(Publikacja [D2])**.
2. Ilość biowęgla zastosowanego w procesie kompostowania determinowała dominujący mechanizm usuwania WWA. Niższa dawka dodatku (1%) sprzyjała stymulacji degradacji mikrobiologicznej zanieczyszczeń, natomiast wyższa dawka (5%) sprzyjała ich immobilizacji poprzez procesy sorpcji, co może wiązać się z ryzykiem ponownego uwalniania WWA podczas długotrwałego starzenia materiału w glebie **(Publikacja [D2])**.
3. Dodatek biowęgla wpływał na specjację pierwiastków potencjalnie toksycznych (PTE) w kompostowanym osadzie ściekowym, przy czym obserwowany efekt zależał zarówno od dawki biowęgla, jak i właściwości poszczególnych PTE. Dodatek 1% biowęgla sprzyjał skutecznej immobilizacji Ni, natomiast wyższa dawka (5%) przyczyniała się przede wszystkim do stabilizacji Cu i Zn. Mechanizm był związany zarówno z właściwościami powierzchniowymi biowęgla, jak i jego wpływem na aktywność mikroorganizmów **(Publikacja [D3])**.
4. Wyższy (5%) dodatek biowęgla do kompostowania osadu ściekowego zmniejszył toksyczność względem bakterii, jak również stymulował wzrost korzeni roślin oraz rozrodczość bezkręgowców w większym stopniu niż niższy (1%) udział biowęgla **(Publikacja [D3])**.

5. Parametry otrzymania biowęgla, takie jak rodzaj surowca oraz temperatura pirolizy, w istotny sposób determinowały biodostępność i trwałość WWA podczas kompostowania, a także mechanizm ich usuwania **(Publikacja [D4])**.
6. Rodzaj surowca wykorzystywanego do otrzymania biowęgla różnicował mechanizmy oddziaływania z WWA. Biowęgle otrzymane z osadu ściekowego sprzyjały przede wszystkim procesom adsorpcji i sekwestracji zanieczyszczeń w matrycy kompostu, natomiast biowęgle wytworzone z biomasy stymulowały procesy biodegradacji WWA **(Publikacja [D4])**.
7. Właściwości biowęgla wynikające z parametrów jego produkcji wpływały również na poziom toksyczności kompostu. Biowęgle otrzymane w temperaturze 700 °C skuteczniej ograniczały toksyczność względem bakterii i roślin niż materiały wytworzone w niższej temperaturze pirolizy **(Publikacja [D5])**.
8. W kontekście oddziaływania na bezkręgowce glebowe korzystniejsze okazały się biowęgle otrzymane z biomasy (wierzby), które w większym stopniu stymulowały rozrodczość *Folsomia candida* niż biowęgle wytworzone z osadu ściekowego **(Publikacja [D5])**.
9. Uzyskane wyniki wskazują, że dobór parametrów otrzymania biowęgla powinien być dostosowany do zamierzonego celu jego zastosowania. Biowęgle bogate we frakcję mineralną, otrzymane z osadu ściekowego, mogą być szczególnie przydatne w działaniach ukierunkowanych na zwiększenie plonu roślin oraz procesy fitostabilizacji, natomiast biowęgle otrzymane z biomasy, charakteryzujące się wyższą zawartością węgla organicznego, mogą skuteczniej wspierać procesy rewitalizacji gleb poprzez stymulację aktywności bezkręgowców glebowych **(Publikacja [D5])**.

Literatura

[1] M. Ayaz, S.T. Muntaha, E. Baltrėnaitė-Gedienė, Z. Kriaučiūnienė, Biochar and carbon-negative technologies: exploring opportunities for climate change mitigation, Biochar. 7 (2025) 1. https://doi.org/10.1007/S42773-024-00421-3.

[2] S. Kumari, I. Širić, S.A. Fayssal, Biochar as a versatile resource for achieving sustainability in agri-food chains, AgroEnvironmental Sustain. 12 (2023) 76. https://doi.org/10.59983/S20230101010.

[3] A. Mukherjee, B.R. Patra, J. Podder, A.K. Dalai, Synthesis of biochar from lignocellulosic biomass for diverse industrial applications and energy harvesting: Effects of pyrolysis conditions on the physicochemical properties of biochar, Front. Mater. 9 (2022) 870184. https://doi.org/10.3389/FMATS.2022.870184.

[4] X.F. Tan, S.S. Zhu, R.P. Wang, Y. Di Chen, P.L. Show, F.F. Zhang, S.H. Ho, Role of biochar surface characteristics in the adsorption of aromatic compounds: Pore structure and functional groups, Chinese Chem. Lett. 32 (2021) 2939. https://doi.org/10.1016/j.cclet.2021.04.059.

[5] J. Feng, I.T. Burke, X. Chen, D.I. Stewart, Assessing metal contamination and speciation in sewage sludge: implications for soil application and environmental risk, Rev. Environ. Sci. Bio/Technology. 22 (2023) 1037. https://doi.org/10.1007/S11157-023-09675-Y.

[6] R. Molaey, L. Appels, H. Yesil, A.E. Tugtas, B. Çalli, Sustainable heavy metal removal from sewage sludge: A review of bioleaching and other emerging technologies, Sci. Total Environ. 955 (2024) 177020. https://doi.org/10.1016/J.SCITOTENV.2024.177020.

[7] M.D. Hatinoğlu, F.D. Sanin, Sewage sludge as a source of microplastics in the environment: A review of occurrence and fate during sludge treatment, J. Environ. Manage. 295 (2021) 113028. https://doi.org/10.1016/j.jenvman.2021.113028.

[8] M. Patra, S.K. Dubey, Understanding the spread of antibiotic resistance in vegetables cultivated with sewage sludge: implications for food safety and human health, Environ. Syst. Res. 13 (2024) 21. https://doi.org/10.1186/s40068-024-00347-6.

[9] B. Tomczyk, A. Siatecka, Y. Gao, Y.S. Ok, A. Bogusz, P. Oleszczuk, The convertion of sewage sludge to biochar as a sustainable tool of PAHs exposure reduction during agricultural utilization of sewage sludges, J. Hazard. Mater. 392 (2020) 122416. https://doi.org/10.1016/j.jhazmat.2020.122416.

[10] R. K, S. Kumar, B.R. Yadav, From pollutant to powerhouse: The untapped potential of sewage sludge and wastewater, EMBO Rep. 24 (2023). https://doi.org/10.15252/embr.202358201.

[11] H. Lü, X.H. Chen, C.H. Mo, Y.H. Huang, M.Y. He, Y.W. Li, N.X. Feng, A. Katsoyiannis, Q.Y. Cai, Occurrence and dissipation mechanism of organic pollutants during the composting of sewage sludge: A critical review, Bioresour. Technol. 328 (2021) 124847. https://doi.org/10.1016/J.BIORTECH.2021.124847.

[12] A. Sharma, R. Soni, S.K. Soni, From waste to wealth: exploring modern composting innovations and compost valorization, J. Mater. Cycles Waste Manag. 26 (2023) 20. https://doi.org/10.1007/s10163-023-01839-w.

[13] P.A. Rivier, D. Jamniczky, A. Nemes, A. Makó, G. Barna, N. Uzinger, M. Rékási, C. Farkas, Short-term effects of compost amendments to soil on soil structure, hydraulic properties, and water regime, J. Hydrol. Hydromechanics. 70 (2022) 74.

https://doi.org/10.2478/johh-2022-0004.

[14] A. Doughmi, H. Addi, S. Azzouzi, G. Elkafz, F. Benradi, E. Cherkaoui, M. Khamar, A. Nounah, M. Halim, E. Jalil, A. Zouahri, Transforming sewage sludge into a safe circular economy agronomic inputs through (co-)composting: Nutrient value, soil-structure benefits, and contaminant control, Ecol. Eng. Environ. Technol. 27 (2026) 207–221. https://doi.org/10.12912/27197050/215461.

[15] M. Urbaniak, A. Baran, J. Giebułtowicz, A. Bednarek, L. Serwecińska, The occurrence of heavy metals and antimicrobials in sewage sludge and their predicted risk to soil — Is there anything to fear?, Sci. Total Environ. 912 (2024) 168856. https://doi.org/10.1016/j.scitotenv.2023.168856.

[16] V. Pelagalli, M. Langone, S. Matassa, M. Race, R. Tuffi, S. Papirio, P.N.L. Lens, M. Lazzazzara, A. Frugis, L. Petta, G. Esposito, Pyrolysis of municipal sewage sludge: challenges, opportunities and new valorization routes for biochar, bio-oil, and pyrolysis gas, Environ. Sci. Water Res. Technol. 10 (2024) 2282. https://doi.org/10.1039/d4ew00278d.

[17] T.Y.A. Fahmy, Y. Fahmy, F. Mobarak, M. El-Sakhawy, R.E. Abou-Zeid, Biomass pyrolysis: past, present, and future, Environ. Dev. Sustain. 22 (2020) 17. https://doi.org/10.1007/s10668-018-0200-5.

[18] M. Ebrahimi, S. Gholipour, G. Mostafaii, F. Yousefian, Biochar-amended food waste compost: A review of properties, Results Eng. 24 (2024) 103118. https://doi.org/10.1016/J.RINENG.2024.103118.

[19] M.K. Nguyen, C. Lin, H.G. Hoang, P. Sanderson, B.T. Dang, X.T. Bui, N.S.H. Nguyen, D.V.N. Vo, H.T. Tran, Evaluate the role of biochar during the organic waste composting process: A critical review, Chemosphere. 299 (2022) 134488.

https://doi.org/10.1016/J.CHEMOSPHERE.2022.134488.

[20] R. Tang, S. Yao, Y. Liu, T. Ren, J. Ma, X. Gong, G. Li, R. Ma, J. Yuan, Iron-modified biochar enhanced nitrogen retention during composting:bridging chemisorption and microbiome modulation, Chem. Eng. J. 513 (2025) 162761. https://doi.org/10.1016/J.CEJ.2025.162761.

[21] B.J. Parasar, N. Agarwala, Unravelling the role of biochar-microbe-soil tripartite interaction in regulating soil carbon and nitrogen budget: a panacea to soil sustainability, Biochar. 7 (2025) 1. https://doi.org/10.1007/S42773-024-00411-5.

[22] X. Guo, H. Liu, J. Zhang, The role of biochar in organic waste composting and soil improvement: A review, Waste Manag. 102 (2020) 884. https://doi.org/10.1016/j.wasman.2019.12.003.

[23] K. Lu, L. Wang, Y. Pei, K. Zhang, W. Liu, M. Zhu, Y. Duan, Q. Feng, M. Liu, Different pathways in promoting humic acid formation of multi-source biochar addition between fiber and livestock manure type solid waste composting, Int. J. Biol. Macromol. 315 (2025) 144592. https://doi.org/10.1016/J.IJBIOMAC.2025.144592.

[24] X. Gu, H. Li, Y. Shi, C. Sun, J. Li, S. Li, Magnesium modified biochar facilitates favorable nitrogen conversion to mitigate ammonia and nitrous oxide emissions during pig manure composting, Chem. Eng. J. 504 (2025) 159073. https://doi.org/10.1016/J.CEJ.2024.159073.

[25] B.P. Harrison, Z. Moo, E. Perez-Agredano, S. Gao, X. Zhang, R. Ryals, Biochar-composting substantially reduces methane and air pollutant emissions from dairy manure, Environ. Res. Lett. 19 (2024) 014081. https://doi.org/10.1088/1748-9326/ad1ad2.

[26] D. Castro-Herrera, K. Prost, D.G. Kim, F. Yimer, M. Tadesse, M. Gebrehiwot, N. Brüggemann, Biochar addition reduces non-CO2 greenhouse gas emissions during composting of human excreta and cattle manure, J. Environ. Qual. 52 (2023) 814. https://doi.org/10.1002/JEQ2.20482.

[27] H.T. Tran, N.S. Bolan, C. Lin, Q.A. Binh, M.K. Nguyen, T.A. Luu, V.G. Le, C.Q. Pham, H.G. Hoang, D.V.N. Vo, Succession of biochar addition for soil amendment and contaminants remediation during co-composting: A state of art review, J. Environ. Manage. 342 (2023) 118191. https://doi.org/10.1016/J.JENVMAN.2023.118191.

[28] S. Qian, X. Zhou, Y. Fu, B. Song, H. Yan, Z. Chen, Q. Sun, H. Ye, L. Qin, C. Lai, Biochar-compost as a new option for soil improvement: Application in various problem soils, Sci. Total Environ. 870 (2023) 162024. https://doi.org/10.1016/J.SCITOTENV.2023.162024.

[29] K.N. Palansooriya, P.D. Dissanayake, A. El-Naggar, E. Gayesha, H. Wijesekara, N. Krishnamoorthy, Y. Cai, S.X. Chang, Biochar-based controlled-release fertilizers for enhancing plant growth and environmental sustainability: a review, Biol. Fertil. Soils. 61 (2025) 701. https://doi.org/10.1007/S00374-025-01888-3.

[30] P. Godlewska, H.P. Schmidt, Y.S. Ok, P. Oleszczuk, Biochar for composting improvement and contaminants reduction. A review, Bioresour. Technol. 246 (2017) 193. https://doi.org/10.1016/j.biortech.2017.07.095.

[31] I. Mikajlo, T.Z. Lerch, B. Louvel, J. Hynšt, J. Záhora, B. Pourrut, Composted biochar versus compost with biochar: effects on soil properties and plant growth, Biochar. 6 (2024) 1. https://doi.org/10.1007/S42773-024-00379-2.

[32] N. Akdeniz, A systematic review of biochar use in animal waste composting,

Waste Manag. 88 (2019) 291. https://doi.org/10.1016/J.WASMAN.2019.03.054.

[33] R. Xiao, M.K. Awasthi, R. Li, J. Park, S.M. Pensky, Q. Wang, J.J. Wang, Z. Zhang, Recent developments in biochar utilization as an additive in organic solid waste composting: A review, Bioresour. Technol. 246 (2017) 203. https://doi.org/10.1016/J.BIORTECH.2017.07.090.

[34] W. Buss, Pyrolysis solves the issue of organic contaminants in sewage sludge while retaining carbon - Making the case for sewage sludge treatment via pyrolysis, ACS Sustain. Chem. Eng. 9 (2021) 10048. https://doi.org/10.1021/acssuschemeng.1c03651.

[35] J. Poluszyńska, E. Jarosz-Krzemińska, E. Helios-Rybicka, Studying the effects of two various methods of composting on the degradation levels of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge, Water. Air. Soil Pollut. 228 (2017) 1. https://doi.org/10.1007/S11270-017-3481-7.

[36] N. Ozaki, A. Nakazato, K. Nakashima, T. Kindaichi, A. Ohashi, Loading and removal of PAHs, fragrance compounds, triclosan and toxicity by composting process from sewage sludge, Sci. Total Environ. 605–606 (2017) 860. https://doi.org/10.1016/j.scitotenv.2017.06.165.

[37] D. Vrábl, K. Chamrádová, K. Smutná, I. Koutník, J. Rusín, L. Repecká, A. Gavlová, M. Navrátil, R. Chalupa, B. Tenklová, J. Pavlíková, M. Vráblová, Composting of waste biomass into substrates with enhanced humic acid content and optimized water holding capacity, J. Environ. Chem. Eng. 13 (2025) 117217. https://doi.org/10.1016/j.jece.2025.117217.

[38] M. Kopeć, B. Smreczak, A. Ukalska-Jaruga, M. Mierzwa-Hersztek, K. Gondek, Changes of PAHs and C humic fractions in composts with sewage sludge and

biochar amendment, Desalin. Water Treat. 97 (2017) 234. https://doi.org/10.5004/dwt.2017.21629.

[39] H. Jia, D. Chu, X. You, Y. Li, C. Huang, J. Zhang, X. Zeng, H. Yao, Z. Zhou, Biochar improved the composting quality of seaweeds and cow manure mixture and altered the microbial community, Front. Microbiol. 13 (2022) 1064252. https://doi.org/10.3389/fmicb.2022.1064252.

[40] N. Wang, X. Bai, D. Huang, M. Shao, Q. Chen, Q. Xu, Insights into the influence of digestate-derived biochar upon the microbial community succession during the composting of digestate from food waste, Chemosphere. 316 (2023) 137786. https://doi.org/10.1016/J.CHEMOSPHERE.2023.137786.

[41] O. Roques, J.P. Bedell, J. Le Maux, L. Wiest, S. Nélieu, C. Mougin, N. Cheviron, O. Santini, V. Lecomte, R. Bayard, Assessing the potential ecotoxicological risk of different organic amendments used in agriculture: Approach using acute toxicity tests on plants and earthworms, Arch. Environ. Contam. Toxicol. 84 (2023) 248. https://doi.org/10.1007/S00244-023-00979-2.

[42] B. Mohamadi, B. Akbari-Adergani, Y. Mazaheri, N. Akbari, B. Basaran, P. Sadighara, A systematic study of the assessment of polycyclic aromatic hydrocarbons (PAHs) in green houses and farms.“A review,” Int. J. Veg. Sci. 31 (2025) 135. https://doi.org/10.1080/19315260.2024.2447773.

[43] A. Dhara, R. Dutta, A review on sources and distribution of polycyclic aromatic hydrocarbons (PAHs) in wetland ecosystem: focusing on plant-biomonitoring and phytoremediation, Environ. Sci. Pollut. Res. 32 (2025) 8743. https://doi.org/10.1007/S11356-025-36240-7.

[44] Environmental Protection Agency (EPA), Appendix A: priority pollutants, Off.

Fed. Regist. 47 (1982) 52309.

[45] M. Mohanty, J. Mohanty, S. Priyadarsini, J.M. Rodríguez-Díaz, S. Yadav, M.M.S. Cabral-Pinto, H. Nath, D.K. Ram, G. Koteswara Reddy, A.P. Das, Environmental hydrocarbon pollutants: Sources, transport, and effect on human health, in: Environ. Hydrocarb. Pollut. Zero Waste Approach Towar. a Sustain. Waste Manag., Springer, Cham, 2025: p. 21. https://doi.org/10.1007/978-3-031-81615-4_2.

[46] D. He, T. Zhu, J. Sun, X. Pan, J. Li, H. Luo, Emerging organic contaminants in sewage sludge: Current status, technological challenges and regulatory perspectives, Sci. Total Environ. 955 (2024) 177234. https://doi.org/10.1016/j.scitotenv.2024.177234.

[47] M. Alipour, H. Asadi, C. Chen, A.A. Besalatpour, Fate of organic pollutants in sewage sludge during thermal treatments: Elimination of PCBs, PAHs, and PPCPs, Fuel. 319 (2022) 123864. https://doi.org/10.1016/j.fuel.2022.123864.

[48] A. Balkrishna, P. Kaushik, S. Singh, P. Agrahari, B. Kumar, P. Kumar, V.P. Arya, Potential use of sewage sludge as fertilizer in organic farming, Clean. Waste Syst. 10 (2025) 100245. https://doi.org/10.1016/j.clwas.2025.100245.

[49] Q. Lu, Z. Jiang, W. Feng, C. Yu, F. Jiang, J. Huang, J. Cui, Exploration of bacterial community-induced polycyclic aromatic hydrocarbons degradation and humus formation during co-composting of cow manure waste combined with contaminated soil, J. Environ. Manage. 326 (2023) 116852. https://doi.org/10.1016/J.JENVMAN.2022.116852.

[50] G. Zhang, X. Guo, Y. Zhu, X. Liu, Z. Han, K. Sun, L. Ji, Q. He, L. Han, The effects of different biochars on microbial quantity, microbial community shift,

enzyme activity, and biodegradation of polycyclic aromatic hydrocarbons in soil, Geoderma. 328 (2018) 100. https://doi.org/10.1016/J.GEODERMA.2018.05.009.

[51] S. Ye, G. Zeng, H. Wu, J. Liang, C. Zhang, J. Dai, W. Xiong, B. Song, S. Wu, J. Yu, The effects of activated biochar addition on remediation efficiency of co-composting with contaminated wetland soil, Resour. Conserv. Recycl. 140 (2019) 278. https://doi.org/10.1016/J.RESCONREC.2018.10.004.

[52] A. Ukalska-Jaruga, G. Debaene, B. Smreczak, Dissipation and sorption processes of polycyclic aromatic hydrocarbons (PAHs) to organic matter in soils amended by exogenous rich-carbon material, J. Soils Sediments. 20 (2019) 836. https://doi.org/10.1007/s11368-019-02455-8.

[53] X. Su, R. Zhang, H. Cao, D. Mu, L. Wang, C. Song, Z. Wei, Y. Zhao, Adsorption of humic acid from different organic solid waste compost to phenanthrene, is fluorescence excitation or quenching?, Environ. Pollut. 347 (2024) 123712. https://doi.org/10.1016/j.envpol.2024.123712.

[54] S. Lamichhane, K.C. Bal Krishna, R. Sarukkalige, Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: A review, Chemosphere. 148 (2016) 336. https://doi.org/10.1016/J.CHEMOSPHERE.2016.01.036.

[55] Q. Aemig, N. Doussiet, A. Danel, N. Delgenès, J. Jimenez, S. Houot, D. Patureau, Organic micropollutants' distribution within sludge organic matter fractions explains their dynamic during sewage sludge anaerobic digestion followed by composting, Environ. Sci. Pollut. Res. 26 (2019) 5820. https://doi.org/10.1007/s11356-018-4014-7.

[56] Y. Guo, E.R. Rene, J. Wang, W. Ma, Biodegradation of polyaromatic hydrocarbons and the influence of environmental factors during the co-composting

of sewage sludge and green forest waste, Bioresour. Technol. 297 (2020) 122434. https://doi.org/10.1016/J.BIORTECH.2019.122434.

[57] K. Jomova, S.Y. Alomar, E. Nepovimova, K. Kuca, M. Valko, Heavy metals: toxicity and human health effects, Arch. Toxicol. 99 (2024) 153. https://doi.org/10.1007/s00204-024-03903-2.

[58] R. Nieder, D.K. Benbi, Potentially toxic elements in the environment - A review of sources, sinks, pathways and mitigation measures, Rev. Environ. Health. 39 (2024) 561. https://doi.org/10.1515/REVEH-2022-0161.

[59] X. Chen, Y. Zhao, C. Zhang, D. Zhang, C. Yao, Q. Meng, R. Zhao, Z. Wei, Speciation, toxicity mechanism and remediation ways of heavy metals during composting: A novel theoretical microbial remediation method is proposed, J. Environ. Manage. 272 (2020) 111109. https://doi.org/10.1016/J.JENVMAN.2020.111109.

[60] M.N. Georgaki, S. Tsokkou, A. Keramas, T. Papamitsou, S. Karachrysafi, N. Kazakis, Chromium supplementation and type 2 diabetes mellitus: an extensive systematic review, Environ. Geochem. Health. 46 (2024) 515. https://doi.org/10.1007/s10653-024-02297-5.

[61] Kiran, R. Bharti, R. Sharma, Effect of heavy metals: An overview, Mater. Today Proc. 51 (2022) 880. https://doi.org/10.1016/J.MATPR.2021.06.278.

[62] Y. Gao, S. Wang, W. Tan, B. Xi, Dynamics of nutrient elements and potentially toxic elements during composting with different organic wastes, Front. Sustain. Food Syst. 7 (2023) 1181392. https://doi.org/10.3389/fsufs.2023.1181392.

[63] Y. Duan, J. Yang, Y. Guo, X. Wu, Y. Tian, H. Li, M.K. Awasthi, Pollution control

in biochar-driven clean composting: Emphasize on heavy metal passivation and gaseous emissions mitigation, J. Hazard. Mater. 420 (2021) 126635. https://doi.org/10.1016/J.JHAZMAT.2021.126635.

[64] X. Chen, Z. Du, D. Liu, L. Wang, C. Pan, Z. Wei, L. Jia, R. Zhao, Biochar mitigates the biotoxicity of heavy metals in livestock manure during composting, Biochar. 4 (2022) 1. https://doi.org/10.1007/S42773-022-00174-X.

[65] J. Ali, M. Tuzen, Q. ul ain Shaikh, W.B. Jatoi, X. Feng, G. Sun, T.A. Saleh, A review of sequential extraction methods for fractionation analysis of toxic metals in solid environmental matrices, TrAC Trends Anal. Chem. 173 (2024) 117639. https://doi.org/10.1016/J.TRAC.2024.117639.

[66] G. Dede, Z. Banu Sasmaz, S. Ozdemir, C. Caner, C. Dede, Investigation of heavy metal and micro-macro element speciation in biomass ash enriched sewage sludge compost, J. Environ. Manage. 344 (2023) 118330. https://doi.org/10.1016/J.JENVMAN.2023.118330.

[67] X. Wang, T. Chen, G. Zheng, Preservation of nitrogen and sulfur and passivation of heavy metals during sewage sludge composting with KH2PO4 and FeSO4, Bioresour. Technol. 297 (2020) 122383. https://doi.org/10.1016/j.biortech.2019.122383.

[68] M.R. Rehana, B. Joseph, R. Gladis, Heavy metal stabilization in sewage sludge composting process, Curr. J. Appl. Sci. Technol. 39 (2020) 38. https://doi.org/10.9734/cjast/2020/v39i1930789.

[69] R. Cai, Y. Wang, R. Li, Study on the transformation mechanism of heavy metals and phosphorus and their bioavailability during sludge composting under functional membrane coverage, Chem. Eng. J. 523 (2025) 168735.

https://doi.org/10.1016/j.cej.2025.168735.

[70] S. Xu, L. Li, J. Zhan, X. Guo, Variation and factors on heavy metal speciation during co-composting of rural sewage sludge and typical rural organic solid waste, J. Environ. Manage. 306 (2022) 114418. https://doi.org/10.1016/j.jenvman.2021.114418.

[71] W. Liu, R. Huo, J. Xu, S. Liang, J. Li, T. Zhao, S. Wang, Effects of biochar on nitrogen transformation and heavy metals in sludge composting, Bioresour. Technol. 235 (2017) 43. https://doi.org/10.1016/J.BIORTECH.2017.03.052.

[72] S. Guo, J. Wei, Y. Zhang, Z. Bao, Y. Wei, B. Zhu, J. Liu, Effects and mechanisms of different types of biochar on heavy metal passivation during sludge composting, Bull. Environ. Contam. Toxicol. 113 (2024) 1. https://doi.org/10.1007/S00128-024-03921-X.

[73] M. Zhao, S. Zhong, X. Zhou, Z. Yu, Biochar derived from animal and plant facilitates synergistic transformation of heavy metals and phosphorus in sewage sludge composting, Environ. Pollut. 357 (2024) 124396. https://doi.org/10.1016/J.ENVPOL.2024.124396.

[74] W. Quan, J. Zhang, Y. Wu, Y. Gong, K. Yang, L. Li, J. Gao, K. Yang, H. Cheng, Effect of biochars derived from plant and animal manure on heavy metal immobilization in sewage sludge during composting, Environ. Technol. Innov. 41 (2026) 104791. https://doi.org/10.1016/j.eti.2026.104791.

[75] M.K. Awasthi, Q. Wang, H. Huang, R. Li, F. Shen, A.H. Lahori, P. Wang, D. Guo, Z. Guo, S. Jiang, Z. Zhang, Effect of biochar amendment on greenhouse gas emission and bio-availability of heavy metals during sewage sludge co-composting, J. Clean. Prod. 135 (2016) 829.

https://doi.org/10.1016/J.JCLEPRO.2016.07.008.

[76] W. Qin, A. Shahab, X. Sun, J. Li, K. Li, H. Xiao, Enhancing municipal sludge composting efficiency: The synergistic impacts of montmorillonite and coconut shell biochar additives on heavy metal passivation and microbial community succession, J. Environ. Chem. Eng. 13 (2025) 117155. https://doi.org/10.1016/j.jece.2025.117155.

[77] X. Qiu, G. Zhou, H. Wang, X. Wu, The behavior of antibiotic-resistance genes and their relationships with the bacterial community and heavy metals during sewage sludge composting, Ecotoxicol. Environ. Saf. 216 (2021) 112190. https://doi.org/10.1016/j.ecoenv.2021.112190.

[78] L. Liu, Q. Ye, Q. Wu, T. Liu, S. Peng, Effect of biochar addition on sludge aerobic composting and greenbelt utilization, Environ. Technol. Innov. 21 (2021) 101279. https://doi.org/10.1016/J.ETI.2020.101279.

[79] X. Qiu, M. Feng, R. Chen, J. Chen, X. Zheng, X. Mao, W. Song, G. Zhou, Phosphoric acid modified biochar enhanced heavy metals passivation via accelerating humification and bioremediation in sewage sludge composting, Environ. Technol. Innov. 39 (2025) 104275. https://doi.org/10.1016/j.eti.2025.104275.

[80] J.A. Antonangelo, X. Sun, H. Zhang, The roles of co-composted biochar (COMBI) in improving soil quality, crop productivity, and toxic metal amelioration, J. Environ. Manage. 277 (2021) 111443. https://doi.org/10.1016/j.jenvman.2020.111443.

[81] L. Chen, Y. Chen, Y. Li, H. Jiang, Y. Liu, Y. Yuan, J. Wang, H. Li, Y. Chen, Passivation of heavy metals during co-composting of Camellia oleifera by-

products and river sediment with the additives of MnO2-loaded biochar, Ind. Crops Prod. 215 (2024) 118697. https://doi.org/10.1016/J.INDCROP.2024.118697.

[82] Z. Wang, M. Zhang, J. Li, J. Wang, G. Sun, G. Yang, J. Li, Effect of biochar with various pore characteristics on heavy metal passivation and microbiota development during pig manure composting, J. Environ. Manage. 352 (2024) 120048. https://doi.org/10.1016/J.JENVMAN.2024.120048.

[83] M. Wang, Y. Wu, J. Zhao, Y. Liu, L. Gao, Z. Jiang, J. Zhang, W. Tian, Comparison of composting factors, heavy metal immobilization, and microbial activity after biochar or lime application in straw-manure composting, Bioresour. Technol. 363 (2022) 127872. https://doi.org/10.1016/J.BIORTECH.2022.127872.

[84] W. Yang, Y. Zhong, Z. Lu, D. Lin, Q. Zhuo, H. Zeng, D. Yang, Z. Chen, Synthesis of biochar-loaded green synthetic iron nanocomposite and passivation mechanism of cadmium in pig manure aerobic composting, Environ. Technol. Innov. 40 (2025) 104377. https://doi.org/10.1016/J.ETI.2025.104377.

[85] X. Cao, P.N. Williams, Y. Zhan, S.A. Coughlin, J.W. McGrath, J.P. Chin, Y. Xu, Municipal solid waste compost: Global trends and biogeochemical cycling, Soil Environ. Heal. 1 (2023) 100038. https://doi.org/10.1016/J.SEH.2023.100038.

[86] F. Carraturo, A. Siciliano, A. Giordano, F. Di Capua, F. Barone, E. Casaletta, F. Cicotti, M. Guida, F. Adani, Ecotoxicological assessment of waste-derived organic fertilizers and long-term monitoring of fertilized soils using a multi-matrix and multi-species approach, Sci. Total Environ. 912 (2024) 169341. https://doi.org/10.1016/J.SCITOTENV.2023.169341.

[87] S.A. Tsabedze, B. Otieno, A.R. Thomas, S.T. Getahun, Phytotoxicity and quality in compost: a concise review of sewage sludge and green waste applications, J.

Mater. Cycles Waste Manag. 27 (2025) 4041. https://doi.org/10.1007/S10163-025-02334-0.

[88] S. Albert, E. Bloem, Ecotoxicological methods to evaluate the toxicity of bio-based fertilizer application to agricultural soils – A review, Sci. Total Environ. 879 (2023) 163076. https://doi.org/10.1016/J.SCITOTENV.2023.163076.

[89] E. Abban-Baidoo, D. Manka'abusi, L. Apuri, B. Marschner, K.A. Frimpong, Biochar addition influences C and N dynamics during biochar co-composting and the nutrient content of the biochar co-compost, Sci. Rep. 14 (2024) 1. https://doi.org/10.1038/s41598-024-67884-z.

[90] M. Kopeć, A. Baran, M. Mierzwa-Hersztek, K. Gondek, M.J. Chmiel, Effect of the addition of biochar and coffee grounds on the biological properties and ecotoxicity of composts, Waste and Biomass Valorization. 9 (2018) 1389. https://doi.org/10.1007/S12649-017-9916-Y.

[91] I. Hilber, F. Blum, J. Leifeld, H.P. Schmidt, T.D. Bucheli, Quantitative determination of PAHs in biochar: A prerequisite to ensure its quality and safe application, J. Agric. Food Chem. 60 (2012) 3042–3050. https://doi.org/10.1021/JF205278V.

[92] G. Cornelissen, A. Pettersen, D. Broman, P. Mayer, G.D. Breedveld, Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations, Environ. Toxicol. Chem. 27 (2008) 499. https://doi.org/10.1897/07-253.1.

[93] S.B. Hawthorne, M.T.O. Jonker, S.A. Van Der Heijden, C.B. Grabanski, N.A. Azzolina, D.J. Miller, Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with

polyoxymethylene, Anal. Chem. 83 (2011) 6754. https://doi.org/10.1021/ac201411v.

[94] S.B. Hawthorne, C.B. Grabanski, D.J. Miller, Measured partitioning coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: Part 1. KOC values, Environ. Toxicol. Chem. 25 (2006) 2901. https://doi.org/10.1897/06-115R.1.

[95] M. Pueyo, J. Mateu, A. Rigol, M. Vidal, J.F. López-Sánchez, G. Rauret, Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils, Environ. Pollut. 152 (2008) 330. https://doi.org/10.1016/J.ENVPOL.2007.06.020.

[96] S. Mukherjee, B. Sarkar, V.K. Aralappanavar, R. Mukhopadhyay, B.B. Basak, P. Srivastava, O. Marchut-Mikołajczyk, A. Bhatnagar, K.T. Semple, N. Bolan, Biochar-microorganism interactions for organic pollutant remediation: Challenges and perspectives, Environ. Pollut. 308 (2022) 119609. https://doi.org/10.1016/J.ENVPOL.2022.119609.

[97] B. Xiao, J. Jia, W. Xu, S. Ji, B. Zhang, W. Wang, Y. Ma, X. Gao, Enhanced biodegradation of polycyclic aromatic hydrocarbons in contaminated soils using biochar-immobilized mixed bacteria: Mechanisms and microbial responses, Water, Air, Soil Pollut. 236 (2025) 453. https://doi.org/10.1007/s11270-025-08111-x.

[98] Y. Chen, Y. Xu, F. Qu, F. Hou, H. Chen, X. Li, Effects of different loading rates and types of biochar on passivations of Cu and Zn via swine manure composting, J. Arid Land. 12 (2020) 1056. https://doi.org/10.1007/S40333-020-0026-5.

[99] Y. Kong, R. Ma, G. Li, G. Wang, Y. Liu, J. Yuan, Impact of biochar, calcium magnesium phosphate fertilizer and spent mushroom substrate on humification and

heavy metal passivation during composting, Sci. Total Environ. 824 (2022) 153755. https://doi.org/10.1016/J.SCITOTENV.2022.153755.

[100] Z. Jiao, R. Li, K. Zhang, Y. Zhang, Y. Guo, S. Chang, Y. Chang, Y. Wei, Z. Kang, Y. Qiao, J. Li, From carbon sequestration perspective: Adsorption of minerals enhances the stabilization of organic fractions in composting, Environ. Technol. Innov. 37 (2025) 104023. https://doi.org/10.1016/J.ETI.2025.104023.

[101] X. Guo, H. Liu, S. Wu, Humic substances developed during organic waste composting: Formation mechanisms, structural properties, and agronomic functions, Sci. Total Environ. 662 (2019) 501. https://doi.org/10.1016/J.SCITOTENV.2019.01.137.

[102] S. Kukowska, K. Szewczuk-Karpisz, Biochar and zeolite uses in improving immobilization of nutrients and pollutants in soils, Sep. Purif. Rev. 54 (2025) 354. https://doi.org/10.1080/15422119.2024.2426157.

[103] Y. Zhang, Y. Zheng, Y. Yang, J. Huang, A.R. Zimmerman, H. Chen, X. Hu, B. Gao, Mechanisms and adsorption capacities of hydrogen peroxide modified ball milled biochar for the removal of methylene blue from aqueous solutions, Bioresour. Technol. 337 (2021) 125432. https://doi.org/10.1016/J.BIORTECH.2021.125432.

[104] M. Zhang, L. Shu, X. Guo, X. Shen, H. Zhang, G. Shen, B. Wang, Y. Yang, S. Tao, X. Wang, Impact of humic acid coating on sorption of naphthalene by biochars, Carbon N. Y. 94 (2015) 946. https://doi.org/10.1016/J.CARBON.2015.07.079.

[105] J. Du, Y. Zhang, B. Hu, M. Qv, C. Ma, M. Wei, H. Zhang, Insight into the potentiality of big biochar particle as an amendment in aerobic composting of

sewage sludge, Bioresour. Technol. 288 (2019) 121469. https://doi.org/10.1016/J.BIORTECH.2019.121469.

[106] Z. Luo, B. Yao, X. Yang, L. Wang, Z. Xu, X. Yan, L. Tian, H. Zhou, Y. Zhou, Novel insights into the adsorption of organic contaminants by biochar: A review, Chemosphere. 287 (2022) 132113. https://doi.org/10.1016/J.CHEMOSPHERE.2021.132113.

[107] M. Fan, C. Li, Y. Shao, S. Zhang, M. Gholizadeh, X. Hu, Pyrolysis of cellulose: Correlation of hydrophilicity with evolution of functionality of biochar, Sci. Total Environ. 825 (2022) 153959. https://doi.org/10.1016/J.SCITOTENV.2022.153959.

[108] X. Jia, B. Zhang, Y. Han, J. Guan, H. Gao, P. Guo, Role of reactive oxygen species (ROS) on biochar enhanced chromium phytoremediation in the soil–plant system: Exploration on detoxification mechanism, Environ. Int. 199 (2025) 109471. https://doi.org/10.1016/J.ENVINT.2025.109471.

[109] M. Abbas, M. Adil, S. Ehtisham-ul-Haque, B. Munir, M. Yameen, A. Ghaffar, G.A. Shar, M. Asif Tahir, M. Iqbal, Vibrio fischeri bioluminescence inhibition assay for ecotoxicity assessment: A review, Sci. Total Environ. 626 (2018) 1295–1309. https://doi.org/10.1016/J.SCITOTENV.2018.01.066.

[110] L.H. Mortensen, C. Cruz-Paredes, J. Qin, R. Rønn, M. Vestergård, Effect of ash application on the decomposer food web and N mineralization in a Norway spruce plantation, Sci. Total Environ. 715 (2020) 136793. https://doi.org/10.1016/J.SCITOTENV.2020.136793.

[111] R.E. Reitsema, P. Meire, J. Schoelynck, The future of freshwater macrophytes in a changing world: Dissolved organic carbon quantity and quality and its interactions with macrophytes, Front. Plant Sci. 9 (2018) 629.

https://doi.org/10.3389/FPLS.2018.00629.

[112] Y. Sun, X. Xiong, M. He, Z. Xu, D. Hou, W. Zhang, Y.S. Ok, J. Rinklebe, L. Wang, D.C.W. Tsang, Roles of biochar-derived dissolved organic matter in soil amendment and environmental remediation: A critical review, Chem. Eng. J. 424 (2021) 130387. https://doi.org/10.1016/J.CEJ.2021.130387.

[113] L. Comensoli, S. Bindschedler, P. Junier, E. Joseph, Iron and fungal physiology: A review of biotechnological opportunities, Adv. Appl. Microbiol. 98 (2017) 31. https://doi.org/10.1016/BS.AAMBS.2016.11.001.

[114] Z. Chen, A. Kumar, Y. Fu, B.P. Singh, T. Ge, H. Tu, Y. Luo, J. Xu, Biochar decreased rhizodeposits stabilization via opposite effects on bacteria and fungi: diminished fungi-promoted aggregation and enhanced bacterial mineralization, Biol. Fertil. Soils. 57 (2021) 533. https://doi.org/10.1007/S00374-020-01539-9.

Życiorys naukowy

W 2014 roku ukończyłam II Liceum Ogólnokształcące im. Adama Mickiewicza w Skarżysku-Kamiennej, a w październiku tego roku rozpoczęłam studia licencjackie na kierunku Chemia, specjalność Chemia kryminalistyczna, na Wydziale Chemii Uniwersytetu Marii Curie-Skłodowskiej w Lublinie. W 2017 roku obroniłam z wynikiem bardzo dobrym pracę dyplomową pt. „*Metody chemiczne i fizykochemiczne identyfikacji fałszerstw wyrobów z metali*" przygotowaną pod kierunkiem dr. Andrzeja Persony. W 2019 roku otrzymałam tytuł magistra po obronie pracy magisterskiej pt. „*Wpływ warunków syntezy na strukturę i właściwości adsorpcyjne modyfikowanych SBA-15 z odwzorowaniem jonów Pd (II)*" z wynikiem bardzo dobrym. Praca magisterska została zrealizowana pod kierunkiem prof. dr. hab. Ryszarda Dobrowolskiego. W trakcie studiów licencjackich i magisterskich co roku otrzymywałam stypendium rektora dla najlepszych studentów UMCS.

W październiku 2020 roku rozpoczęłam studia doktoranckie w Szkole Doktorskiej Nauk Ścisłych i Przyrodniczych UMCS. Badania będące podstawą rozprawy doktorskiej pt.: „*Optymalizacja procesu kompostowania osadów ściekowych przy zastosowaniu biowęgli i biowęgli projektowanych w celu otrzymania kompostów o zredukowanym ryzyku środowiskowym i podwyższonych właściwościach nawozowych*" zrealizowałam w Katedrze Radiochemii i Chemii Środowiskowej pod kierunkiem prof. dr. hab. Patryka Oleszczuka. Mój dorobek naukowy obejmuje sześć publikacji naukowych indeksowanych na liście JCR, pięć komunikatów na konferencjach krajowych oraz dwa komunikaty na konferencjach międzynarodowych.

Dorobek naukowy

- **Publikacje międzynarodowe**

[1] Tomczyk B., Siatecka A., Jędruchniewicz K., **Sochacka A.**, Bogusz A., Oleszczuk P., 2020. Polycyclic aromatic hydrocarbons (PAHs) persistence, bioavailability and toxicity in sewage-sludge or sewage sludge-derived biochar-amended soil. Science of the Total Environment. 747, 141123. https://doi.org/10.1016/j.scitotenv.2020.141123 (IF: 8,0; MNISW: 200)

[2] **Rombel A.,** Krasucka P., Oleszczuk P., 2021. Sustainable biochar-based soil fertilizers and amendments as a new trend in biochar research. Science of the Total Environment. 816, 151588. https://doi.org/10.1016/J.SCITOTENV.2021.151588 (IF: 8,2; MNiSW: 200)

[3] Krasucka P., **Rombel A.**, Xang X.J., Rakowska M., Xing B., Oleszczuk P., 2022. Adsorption and desorption of antiviral drugs (ritonavir and lopinavir) on sewage sludges as a potential environmental risk. Journal of Hazardous Materials. 425, 127901. https://doi.org/10.1016/J.JHAZMAT.2021.127901 (IF: 12,2; MNiSW: 200)

[4] **Rombel A.**, Różyło K., Oleszczuk P., 2024. The high dose of biochar reduces polycyclic aromatic hydrocarbons losses during co-composting of sewage sludge and wheat straw. Journal of Environmental Management. 351, 119628. https://doi.org/10.1016/J.JENVMAN. 2023.119628 (IF: 8,0; MNiSW: 200)

[5] **Rombel A.,** Różyło K., Ok Y.S., Oleszczuk P., 2025. Influence of biochar characteristics on polycyclic aromatic hydrocarbons content during co-composting of sewage sludge. Bioresource Technology. 423, 132220. https://doi.org/10.1016/J.BIORTECH.2025.132220 (IF: 9,7; MNiSW: 140)

[6] **Rombel A.**, Raczkiewicz M., Pan B., Oleszczuk P., 2026. Stage-dependent effects of willow- and sewage sludge-derived biochar on compost ecotoxicity across multiple trophic levels. Journal of Environmental Chemical Engineering. 14, 121924. https://doi.org/10.1016/j.jece.2026.121924 (IF**:** 7,2; MNiSW: 100)

- **Projekty badawcze**

OPUS-18 (Narodowe Centrum Nauki) – doktorant w projekcie badawczym pt. „*Optimization of the composting process of sewage sludge using biochars and engineered (smart) biochars to obtain composts with reduced environmental risk and increased fertilizing properties*”

- **Konferencje krajowe**

[1] współautorstwo posteru naukowego pt.: „*Adsorpcja i desorpcja leków antywirusowych przez osady ściekowe jako potencjalne zagrożenie dla środowiska*” (autorzy**: A. Rombel**, P. Krasucka, P. Oleszczuk) na XIV Interdyscyplinarnej Konferencji Naukowej TYGIEL 2022 „Interdyscyplinarność kluczem do rozwoju” odbywającej się w dniach 24 – 27 marca 2022r. w Lublinie;

[2] współautorstwo posteru naukowego pt.: „*Wpływ surowca (wierzba, osad ściekowy) na efektywność adsorpcji Cd, Cu i Zn po modyfikacji nadtlenkiem wodoru*” (autorzy: K. Jędruchniewicz, **A. Rombel**, P. Oleszczuk) na XIV Konferencji Naukowo-Technicznej odbywającej się w dniach 18 – 21 października 2022 r. w Ustroniu;

[3] współautorstwo posteru naukowego pt.: „*Dawka biowęgla determinuje straty wielopierścieniowych węglowodorów aromatycznych podczas współkompostowania z osadem ściekowym i słomą*” (autorzy: **A. Rombel**, K. Jędruchniewicz, P. Oleszczuk) na

XV Interdyscyplinarnej Konferencji Naukowej TYGIEL 2023 „Interdyscyplinarność kluczem do rozwoju) odbywającej się w dniach 23 – 26 marca 2023 r. w Lublinie;

[4] współautorstwo posteru naukowego pt.: „*Adsorpcja wybranych pierwiastków śladowych przez biowęgle otrzymane z różnych surowców i w zróżnicowanych warunkach*" (autorzy: **A. Rombel**, P. Oleszczuk) na konferencji naukowej „Fizykochemia granic faz – metody instrumentalne" odbywającej się w dniach 16 – 20 kwietnia 2023 r. w Lublinie;

[5] współautorstwo posteru naukowego pt.: „*Straty całkowitej i biodostępnej zawartości wielopierścieniowych węglowodorów aromatycznych w zależności od dawki biowęgla dodanego do współkompostowania osadu ściekowego i słomy*" (autorzy: **A. Rombel**, P. Oleszczuk) na konferencji naukowej „III Kongres Młodej Nauki" odbywającej się w dniach 6 – 8 lipca 2023 r. w Gdańsku.

- **Konferencje międzynarodowe**

[1] współautorstwo posteru naukowego pt.: "Modification *of biochar with hydrogen peroxide affects differently biochar capacity to heavy metals depending on feedstock (sewage sludge versus biomass)*" (autorzy: **A. Rombel**, K. Jędruchniewicz, P. Oleszczuk) na *Asia Pacific Biochar Conference* 2022 odbywającej się w dniach 24 – 27 października 2022 r. w Seulu (Korea Południowa);

[2] współautorstwo posteru naukowego pt.: „*Effect of the biochar dose on the availability of heavy metals during co-composting with sewage sludge*" (autorzy: **A. Rombel**, K. Jędruchniewicz, P. Oleszczuk) na *1st Joint International Conference ICOBTE & ICHMET* 2023 odbywającej się w dniach 6 – 10 września 2023 r. w Wuppertal (Niemcy).

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D1

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Review

Sustainable biochar-based soil fertilizers and amendments as a new trend in biochar research

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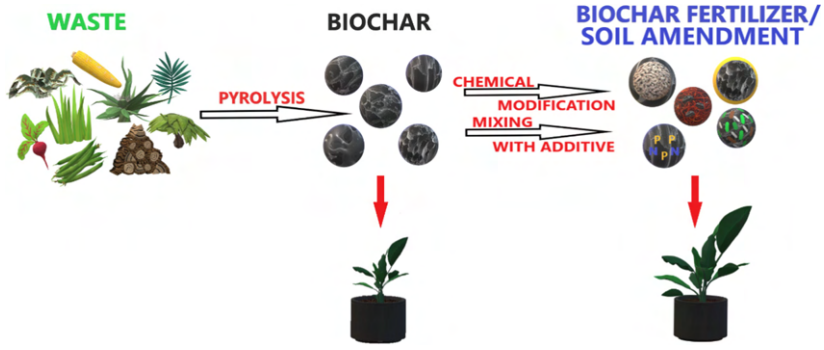
HIGHLIGHTS

- The increasing demand for food forces an increase in the amount of used fertilizers.
- An overview of the types of BC-based fertilizers and BC-compost soil amendments was presented.
- BC after wastewater treatment as an effective fertilizer in line with circular economy
- Compost-BC mixture as a new path in sustainable agriculture

GRAPHICAL ABSTRACT



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ABSTRACT

Today's world is struggling with many environmental problems. Due to the ever-growing size of the population, it is necessary to produce more and more food. The consequence of such a large demand for food is excessive fertilization of soils, often in an uncontrolled manner. The paper presents an overview of the different types of biochar (BC) fertilizers obtained by: coating BCs with a protective layer, coating commercial fertilizers with a layer of BCs, or mixing BCs with commercial fertilizers. Although the use of these new types of fertilizers has a positive effect on soil properties and crop yields, the production and use of "simple" inorganic fertilizers are dominant. The solution to starting the change of this trend may be the use of BC-compost systems as an effective soil amendment, due to the fact that composts are still the most frequently used products by farmers. The review summarized two types of BC-compost soil amendments: BC mixed with ready-made compost and BC co-composted with compost raw material. These types of soil amendments contribute to a significant reduction in the consumption of commercial inorganic fertilizers, and thus less pollution of the natural environment, while allowing for a high yield of safe food.

Contents

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1. Introduction

Global population growth increases the demand for food. Together with the limited amount of arable land, this creates the need to intensify and improve the quality of the obtained crops. To cope with this challenge, natural and synthetic fertilizers are used (Czekała et al., 2019; Hazra, 2016). Soil fertilization consists in introducing appropriate mineral and/or organic substances into it in order to enrich it with nutrients for plants, which has a significant impact on their development (Igalavithana et al., 2015). The role of fertilizers is therefore to provide nutrients (mainly nitrogen (N), potassium (K), and phosphorus (P), but not only), as their properties determine the fertility of the soil (Czekała et al., 2019). In addition to nutrients, substances that improve the structure of the soil or support appropriate microbiota can be introduced into the soil along with fertilizers. These treatments improve the physical (e.g. water retention or aeration), chemical, and biological properties of arable soils, indirectly affecting their fertility (Czekała et al., 2019).

The fertilizer market is constantly developing. The amounts of produced and sold fertilizers are growing every year (Zalewski and Piwowar, 2018). Data on global fertilizer consumption indicate that in 2017, the global consumption of mineral fertilizers amounted to 185 million tonne (Zalewski and Piwowar, 2018), thus increasing 6 times compared to 1960. In developing countries (China, India, Brazil), the use of fertilizers has increased even 34 times over these years. Due to the increase in consumption, the global value of exports of mineral fertilizers has also risen. Compared to 2005, in 2016 it increased by 77%, reaching the level of USD 50 billion. According to estimates, nitrogen fertilizers account for 57% of the total amount of fertilizer used (Zalewski and Piwowar, 2018). Importantly, only 20–30% of nitrogen from nitrogen fertilizers is absorbed and used by plants (Naz and Sulaiman, 2016; Zhao et al., 2019). The rest is released to the natural environment, which causes negative ecological effects (including eutrophication of waters).

On the one hand, the use of fertilizers has many advantages and brings many economic benefits. On the other hand, these products are recognized as the main source of pollution of the water and soil environment. The most dangerous effects of using fertilizers are related to the too rapid release of nutrients into the soil (Shaviv, 2001). Plants are unable to use excess nutrients, which results in their leaching into the soil/water and subsequent loss. The excessive use of fertilizers may also lower the pH of the soil, and thus indirectly increase the mobility and bioavailability of heavy metals in them (Haygarth and Jarvis, 2002). Therefore, one of the greatest challenges of the 21st century is not only the production of environmentally safe and effective fertilizers, but also their rational use and management. One of the solutions may be the use of organic (natural) fertilizers (Czekała et al., 2019). Manure and liquid manure, i.e. waste from livestock farming, are most often used as natural fertilizers (soil amendments) (Ketema and Bauer, 2011). Other types of animal and plant waste (urine, feces, leaves, sawdust, straw, grasses), composts and vermicomposts (compost produced with earthworms), and sewage sludge (Hazra, 2016; Kłapeć and Cholewa, 2012) are also widely used as fertilizers or soil amendments. However, production of fertilizers from (mainly) organic wastes (e.g. in animal waste or sewage sludge) is not a perfect solution. It is well known that these kinds of materials may contain many different biological and chemical pollutants. Animal waste/sewage sludge may contain bacteria, fungi, viruses, invasive forms of parasites, antibiotics, pesticides, or heavy metals (Kłapeć and Cholewa, 2012). It still makes these materials very controversial and needs numerous research regarding to risk assessment. However, the idea is worth of considering in the future. The risk associated with the production of BCs from sewage sludge and other contaminated biomass (e.g. animal manure) has already been widely described in the literature (Ahmad et al., 2022; Ginebra et al., 2022; Godlewska and Oleszczuk, 2022; Xiao et al., 2022) and the current aim is to minimize this risk and completely sanitize this type of waste before use as a fertilizer. For this reason, a practice that is often promoted nowadays is mixing organic fertilizers with biochars (BCs), whose task is to improve the fertilizing properties and immobilize pollutants in conventional fertilizers (Kończak and Oleszczuk, 2018; Stefaniuk et al., 2018; Stefaniuk and Oleszczuk, 2016).

Scientists are constantly searching for new fertilizers and their forms that will ensure more effective action by slowly releasing nutrients into the soil, thus preventing the loss of minor elements and macrominerals (Lateef et al., 2019). When studying the mechanism of slow release of nutrients from fertilizers, two factors should be taken into account: matching the amount of nutrients to the needs of the plant and maintaining the availability of nutrients (Shaviv, 2001). With this direction of development of the fertilizer industry in mind, several types of fertilizers/nano-fertilizers, including slow-release ones, have been developed in recent years (Azeem et al., 2014; Diacono and Montemurro, 2010; Rahman et al., 2014; Yang et al., 2021). They are obtained on the basis of zeolites (Lateef et al., 2016) or BCs (Ding et al., 2016), often covered with a polymeric coating (Costa et al., 2013). BC-based fertilizers are particularly attractive because they can be produced from natural and waste materials, also those of agricultural origin. Additionally, BC-based fertilizers are often characterized by a slow release of nutrients, which is in opposition to the use of commercial fertilizers or composts. Thus, BC-based fertilizers fit in with the current trends of sustainable development and the creation of a circular economy (Dahal et al., 2018) as well as obtaining environmentally friendly fertilizers (Lateef et al., 2019; Xie et al., 2015) (as schematically shown in Fig. 1).

Another way of fertilization is also important, which consists in the use of mixed/co-composted BCs with composts, which play the role of soil amendments, due to the most often high dose of their addition to the soil (doses in the order of %). This type of fertilization is important because research shows (NUTRIMAN, 2021) that still the majority of farmers use compost for fertilization. It is clear that it often contain

Fig. 1. The idea of a circular economy in the context of using biochar-based fertilizers.

pollutants (such as pesticides, heavy metals, or pathogens) that contribute to the contamination of the soil environment. An innovative method is the addition of BCs, which show a synergistic effect in combination with compost/compost raw material and contribute to the creation of a safer, but still effective soil amendment.

2. Biochar-based fertilizers

Biochar is a solid, characterized by a high degree of aromaticity and often high porosity (Fig. 2), obtained by thermal decomposition of biomass under oxygen-limited conditions (Wang et al., 2017).

There are many raw materials that are used in the production of BCs, such as: wood chips (Lucchini et al., 2014), corn cobs or stalks (Lateef et al., 2019), wheat residues (Chun et al., 2004), sugar beet tailings (Yao et al., 2011), rice straw (Peng et al., 2011), manure (Hoseini et al., 2021), sewage sludge (Tomczyk et al., 2020), and biogas residues (Stefaniuk and Oleszczuk, 2016). Various types of thermochemical technology are used for the production of BCs, i.e. pyrolysis (slow and fast), gasification, hydrothermal carbonization, torrefaction, or microwave-assisted pyrolysis (Hossain et al., 2020; Xie et al., 2015). BC obtained by different conversion methods usually has different properties (Jindo et al., 2020). The composition and physicochemical properties

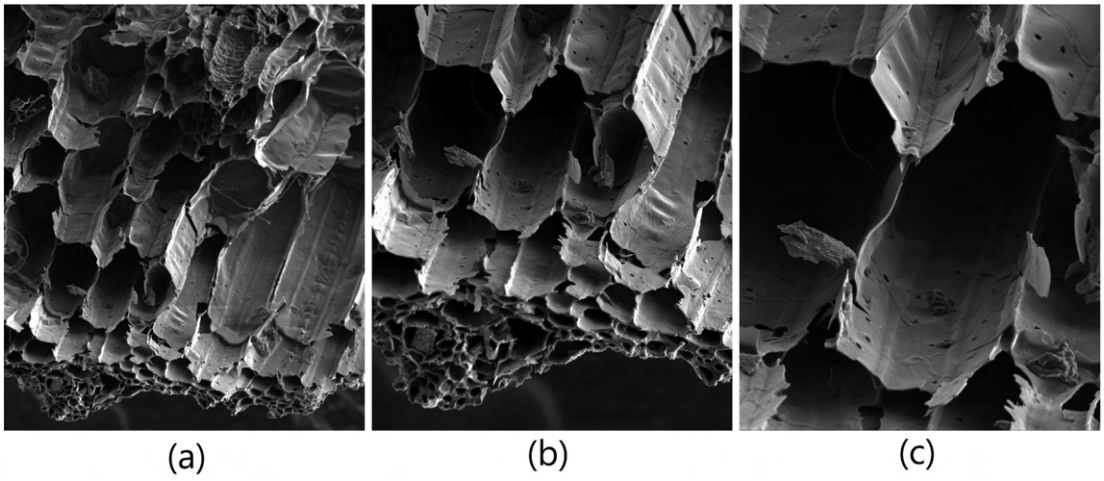

Fig. 2. Pore structure of a particle of willow-derived BC characterized by SEM imaging at (a) 500×, (b) 1000× and (c) 2000× magnification.

of BC largely depend on the type of biomass used for synthesis (Finalis et al., 2020) and on the production conditions (including temperature, heating rate, pressure, pyrolysis duration, packing density of raw material, etc.) (Guo, 2015). Numerous studies indicate that BCs produced from various types of biomass may contain humic and fulvic-like materials (Lin et al., 2012), bioavailable phosphorus, sodium, magnesium, nitrogen, and potassium (Masto et al., 2013; Mukherjee and Zimmerman, 2013). BC is often characterized by a high specific surface area (S_{BET}) and the presence of functional groups on the surface (hydroxyl, carboxyl, carbonyl, and others) (Wang et al., 2017). Due to the diversity of functional groups on the surface of BCs, it has been demonstrated that they have the ability to adsorb various nutrient ions, including nitrate, ammonium, potassium, manganese and phosphate ions (Fatima et al., 2021; Kimetu and Lehmann, 2010; Mizuta et al., 2004). However, different mechanisms (Sim et al., 2021) are responsible for the adsorption of different ions on the BCs surface. Due to the fact that the BCs surface is usually negatively charged, anion adsorption is difficult. Though, research (Ahmad et al., 2018) shows that phosphate ions PO_4^{3-} can bind with metal cations (e.g. magnesium or iron (III)) and thus adsorb "indirectly" on the BC surface. In the paper of Fatima et al. (2021) authors indicate that BC obtained at higher temperature (700 °C) demonstrate a better affinity for nitrates, while the low-temperature one (300 °C) for phosphates. Additionally, in this work has been shown that chemisorption is the main mechanism for nitrates adsorption, while pore diffusion and chemisorption are the dominant mechanisms in the case of phosphates. Thus anion adsorption on pristine BCs is complex and depends on many factors. The mechanisms of adsorption of various ions on the BC surface can be also based on cation exchange, precipitation, complexation, cation-π interaction, π-π electron donor-acceptor interactions or physical adsorption (Sim et al., 2021).

Biochars increase the availability of potassium by slowing down the process of leaching it from the soil, and increase nitrogen retention by reducing leaching and gas emissions (Hossain et al., 2020). Due to its properties, BC is increasingly used as a fertilizer for plants (Ahmad et al., 2014). The ability of BC to improve soil fertility depends on the processes of the oxidation (aging) of its surface. This is a slow process that contributes to increased cation exchange capacity (CEC) and nutrient retention (Cheng et al., 2008). Moreover, the addition of BC to soil has a positive effect on its properties and environmental functions (Woolf et al., 2010), such as reducing soil acidity, improving the respiratory metabolism of soil microorganisms, and increasing the content of organic matter (Igalavithana et al., 2015; Laird et al., 2010; Shi et al., 2020). In addition, it has been proven that the unique structure and high aromaticity of BCs can improve the water holding capacity (WHC) and promote the immobilization of heavy metals, organic acids, and pesticides in the soil, which reduces soil toxicity to various organisms (Ćwieląg-Piasecka et al., 2018; Sajjadi et al., 2019; Yousaf et al., 2016). BC introduced with fertilizer may contribute to carbon sequestration and reduction of greenhouse gas emissions (Woolf et al., 2010; Xiang, Qi et al., 2020).

2.1. Pristine and chemically modified biochars

Pristine BCs are the easiest to obtain and the least chemically complex among biochar fertilizers. Nevertheless, it has been proven that in this simplest form they can be used as fertilizers. In the literature, there are many examples of the use of pristine BCs in soil fertilization (Farooque et al., 2020; Hossain et al., 2020; Liang et al., 2021). Moreover, a number of review works in this area have been published (Ding et al., 2016; Xie et al., 2015). In this work, however, the focus was on more complex biochar systems and modified BCs. Fig. 3 proposes a classification of biochar-based fertilizers according to the type of modifications they can undergo.

Table 1 presents information on the raw material from which BC was obtained, the method/approach of its modification and the effect of the prepared fertilizer on soil and/or plants.

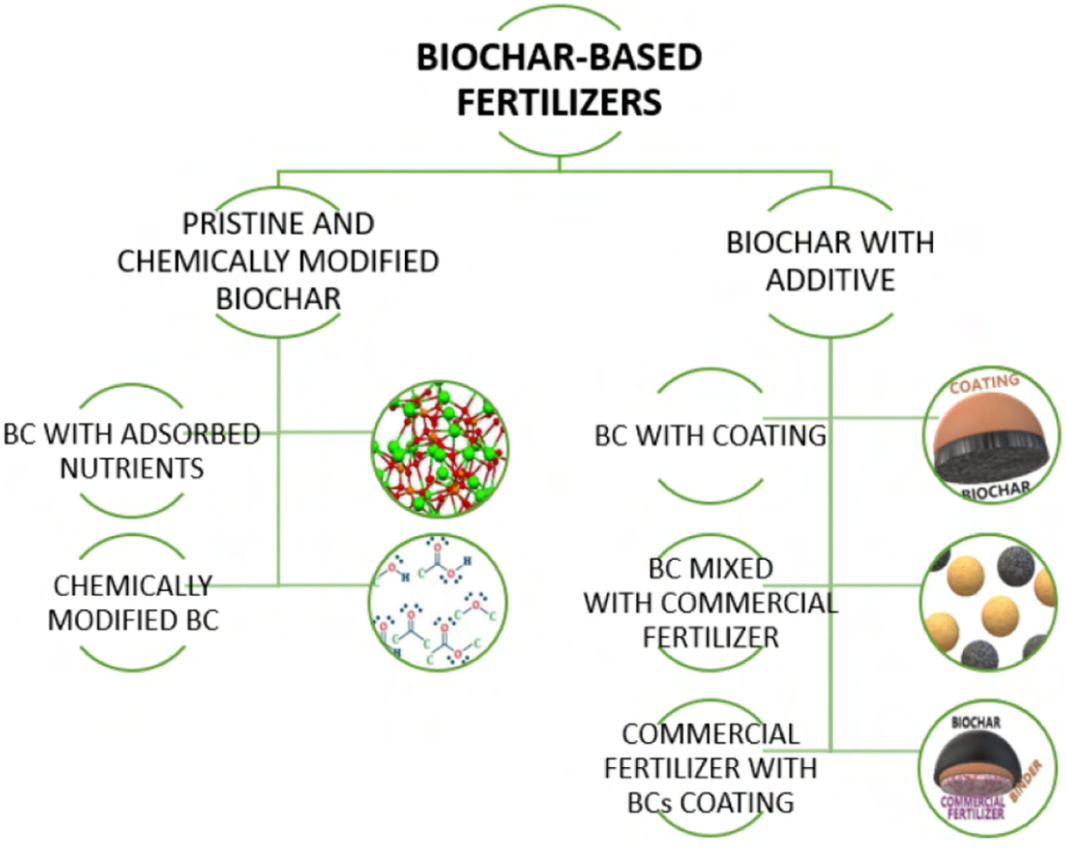

Fig. 3. Types of biochar-based fertilizers.

Table 1
Positive effects of adding BC-based fertilizers to soil.

BC feedstock	Modification/approach	Effect	Reference
Corncob	Nutrients adsorption	Slow release of nutrients, soil fertility improvement, reduce nutrient leaching and volatilization	(Lateef et al., 2019, Lateef et al., 2016)
Sugar beet tailings	Phosphate adsorption	High content of nutrients, increasing yields	(Yao et al., 2011)
Corncobs	Soaking in maize silage digestate	Doubled yield biomass, increasing bioavailable N content	(Dietrich et al., 2020)
Anaerobic digester sludge	Soaking in NH_4^+ solution and primary effluent solution	Showing similar N adsorption capacity from wastewater to laboratory-prepared solutions, ability to treat water/wastewater	(Tang et al., 2019)
Spruce sawdust	Soaking in HNO_3 and Na_2CO_3 solutions	Ammonium adsorption from wastewater, increasing germination, higher fresh biomass of plants	(Shang et al., 2018)
Sugarcane residue	Soaking in KOH and H_3PO_4 solutions; granulation with bentonite clay	Increasing K and P content, increasing yields, greater P efficiency use by plants	(Borges et al., 2020)
Cow dung	Soaking in $MgCl_2$ solution	Phosphate adsorption from wastewater, increasing soil pH, soil quality, moisture and fertility improvement, increasing organic C and bioavailable P content, plant height and weight improvement	(Chen, Qin et al., 2018)
Poultry litter, pig manure, sewage sludge	Mg^{2+} enrichment	P recovery from wastewater, soil properties improvement	(Nardis et al., 2020)
Peanut shells, sugarcane bagasse	Soaking in $MgCl_2$ or $CaCl_2$ solutions	P recovery from sewage sludge; high content of nutrients, in particular P	(Fang et al., 2020)
Wheat straw	Bio-oil coating	Better absorption and use of nutrients by plants, slower release of nutrients	(Ye et al., 2019)
Cotton straw	Coating with natural substances incl. Starch, cellulose, chitosan	P-release rate reduced up to 50%, better degradability of the fertilizer in the soil, higher growth, plant weight and root length	(An et al., 2021b)
Pine tree sawdust and switchgrass	Mixing with triple superphosphate (TSP) and bone meal	Significant improvement the slow release of nutrients into the soil	(Zhao et al., 2016)
Wheat straw	Mixing with diammonium phosphate, potassium chloride and bentonite	Increase (10%) in grain yield, N use efficiency, C, N and P content	(Zheng et al., 2017)
Poultry litter	Mixing with TSP or H_3PO_4 with or without MgO addition	Ensuring a slow release of P, higher dry mass of plant shoots, the addition of MgO increases the content of Mg and provides better efficiency of P use by plants	(Lustosa Filho et al., 2020)
Peanut shell pellets and the oil	Mixing with urea	Root and plant mass increasing, better plant nutrient binding, growth promotion	(Magrini-Bair et al., 2009)
Wood chips	Mixing and coating with TSP	Slowing down the P release into the soil (coating proved to be more effective than mixing)	(Pogorzelski et al., 2020)
Medicinal plant, willow, wood shavings	Coating urea-phosphorite flour-brown coal fertilizer	The wheat yield was 35% higher than with fertilizer without BC layer and 55% better than with commercial NPK fertilizer	(Mikos-Szymańska et al., 2019)
Rice husks	Mixing with urea or coating the urea with a BC layer	Slower N release	(Petrus et al., 2020)
Rice straw, vinasse, chicken manure, *Phyllostachys pubescens, Arundo donax,* sugarcane bagasse	Coating urea with a BC layer, using a binder (starch) and an additional protective layer	Reduction of N release and elution, better results were obtained with BC with an additional protective layer	(Jia et al., 2020)
Rice straw	BC mixed with humic acid and bentonite along with starch as a binder formed a coating to cover the compound fertilizer	Reduction of N leaching losses and rate, increase in the height of plant (rice) stems	(Dong et al., 2020)

2.1.1. Biochars with adsorbed nutrients

Despite their numerous advantages, BCs are usually too low in nutrients and have poor nutrient release capacity when added to soil (Ding et al., 2016). As a result, pristine BCs positively affect the values of poor quality soils only. The nutrient content of BCs can be increased by adsorbing ions on them. This can be done by adsorbing nutrients from a specially prepared solution (Lateef et al., 2019) or using raw material/biochar to adsorb nutrients from wastewater contaminated with these substances (Xiang, Zhang et al., 2020). In the latter case, BC has a dual use. Firstly, it can be used as an adsorbent for purifying water/wastewater from excess nutrients (such as NH_4^+, PO_4^{3-}, NO_3^-, which cause e.g. water eutrophication), while after the adsorption process, BC with adsorbed ions can be used as a natural fertilizer. The whole process, starting with obtaining BC from waste, then removing excess pollutants from water, and using BC elsewhere as a fertilizer, fits perfectly into the idea of circular economy and sustainable development.

Examples of this type of research include the works by Lateef et al. (2019, 2016), where BCs obtained from corn cobs at a temperature of 300–400 °C were used for the adsorption of nutrients. The material was introduced into a 5% aqueous solution of macrominerals (N, P, K, Ca, Mg) and minor elements (Na, Zn, Fe). Subsequently, the kinetic of nutrients release to the soil from obtained materials was investigated. The rate of nutrient release was rapid in the initial stage, and then slowed down at the second stage until a plateau was achieved. Thus, BC enriched with nutrients can be an effective slow-release fertilizer. Additionally, the tested biochar materials had a positive effect on soil fertility, reduced leaching and loss of nutrients, which can be a common phenomenon when using conventional fertilizers.

Yao et al. (2011) suggested the use of pristine BC, obtained by pyrolysis of sugar beet tailings at 600 °C, for adsorbing nutrients from water. They compared the ability of BC prepared in this way to remove phosphates from water to that of activated carbon. Specially prepared phosphate solutions (20 mg L^{-1} P) were used in the experiment. The results showed that BCs demonstrated a much better ability to remove phosphates from water (at a level of 73%) than activated carbon (which even released a small amount of P to the solution instead of removing it). This shows that BCs can be successfully used to purify water from nutrients. These data show that the P-loaded BC prepared in this way, used for soil remediation, can provide a good source of nutrients for crops and increase the yield. Unfortunately, the authors did not conduct a P-desorption experiment on BC, which could provide information on the kinetics of nutrient release from these fertilizers.

Dietrich et al. (2020) prepared pristine BC using corn cobs and pyrolyzing them at 450 °C. Then, in order to enrich BC with nutrients, it was wrapped in polypropylene fabric and immersed in maize silage digestate containing 0.53% N and 0.71% K. Pristine BC (control) and

nutrient-loaded BC were used as a soil additive at a dose of 5%, and maize (*Zea mays L.*) was used as a test plant. The addition of enriched BC to the soil more than doubled the plant biomass compared to the control. Additionally, when using nutrient-loaded BC, the amount of N bioavailable for plants in the soil was significantly increased. It should be noted that application of such a high dose of BC to the soil is not practical and recommended. So these studies are hard to compare to the results for standard doses of commercial fertilizers.

Tang et al. (2019) obtained pristine BC by pyrolysis of anaerobic digester sludge at 350–550 °C. BC was enriched with nutrients by being soaked in a synthetically prepared solution of NH_4^+ ions or a solution of real municipal wastewater (primary effluent). The concentration of NH_4^+-N in both solutions was 45 mg L^{-1}. The results showed that the highest adsorption capacity of the solutions was demonstrated by the BC obtained at 450 °C (1.4 mg g^{-1}). Similar results were obtained for raw wastewater. However, some differences were noted between the adsorption from the solution and the actual wastewater. In the case of wastewater, in the initial period (200–600 min.) there were some fluctuations (greater than in the case of adsorption from solutions) that could have been caused by the presence of other ions (e.g. PO_4^{3-} and NO_3^-) in municipal sewage. The competition for active sites on the BC surface between the PO_4^{3-}, NO_3^-, and NH_4^+ ions could have therefore been the reason for the observed fluctuations. Further research showed (Tang et al., 2019) that N-loaded BCs can be successfully used as effective fertilizers supplying plants with bioavailable N.

2.1.2. Chemically modified biochars

BCs can also be subjected to chemical modifications that change their chemical composition, which usually results in an improvement in its adsorptive and structural properties. The chemicals most frequently used in BC chemical modification are acids (mainly HNO_3, H_2SO_4, HCl, H_3PO_4), bases (mainly KOH and NaOH), and salts (e.g. $FeCl_3$, $Zn(NO_3)_2$, $MgCl_2$, NH_4Cl, $ZnCl_2$). The type of selected modification largely depends on the desired or expected effect.

Shang et al. (2018) obtained BC by pyrolysis of spruce sawdust at 400 °C. BC was then modified in a solution of 6 M HNO_3 in a ratio of 1:10 (*w*/*v*). The obtained material was then subjected to the second modification with 0.5 M Na_2CO_3 in a ratio of 1:20 (w/v) in order to neutralize the pH of the previously obtained material. The studies showed that pristine BC and acid-treated BC had little ability to adsorb NH_4^+ ions. The adsorption capacity of these BCs determined by the authors was 0.85 and 0.31 mg g^{-1}, respectively. Modifying acid-treated BC with Na_2CO_3 increased its adsorption capacity (9.93 mg g^{-1}) compared to pristine and acid-treated BC - 11 and 32 times, respectively (Shang et al., 2018). It was found that such a significant increase in NH_4^+ adsorption after Na_2CO_3 modification was related to the cationic exchange between Na^+ and NH_4^+ ions. It was concluded on the basis of the analysis of the EDS spectrum before and after the adsorption process, where a significant decrease in the amount of Na was observed, and a significant increase in N. The biochar obtained after the adsorption of NH_4^+ (NH_4^+-BC) was then used as a fertilizer in the cultivation of spinach (*Spinacia oleracea L.*). The addition of NH_4^+-BC at a dose of 6.25 g L^{-1} of soil increased seed germination rate by 20% compared to the control soil (without BC). In addition, it was found that after 15 days, the biomass of plants grown in soil with the addition of NH_4^+-BC was greater than that of spinach in soil without BC. The test results confirmed that BC modified in this way can be used as an ecological adsorbent of nitrogen compounds from water contaminated with them, and at the same time it can be a nitrogen fertilizer. It is an approach that fits in perfectly with the idea of circular economy, in which the main role is played by BC obtained from waste.

Borges et al. (2020) used sugarcane residue as a raw material for the production of BC by its fast pyrolysis at 450 °C. The material was then enriched with nutrients. Pristine BC was initially treated with a 17% KOH solution (BC:KOH ratio 1:1 *w*/w) and then neutralized with a 85% H_3PO_4 solution to a pH of 7. The final product (K- and P-enriched BC) was granulated with the addition of 1% of bentonite clay in order to increase the mechanical resistance of fertilizer granules. The enrichment process significantly increased the content of K (from 7 to 207 g kg^{-1}) and P (from 2 to 86 g kg^{-1}) in the obtained fertilizer in comparison to pristine BC. Additionally, the specific surface area of the fertilizer increased from 9.15 mg g^{-1} to 72.4 mg g^{-1}. The verification of the effectiveness of the fertilizer as part of the pot experiment showed an increase in the yield of sugar cane (*Saccharum officinarum*) by 15% and an increase in the efficiency of P use by 10% compared to the classic fertilizer (triple superphosphate, TSP).

Chen, Qin et al. (2018) investigated the possibility of obtaining a fertilizer based on BC enriched with MgO as a carrier of phosphate compounds. As a raw material for the production of BC, powdered cow dung was used, which was soaked in a solution of $MgCl_2$ with a concentration of 3.28 mg L^{-1} in a ratio of 1:5 (*w*/*v*), thus producing BC modified with magnesium oxide (BC-MgO). Phosphate ions (from a solution with a concentration of 600 mg L^{-1}) were then adsorbed on BC-MgO to obtain a magnesium-phosphate fertilizer (BC-MgO/P). The effect of an addition of 2% of the thus obtained fertilizer on the sprouting and growth of lettuce (*Lactuca L.*) was investigated. BC-MgO/P improved soil pH and moisture in comparison to the soil without fertilizer (control). In soil, after the addition of BC-MgO/P, the content of bioavailable P significantly increased from 2.62 mg kg^{-1} (for the control soil) to 27.7 mg kg^{-1}. The addition of BC-MgO/P to the soil improved plant height and biomass. The conducted research has shown that BC modified with magnesium oxide can effectively adsorb P from polluted waters and then be used as an efficient fertilizer. At the same time, by using cow dung as a raw material to obtain BC, this waste is effectively and efficiently managed.

Nardis et al. (2020) enriched BC they obtained at 500 °C from poultry litter, pig manure, or sewage sludge with Mg^{2+} cations (2.67 mol L^{-1}). Subsequently, Mg-loaded BC was used to study the adsorption of P from specially prepared solutions. Mg-P-loaded BC was used in a pot experiment to investigate the effect of this fertilizer on the growth of maize (*Z. mays L.*). The research results showed that Mg-loaded BC obtained from various waste materials can be effectively used for P recovery from water (adsorption capacity, depending on the raw material used, ranged from 34.5 to 68 mg g^{-1}). The fertilizer based on Mg-P-loaded BC, regardless of the raw material used, provided the greatest biomass of shoots and plant height. It also provided plants with the most Mg and an amount of P comparable to that provided by a commercial fertilizer (TSP). Such a strategy for obtaining fertilizers based on enriched BCs can help in the sustainable management of organic residues and can be an ecological solution to the problem of the pollution of water with excess P.

Fang et al. (2020) proposed the use of Mg- or Ca-enriched BC to recover phosphorus from wastewater. Peanut shells or sugarcane bagasse were used in the production of BC. The raw materials were first soaked in solutions of 19% $MgCl_2$ or 34% $CaCl_2$, and then pyrolyzed at a temperature ranging from 450 to 850 °C. The incinerated sewage sludge ash (ISSA) extract was used as the source of phosphate ions. To extract phosphorus from ISSA, a two-step procedure (Fang et al., 2018) was applied involving the use of 0.02 M EDTA solution and 0.2 M H_2SO_4 solution. Subsequently, the extracts were diluted 4 times, the pH was adjusted to 2 and the appropriately prepared BC was added to them. Sugarcane bagasse BC modified with $MgCl_2$ and pyrolyzed at 700 °C showed the highest affinity for P (adsorption capacity of 34.9 mg g^{-1}) among the obtained adsorbents. This biochar was characterized by the highest specific surface area (1440 m^2 g^{-1}) and the highest pore volume (1.57 cm^3 g^{-1}). Research has shown that BC enriched as described above can be successfully used as an effective and environmentally friendly P-fertilizer that provides plants with the necessary nutrients. However, the authors (Fang et al., 2020) suggested the need for detailed further research in this direction in order to confirm this hypothesis.

Nevertheless, there are cases where, despite chemically modifications, BCs have too low nutrient content and/or inappropriate nutrient

release kinetics (Varalta and Sorvari, 2020; Zhao et al., 2016). For example, BC obtained by pyrolysis of cotton straw together with Mg salt and bentonite at a temperature of 500 °C did not show optimal kinetics of nutrient release (An et al., 2021a). After 32 days, 2 g L^{-1} of phosphorus was released from the BC obtained in the above-described manner, while after subsequent modifications (covering with a protective layer), 15% less P was released within almost twice as long (60 days).

In order to obtain an effective BC-based fertilizer, the raw material type as well as the conditions of conducting pyrolysis and modification must be closely monitored and/or BCs must be combined with conventional fertilizers (Igalavithana et al., 2015). The latter method leads to the creation of BC-based fertilizers. This type of fertilizers in which BC acts as a kind of matrix is more suitable for stimulating plant growth (Si et al., 2018) than BC alone, even after modifications. The positive effect of adding BC to fertilizers is explained by a number of mechanisms that directly or indirectly regulate the release of nutrients to the soil. It can be presumed that BCs indirectly improve soil properties, enrich it with organic C, or provide a potentially better environment for root growth (Sohi et al., 2009). The direct influence of BCs consists in slowing down the kinetics of the release of nutrients contained in fertilizers, which is an important feature of an effective fertilizer and fits in with the current trends of modern and sustainable agriculture (Hagemann et al., 2017; Khan et al., 2008).

2.2. Biochars with additives

In order to enrich BCs with nutrients necessary for plants, ensure their slow release, or give them specific properties, they are combined with other ingredients (that constitute a separate phase). This can be achieved by coating BCs themselves, which are the source of nutrients, with a protective layer (An et al., 2021a; Ye et al., 2019), mixing BCs with commercial fertilizers (Lustosa Filho et al., 2020; Magrini-Bair et al., 2009; Zhao et al., 2016; Zheng et al., 2017), or by coating fertilizers with a layer of BCs (Dong et al., 2020; Jia et al., 2020; Mikos-Szymańska et al., 2019; Petrus et al., 2020; Pogorzelski et al., 2020).

2.2.1. Biochars with coating

Coating BCs can be used to regulate the kinetics of the release of nutrients from BCs and to improve the efficiency of their use by plants. This process involves physically encapsulating BC-based fertilizer granules in organic or inorganic hydrophobic materials that act as a diffusion barrier (An et al., 2021a; Chen, Yang et al., 2018). Among coating materials, various polymeric and non-polymeric materials can be found (Blouin et al., 1971; Saleh et al., 2003). The polymer coatings used are acrylic or silicone-acrylic emulsions based on water (Du et al., 2013) or cellulose acetate butyrate (CAB) (Wang et al., 2014). These types of coatings are often non-biodegradable and expensive to prepare (Zhang et al., 2019). In view of the policy of sustainable development, it is recommended to abandon the use of this type of substances (Azeem et al., 2014). In addition to polymer coatings, amines/mixtures of amines with microcrystalline wax, paraffin, or synthetic wax are also used to coat BCs, as well as combinations of mineral oils (Naz and Sulaiman, 2016).

In their research, Ye et al. (2019) used BC obtained from wheat straw by pyrolysis at 400 °C. Biochar was enriched with P and N by soaking it in KH_2PO_4 and KNO_3 solutions. Subsequently, P- and N-enriched BC was covered with a layer of bio-oil. In this way, a fertilizer with a slow release of P and N was obtained which promoted the absorption and use of nutrients by plants. The addition of a bio-oil layer influenced the kinetics of nutrient release, and the rate of their dissolution in water decreased by 15%. In turn, An et al. (2021a) proposed to cover BC obtained from cotton straw (at a temperature of 500 °C) with an additional protective layer consisting of natural substances: starch, cellulose, chitosan, or maltodextrin. The rate of release of P into soils from BC prepared in this way was 50% lower than from pristine BC. The research carried out as part of the pot experiment proved that fresh and dry weight of pepper (*Piper L.*) grown on the soil fertilized with coated BC (a dose of 15 g kg^{-1} of soil) was 35% higher than in the case of fertilization with pristine BC.

2.2.2. Biochars mixed with commercial fertilizer

Mixing commercial inorganic fertilizers (such as triple superphosphate, diammonium phosphate, bone meal, ammonium sulfate, phosphoric (V) acid, ammonium nitrate, and potassium chloride) with BCs is commonly used to enrich BCs with nutrients. The introduction of fertilizers combined with a biochar matrix into the soil allows for obtaining effective slow-release fertilizers at a low cost. Zhao et al. (2016) mixed two types of plant biomass (pine tree sawdust and switchgrass) with two commonly used phosphate fertilizers (triple superphosphate and bone meal) in a ratio of 4:1 (*w*/w). The mixed materials were subsequently pyrolyzed at 500 °C. The obtained enriched biochar fertilizer was compared with commercial fertilizers (TSP and bone meal). The release of P to the soil in the case of commercial phosphate fertilizers was fast - it was 80 mg of P from 1 g of fertilizer within 20 h. The use of the mixture of BC with fertilizer lowered this value to 20 mg from 1 g of fertilizer within 120 h.

Zheng et al. (2017) mixed chemical fertilizers (diammonium phosphate and potassium chloride) with bentonite and BC obtained during wheat straw pyrolysis at a temperature of 350 to 550 °C. The resulting biochar compound fertilizer (BCF) was then mixed using a revolving drum granulation device under a water vapor atmosphere. The results of the pot experiment showed that BCF increased the yield of maize grain (*Z. mays L.*) by more than 10% compared to the use of standard inorganic fertilizer (urea formaldehyde compound fertilizer, 15% N, 15% P, 15% K). Additionally, thanks to the use of BCF, the content of organic C, N, and bioavailable P in the soil increased (by 7%, 7%, and 57%, respectively) compared to fertilization with a commercial fertilizer.

Lustosa Filho et al. (2020) mixed poultry litter with fertilizers (TSP or phosphoric (V) acid) and magnesium oxide. The biomass prepared in this way was subjected to pyrolysis at the temperature of 500 °C in order to obtain BC-based fertilizers. Fertilizer efficiency was tested in a pot experiment during three Marandu grass cultivation cycles. The results showed that the application of TSP in the first cultivation cycle resulted in a P uptake greater by 29% compared to other fertilizers applied. In the subsequent cycles of the experiment with TSP, however, there was a decrease in P uptake compared to BC-based fertilizers. All TSP-based biochars increased the dry weight of grass shoots, which, according to the authors, was associated with a slow release of P. The slow release translated into a gradual absorption of P, which was not observed in the case of fertilization with a traditional fertilizer. In the case of a traditional fertilizer, P release was fast and not conducive to long-term supplementation. The addition of MgO was aimed at reducing the acidity of the material caused by H_3PO_4 and at increasing the content of Mg in the product. It has been demonstrated (Lustosa Filho et al., 2020) that it additionally contributed to increasing the efficiency of P absorption by plants.

Magrini-Bair et al. (2009) tested a biochar-based urea fertilizer obtained from peanut shell pellets by fast pyrolysis at 400 °C with the addition of oil and urea solution. The addition of the fertilizer increased plant biomass in relation to non-fertilized soil to a comparable degree as a commercial NPK fertilizer (Miracle-Gro). It was found that in the soil fertilized with a 5% dose of modified BC-based fertilizer, the height and width of corn stalk was greater by respectively 32% and 46% than in the non-fertilized soil. Thus, biochar obtained from biomass with the addition of urea helped to bind nutrients, provide them to the plant when it needed them, and promote growth. However, it should be noted that application of such a high dose of BC-based fertilizer (5%) to the soil is not practical. Therefore, these studies should not be compared to the results for standard doses of commercial fertilizers.

2.2.3. Commercial fertilizers with BC coating

In addition to mixing BCs with chemical fertilizers, a more complex method of coating chemical fertilizers with a layer of BCs (Petrus et al., 2020) is also used. This approach is aimed at a slower, and therefore

more controlled, release of nutrients into the soil. BCs are a better choice as coating materials than polymeric and non-polymeric substances mentioned in Section 2.2.1., because BCs are much cheaper to prepare and biodegradable (Azeem et al., 2014; Zhang et al., 2014). Additionally, depending on the raw material used for their production, various organic waste can be managed in this way. To improve the efficiency of obtaining this type of fertilizers, natural binders are also used, such as clay, starch, modified starch, lignin, modified lignin, or bentonite (Shi et al., 2020). These compounds or their appropriately prepared solutions are applied directly to the surface of fertilizers, and subsequently, a layer of BC is applied. The aim is to bind BC to the fertilizer surface more permanently. A further modification of this method is the use of subsequent layers/coatings that protect the fertilizer outside (including various types of resins or paraffin) in order to improve its mechanical strength, but also to slow down the release of nutrients (Jia et al., 2020). Unfortunately, the literature lacks information on the thickness of the covering layer, which may be important in modeling or determining the release of nutrients from the fertilizer core.

Pogorzelski et al. (2020) pyrolyzed wood chips at 350 °C, and then applied both the method of mixing them with a fertilizer (TSP) and coating the fertilizer with BC to obtain a BC-based fertilizer (Fig. 4a). The percentage of BC in the fertilizer was 5%, 15%, and 25%. As part of the pot experiment, the effect of the obtained fertilizers on the growth of millet (*Pennisetum glaucum L.*) and maize (*Zea mays L.*) was determined. Increasing the amount of BC in the fertilizer decreased the P release rate. For example, for the coated fertilizer with an addition of 5% of BC, 49% of P was released after 1.5 h, while for the 15% of BC, the release of P was at the level of 30%. The release of P was lower for fertilizers made by coating BC than for those produced by mixing TSP with BC. After 1.5 h, 79–85% of P was released from mixed systems, while 30–49% of P was released from coated systems. Thus, coating fertilizers with biochar prevents rapid P release and its losses. The frequent consequence of P release into the environment is saturation and sorption of P into the solid phase of the soil and the inaccessibility of the element for plants (Benício et al., 2017) even when fertilization is applied.

Mikos-Szymańska et al. (2019) used BC to coat the urea-based fertilizer they prepared. The fertilizer was prepared by mixing phosphorite flour with brown coal, and then the authors used a solution of urea, sulfuric acid, and water as a binder in the fertilizer granulation process. To cover fertilizer granules, three types of BC (from a medicinal plant, willow, or wood shavings) were used; BC constituted 10% of the total weight of the granules. Unfortunately, the authors did not provide the exact conditions of obtaining BC. The model of the obtained fertilizer granule is shown in Fig. 4b. The effect of the obtained fertilizers on spring wheat cv. Varius was tested in a pot experiment. Soil fertilized with the urea fertilizer without BC coating and soil with a commercial NPK fertilizer were used as controls. All doses of fertilizers were determined to contain 2.4 g of N, 1.3 g of P, and 2 g of K. The highest grain yield (4.56 g per plant) was obtained using the urea fertilizer coated with BC from wood chips. It was 35% higher than when using the fertilizer without coating (3.39 g) and 55% higher than when using the commercial NPK fertilizer (2.94 g).

Petrus et al. (2020) compared the efficacy of two BC-based fertilizers obtained from rice husks at 300 °C by slow pyrolysis. The first one (granule model) was obtained by mixing BC (20%, 40%, and 50%) with clay (20%) and urea fertilizer (containing 96% urea) in various proportions (60%, 40%, and 30%, respectively). The second fertilizer (coated model) was prepared by covering the core consisting of a mixture of urea, sludge, and clay (70:20:10, w/w/w) with a layer of BC mixed with clay in various ratios (20%, 50%, and 60% of BC). The granules prepared in this way had a weight of 1 g, and their model is shown in Fig. 4c. The slowest and, at the same time, the most favorable N release from granular fertilizers was observed for the BC:urea:clay ratio equal to 40:40:20. In this case, after 3 days, the amount of N released was 70%, while for the classic urea fertilizer it was 90%. For coated fertilizers, a lower BC:clay ratio (i.e. 20:80) was more favorable for slow N release. For this fertilizer, 45% of N was released over 3 days. This is due to the high hydrophobicity of BC, which increases the brittleness of the coating and, consequently, causes faster nitrogen release to the soil in case of higher biochar:clay ratio.

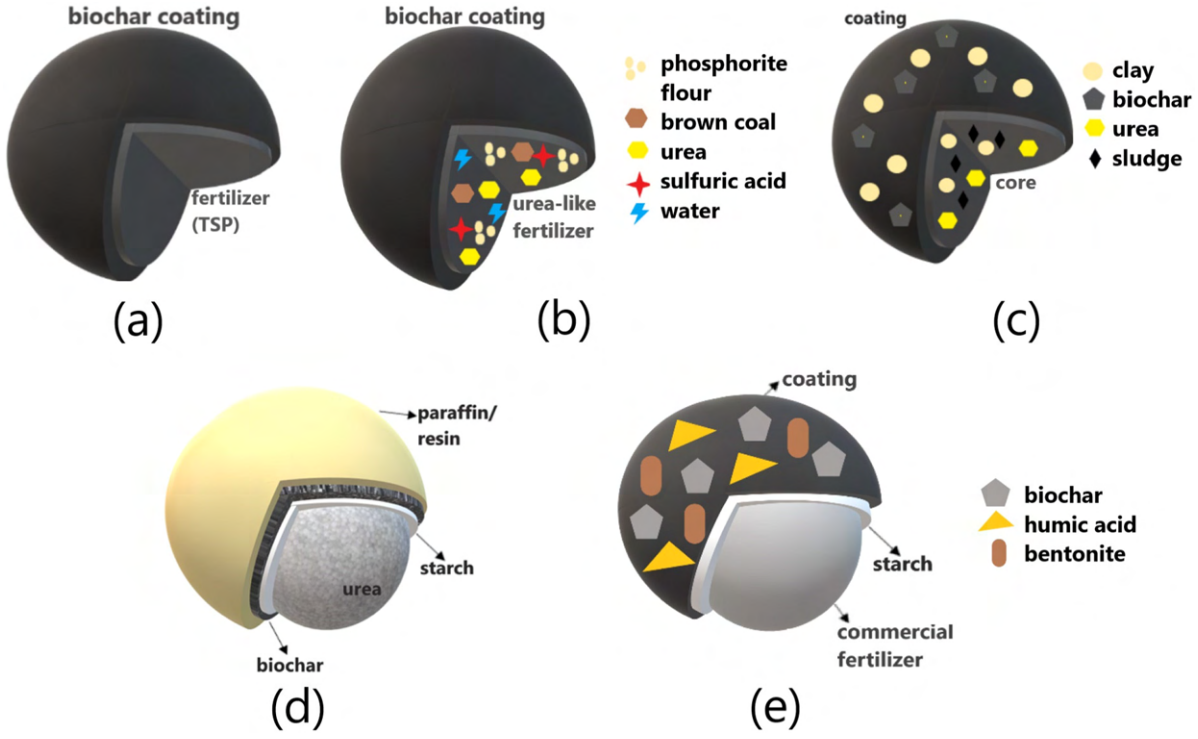

Fig. 4. Models of fertilizer granules prepared by the coating method (based on literature (Dong et al., 2020; Jia et al., 2020; Mikos-Szymańska et al., 2019; Petrus et al., 2020; Pogorzelski et al., 2020)).

Jia et al. (2020) used different types of raw materials (rice straw, vinasse, chicken manure, *Phyllostachys pubescens*, *Arundo donax*, and sugarcane bagasse) to obtain BC and coat urea fertilizer with it. The pyrolysis temperature ranged from 400 to 700 °C. Starch was used as a binder. The research also tested resin and a mixture of resin with paraffin as factors contributing to the reduction of N leaching (Fig. 4d). It has been demonstrated that the slowdown in release is greatest for BCs obtained at higher temperatures (600–700 °C) due to their high specific surface area ($S_{BET} > 130\ m^2\ g^{-1}$). The application of BC coating with an additional protective layer reduced volatilization and leaching of N from the fertilizer by 27% to 42% on the first day compared to the BC-only system.

Dong et al. (2020) used BC obtained from rice straw by slow pyrolysis at a temperature of 400 to 500 °C. Subsequently, BC was mixed with humic acid (obtained from coal) and bentonite in various proportions. During the mixing process, a solution of one of three types of starch (potato, cassava, or corn) was additionally sprayed. The obtained mixture was then used to coat the granules of compound fertilizer containing 15% of N, 15% of K_2O and 15% of P_2O_5 (Fig. 4e). After thorough and even coating with a layer of modified BC, the slow-release fertilizer granules had a diameter of 3 to 5 mm. Preliminary studies showed that coating a fertilizer consisting of 25% of BC, 4% of bentonite, and 10% of humic acid with potato starch as a binder was the most effective solution. This composition of the fertilizer ensured the slowest and at the same time optimal N release from the fertilizer granules: after the first day, 12.8% of N was released, and after 28 days—20.1%. The fertilizer obtained in this way was compared with a commercial fertilizer in a pot experiment using rice (*Oryza sativa* L. cv. Xiuyou No. 5) as a test plant. The dose of the commercial fertilizer was 100 kg ha^{-1}, while the dose of the BC-coated fertilizer was 164 kg ha^{-1} (doses were selected so that the N content in both fertilizers was the same). The use of BC-coated fertilizer reduced the leaching losses of NH_4^+-N by 50% (within 24 days) compared to the use of the commercial fertilizer. The use of the BC-coated fertilizer increased the SPAD (soil-plant analysis development) index at the stages that are most important during rice growth. An increase in stem height of rice plants was also observed, which may have been caused by slower, and therefore more appropriate, nutrient supplementation with the BC-coated fertilizer compared to the commercial fertilizer. The use of both fertilizers (BC-based and commercial) did not ultimately affect the yield of rice grains, as, according to the authors, it requires a better adjustment of the dose of fertilizers.

2.3. Slow-release properties of BC-based fertilizers

Although the results of many studies have shown that BC-based fertilizers exhibit excellent slow-release properties of nutrients, an explanation of the mechanism responsible for this phenomenon is rarely discussed. The authors (Dong et al., 2020; Jia et al., 2020; Lateef et al., 2019; Petrus et al., 2020) often refer to the effect of BC and the impact of its unique properties on the final product (BC-based fertilizer), omitting usually a scientific explanation of this phenomenon. Some attempts have been made to clarify the role (mechanism) of BC in controlled (slow) release of nutrients (Jia et al., 2021; Luo et al., 2021; Vendra Singh et al., 2020) and several types of mathematical models (widely used for kinetic modeling of drug release) have been adopted: Hixson-Crowell model, Baker-Lansdale model or Korsmeyer-Peppas model (Dias et al., 2017; Sim et al., 2021).

Jia et al. (2021) used the fertilizer obtained by coating of urea with BC and observed that leaching of nitrates was much slower compared to unmodified fertilizer. According to author's explanations, the BC binds the nitrogen by adsorption due to its extensive porous structure and the presence of functional groups on the surface. These physiochemical interactions of BC-N and the physical barrier of porous structure hinder/delay release of N into the soil. Wu et al. (2021) explained that the slow release of nutrients from the BC-based fertilizer was also related to the porous structure of BC, and more precisely to the internal forces that stabilized the functional groups containing N and O (mainly phenolic), which delayed the desorption of N from fertilizer to the soil. Mechanism of slow N release from the urea-BC fertilizer was also investigated by Wang et al. (2021). Authors distinguished three steps, which are responsible for N release from this type of fertilizer. The first step involves the release of labile forms of N from urea dispersed on the BC surface. In the second step the N bonded through intermolecular forces and hydrogen bonds with BC are released from the fertilizer. In the last step, N bound by strong chemical bonds is released. According to many studies (An et al., 2021a, 2021b; Sim et al., 2021; Vendra Singh et al., 2020), the mechanism of nutrient release from BC-based fertilizers is mainly based on the diffusion of nutrient molecules on the basis of a concentration gradient and the dissolution of nutrient molecules into the soil.

Advanced research on the mechanisms, and thus far-reaching conclusions, have been proposed by Luo et al. (2021). Authors observed that the slow-P-release from Mg-enriched biochar fertilizer corresponded to the low solubility of Mg—P precipitates that were formed on the BC surface. The effect was enhanced by the occurrence of phosphate ions reprecipitation. However, the mechanism of the slow release of N was regulated by the electrostatic attraction of ammonium ions by the negatively charged BC surface and the confinement effect. Moreover, N compounds could take part in hydrogen bonding with functional groups present on the BC surface, what may delayed N desorption. The slow-release fertilizers based on BCs constitute a new approach in soil fertilization thus issue exploring the mechanisms of their action should be thoroughly investigated in the near future, especially in the context of environmental relevant conditions.

3. Biochar-compost based soil amendments

Composts have been used for many years as natural soil amendments to improve the yield of crops (Jiang et al., 2021). Most often they are used in much higher doses than conventional fertilizers or BC-based fertilizers (doses in the order of %). Composts are an excellent source of nutrients necessary for plants, such as N, K, P, Ca, Mg, or Na, and additionally they stimulate the activity of microorganisms and soil enzymes responsible for the immobilization of nutrients (Bedada et al., 2014). Moreover, composts are cheap and usually readily available. Their disadvantage is the too rapid release of nutrients to the soil, which results in a reduction in their fertilizing efficiency (Godlewska et al., 2017) and risk of environmental pollution, which has been indicated many times in this study. Additionally, composts often contain hazardous organic and inorganic compounds (Smith, 2009) that can contaminate the soil and/or water environment after the compost is applied to the soil. BCs, as previously shown (Ding et al., 2016), tend to be nutrient deficient or contain insufficient amounts of nutrients. However, they have the ability to immobilize pollutants, slow down/regulate the release of nutrients, improve soil properties (pH, WHC, CEC) or carbon sequestration (Kimetu and Lehmann, 2010; Woolf et al., 2010; Yousaf et al., 2016). Thus, the combination of BC and compost seems to be an interesting solution that meets the "win-win" principle, and in the case of binding pollutants, it is also a "multi-win" strategy.

3.1. Biochar-compost mixing

Taking into account the facts described in the introduction to Section 3, applying a mixture of BC and compost together to the soil is a much better solution than applying BC and compost separately. Both components of the mixture show a synergistic effect, mutually improving each other's properties, as well as positively influencing plant growth and the quality of crops (Wang et al., 2019). In order to achieve a synergistic effect, BCs can be either combined (mixed) with ready-made compost, i.e. added after the composting process (Abideen et al., 2020; Azeem et al., 2020; Goldan et al., 2019; Hannet et al., 2021; Radin et al., 2018; Rasool et al., 2021; Zahra et al., 2021)

or co-composted with compost raw material (Awasthi et al., 2017; Bashir et al., 2020; Bello et al., 2021; Luo et al., 2017; Oldfield et al., 2018; Pandit et al., 2020; Wei et al., 2021). Table 2 represents the results that were obtained using the BC-compost system as the soil amendment.

Abideen et al. (2020) mixed BC obtained from wood chips by slow pyrolysis at 750 °C with compost (8.5 g kg^{-1} P, 11 g kg^{-1} K, 7.4 g kg^{-1} Mg) in order to evaluate the effect of this mixture on reed growth parameters (*Phragmites karka*). The mixture was added to the soil at a dose of 1.5%. Simultaneously, control was carried out with an addition of 1.5% of BC alone and without the addition of BC. The results of the research showed that the use of a mixture of BC and compost resulted in the greatest increase in dry and fresh plant biomass among the tested variants. Compared to the use of BC alone, the mixture with compost also gave better results in terms of improving the parameters of the plant.

Goldan et al. (2019) mixed BC produced from sewage sludge (at 500 °C) with compost (0–100% BC) obtained from cattle manure (composted for 2 years). The mixture of BC and compost was applied to the soil at a dose of 0.17% and 1% (5 and 30 t ha^{-1}, respectively) as part of a pot experiment with barley (*Hordeum L.*). The effect of the obtained soil amendment on selected soil parameters, such as organic matter and soil composition, was investigated. In relation to the soil fertilized with BC alone (0% of compost), the use of BC-compost mixtures increased the above-mentioned parameters. The higher dose (30 t ha^{-1}) of the BC-compost amendment was more effective in terms of improving soil properties compared to the dose of 5 t ha^{-1} and BC alone without the addition of compost.

Radin et al. (2018) investigated the effect of BC, compost, and a mixture of BC with compost (30% v/v) on the growth of oil palm seedlings. Compost and BC were obtained from oil palm waste. Biochar was obtained at the temperature from 300 to 350 °C. The application of the mixture of BC with compost to the soil increased the concentration of bioavailable P, the content of K^+, Mg^{2+}, Ca^{2+} ions, and CEC of the soil compared to the soil without fertilizer and to the soil with BC alone. It was found that BC applied to soil alone usually only slightly improved the above-mentioned parameters. In turn, the use of compost (without BC) significantly increased the desired soil parameters, but not as well as when it was used together with BC. For example, after 212 days of cultivation, the amount of bioavailable P in the soil after using 1% of BC was 349 mg kg^{-1}, while in the control soil it was 309 mg kg^{-1}. The use of compost at a dose of 30% increased the content of bioavailable P by 280%, while the use of a mixture of compost and BC (30:1, w/w) by as much as 311% compared to the control soil. Additionally, the use of the mixture of compost with BC increased the soil pH to the value that is optimal for the growth of most plants (from 4.4 to 6.6). Thus, studies have shown that using mixtures of compost with BC is a more effective way to improve soil properties and provide optimal growth conditions for plants than compost and BC used separately.

The effect of compost (commercially available, ZameenDost) and its mixtures with BC (3% and 6%) on the growth of tomatoes (*Solanum lycopersicum L.*) and the development of the fungus *(Alternaria solani*) causing the early blight tomato disease was studied by Rasool et al. (2021) as part of a pot experiment. The tests used BC obtained at a temperature of 500 °C from green waste or from beech wood chips. The mixture of compost and BC obtained from green waste, depending on the proportion of BC, decreased the percent disease index by 57% to 73% compared to the soil without fertilizer. A significant reduction in the incidence of the disease was also noted compared to plants grown on the soil fertilized by compost alone (by 47% to 66%). The introduction of plant growth promoting rhizobacteria (*Bacillus subtilis*) into the system contributed to a further reduction of the percent disease index. The addition of the mixture of BC and compost to the soil also promoted tomato growth. In the soil treated with a mixture of compost and 6% of BC from green waste, the plant height was 30% greater than in the control and 18% greater than in the soil with compost only. The plant supply of N, P, and K was also the highest in this variant of the experiment.

The goal of Zahra et al. (2021) was to determine the effect of a mixture of BC and compost on the soil nutrient profile and the yield of maize (*Z. mays L.*). Cow manure was used as a raw material for the production of BC and compost. The pyrolysis temperature was 480 °C. Soil without fertilizer was used as a control, while BC, compost, and their mixture at a dose of 5 t ha^{-1} were used as additives to soil. The greatest increase in the content of N (0.96%), P (12.53 mg kg^{-1}), and K (208.33 mg kg^{-1})

Table 2
Positive effects of adding BC-compost amendments to soil.

BC feedstock	Modification/approach	Effect	Reference
Wood chips	Mixing with compost	Faster shoot and root growth and a greater leaf surface	(Abideen et al., 2020)
Sewage sludge	Mixing with compost prepared from cattle manure	Higher organic matter and organic C content in the soil	(Goldan et al., 2019)
Oil palm empty fruit bunch	Mixing with compost prepared from oil palm waste	Increase the bioavailable P content, K^+, Mg^{2+}, Ca^{2+} content, enhancing CEC and soil pH	(Radin et al., 2018)
Green waste or beech wood chips	Mixing with commercially available compost	Decreased the % disease (blight tomato) index, promoting tomato growth, greater plant height; the highest N, P, K supply for plant	(Rasool et al., 2021)
Cow manure	Mixing with compost prepared from cow manure	The highest N, P, K supply, increased EC value, the most significant increase in maize height, grain biomass, yield; increased harvest index	(Zahra et al., 2021)
Yellow pine sawdust	Mixing with compost prepared from tree leaves and branches	The highest N and P supply for plant, increased the enzymatic activity, mixture of BC and compost is a better idea than using BC alone when the soil requires remediation	(Azeem et al., 2020)
Hardwood	Mixing with compost prepared from pulp of galip nut	Compost used alone increased content of N and P in the soil, using BC alone resulted in the highest P content in the soil; studies have shown that a mixture of BC and compost is not always the best solution	(Hannet et al., 2021)
Garden peat	Co-composting with manure	Increasing plant height, spike length, dry biomasses of shoot, husks, grains, and roots	(Bashir et al., 2020)
Cotton straw	Co-composting with sewage sludge and wheat straw	Increasing nutrients content, improving the activity of soil microorganisms, facilitating the composting process, shortening the compost maturation time	(Awasthi et al., 2017)
Forest shrub	Co-composting with green waste and cattle manure	Increasing the yield mass, soil CEC; K^+, Mg^{2+}, Ca^{2+}, bioavailable N and P content	(Pandit et al., 2020)
Peanut shells	Co-composting with plant biomass	Increasing the yield mass (even by over 300%), root length and area, organic matter content and CEC	(Luo et al., 2017)
Purchased from company, no information about feedstock	Co-composting with cow manure and corn stalks	Reducing the amount of CO_2 and NH_3 emissions while composting, high amount of NH_4^+-N in the finished product, affecting the transformation of the organic P fractions by microorganisms	(Wei et al., 2021)
Oak residue	Co-composting and mixing with plant biomass and sheep manure	Higher yields, lower environmental impact compared to commercial fertilizer using	(Oldfield et al., 2018)
Rice straw	Co-composting and mixing with cattle manure and corn straw	Both amendments increased the soil fungal diversity index and complexity of the fungi correlation network; BC mixed with compost provide the highest content of N and K	(Bello et al., 2021)

was observed after adding a mixture of BC and compost to the soil (0.4–5 times more than in the control soil). The use of this additive increased the EC value by 11% compared to the control. Among all variants, the increase in plant height, grain biomass, and maize yield was most significant in the case of the addition of the mixture of BC and compost to the soil: by 43%, 15%, and 46%, respectively, compared to the control. The harvest index also increased, reaching the value of 49% compared to 44% recorded for the control. Research has therefore shown that BC and compost can exhibit a synergistic effect, and when used together, they increase crop productivity and improve soil properties.

Azeem et al. (2020) investigated the effect of adding BC, compost, and their mixture to the soil on the activity and biodiversity of soil microorganisms during the growth of tall fescue (*Festuca arundinacea*). BC was obtained from yellow pine sawdust at 350 °C. Compost was obtained from tree leaves and branches. As part of the experiment, two doses of BC (12.5 and 25 t ha^{-1}), compost (a layer of 5 cm on the top layer of soil), and a mixture of BC with compost (12.5 t ha^{-1} BC and 5 cm of compost) were used. Soil without fertilizer was used as a control. The addition of the mixture of BC and compost to the soil provided plants with the highest amount of N and P (respectively, 16% and 13% more than compost used alone and 32% and 51% more than the control). The results showed that the addition of BC alone did not significantly affect the enzymatic activity of the microorganisms, while both the compost and the mixture of BC with compost increased the enzymatic activity. When compost was added to the soil, the activity of urease, dehydrogenase, and β-glucosidase increased by 3%, 77%, and 25%, respectively, and for the mixture of BC and compost - by 6%, 54%, and 54%, respectively. Based on the obtained research results, the authors suggested that in the case of soils requiring remediation (showing low microbial activity or high incidence of plant diseases), compost with BC is the preferred solution. When the soil microflora is functioning properly, BC used alone is a better solution, as it has good effects on soil pH and carbon sequestration (long-term goals). This is a very important conclusion in view of the use of BC-based fertilizers or soil amendments. Research results yet again confirm the necessity to take into account many factors that have an indirect influence on the positive effect when using BC in a mixture with compost.

The effect of a mixture of compost and BC on soil nutrient content was investigated by Hannet et al. (2021). They used BC obtained from hardwood by pyrolysis at 400 °C. The compost was obtained from the pulp of galip nut (*Canarium indicum*) during a 3-month composting process. The field experiment involved using such amendments as: BC alone (5 t ha^{-1}), compost alone (10 t ha^{-1}, 25 t ha^{-1}, 5 t ha^{-1}), and a mixture of BC with compost (5 and 10 t ha^{-1}, respectively). Soil without fertilizer was used as a control. The results demonstrated that the most effective solution was to use the highest dose (35 t ha^{-1}) of compost. It increased to the greatest extent, compared to all other variants, the content of N (by 40% compared to the control) and the available P (almost 2 times more than the control) in the soil. Moreover, the study proved that the addition of BC alone compared to the mixture of BC and compost resulted in a higher P content in the soil. The authors proposed that this could be due to the fact that BC added to the compost could have gained additional specific surface area, on which a greater amount of P, unavailable to plants, was adsorbed, compared to pristine BC. Thus, studies have shown that a mixture of BC and compost is not always a better solution. When planning soil amendments, a number of different factors should be taken into account, such as soil needs, composition of BC/compost and others. It is therefore necessary to constantly conduct new research in this aspect.

3.2. Biochar-organic waste co-composting—COMBI

Another approach to the production of BC-based soil amendments is co-composting. The process involves adding BC to compost raw material (e.g. sewage sludge, manure, agricultural residues) before composting. This allows for obtaining a compost-biochar product with new and specific properties, called COMBI (co-composted biochar). Research shows (Antonangelo et al., 2021) that the use of COMBI has many advantages over BCs and composts used alone. It is presumed that it is also a more advantageous solution than the use of BC-compost mixtures obtained from ready-made ingredients (Antonangelo et al., 2021). The better efficiency of COMBI may be due to the fact that during co-composting, the properties of BCs are modified and composting is improved (Godlewska et al., 2017). Ultimately, this leads to an improvement in the performance of both substrates, i.e. BC and composted raw material, and their synergy in the finished COMBI (Antonangelo et al., 2021).

In the case of BCs, co-composting causes changes in the surface functional groups consisting in increasing the number of negatively charged groups, i.e. acid and oxygenated groups (e.g. carboxyl, lactone, or phenolic) (Hua et al., 2009; Khan et al., 2016). This type of change on the BC surface promotes the immobilization of nutrients and prevents their loss during composting (Kammann et al., 2015). Co-composting also increases the CEC value of biochar materials, which leads to better immobilization of nutrients by BCs (Antonangelo et al., 2021). During co-composting, BCs are also enriched with easily available sources of N and C, and thus the fertilization properties are improved (Antonangelo et al., 2021). Moreover, studies (Wang et al., 2019) show that co-composting with BC facilitates the natural oxidation (aging) of BCs, which contributes to more effective soil fertilization due to the retention of nutrients. It also prevents the leaching of nutrients to other elements of the environment. Composting increases both abiotic oxidation (thanks to high temperatures) and biotic oxidation (thanks to microbial activity) (Sanchez-Monedero et al., 2018).

While the composting process has a positive effect on the properties of BC, BC also has a positive effect on the properties of COMBI. The addition of BC improves the efficiency of the composting process (Godlewska et al., 2017), increases the activity and diversity of microorganisms thanks to better aeration of compost (Antonangelo et al., 2021), as well as contributes to the reduction of greenhouse gas emissions during the process (Antonangelo et al., 2021; Guo et al., 2020). The addition of BC before composting causes the temperature during the process to be higher than in a system without BC (Wei et al., 2014), which results in a higher level of disinfection and the possibility of using raw materials that may pose a biological risk, e.g. sewage sludge or animal manure. One possible mechanism for this is that BC fills the voids between the particles of compost material, which reduces heat loss (Zhang et al., 2014). Due to its high CEC and negatively charged BC surface, it contributes to an increase in the amount of nutrients (mainly K^+, Na^+, Ca^{2+}, Mg^{2+} ions) in the produced compost (Varalta and Sorvari, 2020). BC can also play a protective role for soil microorganisms during composting due to the presence of micro- and macropores in its structure (Sanchez-Monedero et al., 2018). Additionally, BC contributes to a more effective retention of nutrients in compost due to its high retention capacity. The consequence is a higher moisture content in the composter with BC compared to that without BC, which translates into reduced leakage of nutrients (Li et al., 2015). Moreover, biochar material has the ability to adsorb humic substances, thus protecting them against decomposition during composting and increasing the degree of humification (Akdeniz, 2019; Jindo et al., 2016). The benefits of co-composting BC with organic material are presented in Fig. 5.

Bashir et al. (2020) investigated the effect of a soil amendment obtained by co-composting farm yard manure and BC on the growth of wheat. BC was obtained from garden peat at 450 °C (Qayyum et al., 2017). Subsequently, BC was mixed in various proportions with cow manure and composted for 2.5 months. The use of compost prepared in this way had a positive effect on the length of spikes, mass of shoots, roots, and husks. The values of all these parameters increased with the growing proportion of BC in the compost and were significantly higher than in the control soil (without the addition of a fertilizer). Moreover, the compost obtained on the basis of BC reduced the availability of Cd for plants, which was an additional advantage of its use.

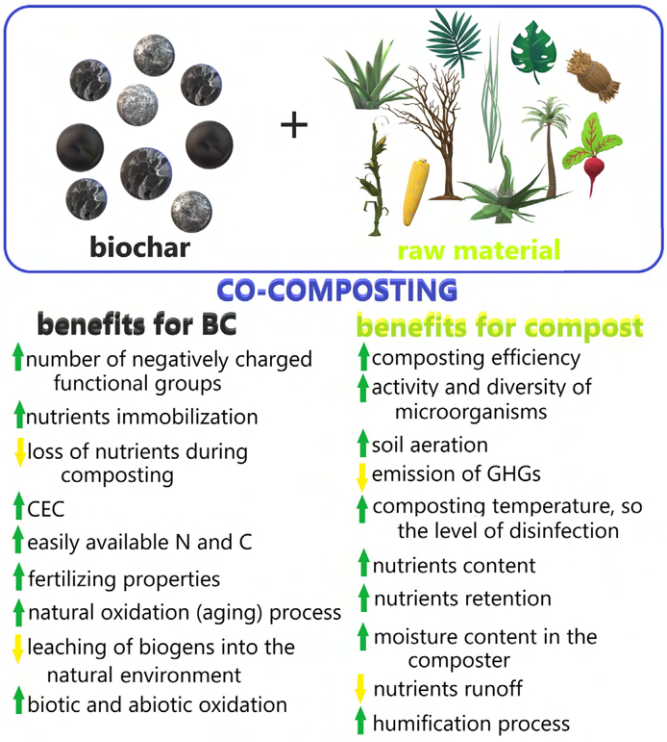

Fig. 5. Benefits of co-composting raw compost material with BC for both components.

Awasthi et al. (2017) used a mixture of sewage sludge, cotton straw, and BC obtained from cotton straw (at a temperature of 500–600 °C) as raw materials for the production of compost. BC was added to the mixture of cotton straw and sewage sludge at doses ranging from 2% to 18% of dry weight. Composting was carried out for 8 weeks. The addition of BC facilitated composting and shortened the maturity period by 3 weeks (the best results were obtained in the case of a 12% addition of BC). The results also showed that with the proportion of BC in the compost mass at the level of 12% and 18%, the nutrient content of the compost increases. Additionally, after adding compost to the soil, the activity of microorganisms was significantly improved.

Studies on the effect of compost obtained from a mixture of green waste, cattle manure, and BC (obtained from forest shrub at a temperature of 600–700 °C) on the growth of maize (*Manakamana-4 variety*) were conducted by Pandit et al. (2020). The experiment was carried out as part of a pot experiment in which compost was applied to the soil at a dose of 60 t ha^{-1}. Soil fertilized with a commercial NPK fertilizer was used as a control. The use of compost with BC resulted in a more than a two-fold increase in the crop weight compared to NPK fertilizer. In addition, an increase in the soil CEC and the content of Mg^{2+}, Ca^{2+}, and K^{+} ions in it (about two-fold) was observed, as well as of the amount of bioavailable N (from 5.1 to 8.7 mg kg^{-1}) and P (from 34.8 to 105.1 mg kg^{-1}).

Luo et al. (2017) studied the effect of BC co-composted with plant biomass (1:1 *w*/w) on soil properties and the growth of two halophytes: sesbania (*Sesbania canabina (Retz.) Pers*) and seashore mallow (*Kosteletzkya virginica*). BC was obtained from peanut shells by pyrolysis at 350 °C for 2 h. The soil amendment was applied to the soil in three doses: 1.5%, 5%, and 10% (w/w), and the soil without fertilizer was the control. An increase in the height of shoots of both plants was recorded only in the case of the lowest dose of compost (in relation to the soil without fertilizer, the parameter increased by 20%). Higher doses of compost (5% and 10%) reduced the height of sesbania shoots (by 24% and 55%, respectively), as well as seashore mallow shoots (by 10% and 50%, respectively). The application of a dose of 1.5% of BC-compost product increased the sesbania biomass 5 times; the 5% dose resulted in a 3-fold increase, and the 10% dose resulted in a reduction of biomass in relation to the soil without fertilizer (by 50%). The results suggest, therefore, that only low doses of compost co-composted with BC resulted in the promotion of plant growth, and the highest dose had a negative effect on many plant parameters. Moreover, after the application of COMBI (at a dose of 1.5%), the content of organic matter and CEC of the soil increased by 63% and 11%, respectively.

Wei et al. (2021) investigated the effect of the addition of BC (purchased from company, dose 10%) or woody peat to a mixture of cow manure and corn stalks (1:0.9 (w/w) on the composting parameters (CO_2 and NH_3 emissions, NH_4^+-N content) and the form of P. The control was compost made from cow manure and corn stalks without any additives. Composting was carried out for 28 days. It was proven that both the addition of wood peat or BC reduced the amount of CO_2 and NH_3 emissions by 10% and 54–64%, respectively, as compared to the control. Additionally, BC showed a positive effect on the amount of NH_4^+-N in the finished compost. It was also proven that both the addition of woody peat or BC had a significant effect on the forms of P and their bioavailability. The addition of BC affected the transformation of the organic P fractions by microorganisms, which contributed to the regulation of the potential availability of P to plants after the application of the amendment to the soil.

Oldfield et al. (2018) compared the effect of soil amendments obtained as a result of (1) co-composting organic waste with BC and (2) mixing BC with finished compost. Biochar was obtained from oak residue by slow pyrolysis at a temperature of 650 °C. As a raw material for the production of composts, the organic fraction of municipal biowaste was used, or a mixture of olive mill waste, olive tree prunings, and sheep manure. The use of mixtures of compost and BC (9:1 w/w; regardless of whether BC was added to compost before or after the composting process) provided plants with a greater amount of nutrients (N, P, K) and organic C than the use of BC alone.

Bello et al. (2021) investigated the effect of co-composted BC and BC mixed with compost on the physicochemical properties of soil and soil microbiome. Biochar was obtained from rice straw as a result of slow pyrolysis at a temperature ranging from 450 to 500 °C, while the compost raw material was a mixture of cattle manure and corn straw. Soil without fertilizer was used as a control, and the test plant was maize (*Zea mays L.*). The soil was fertilized/amended with BC, compost, a mixture of compost and BC, and compost co-composted with BC. The proportion of BC in the compost and in COMBI was 10%, and the soil dose was set at 180 kg N ha^{-1}. The results showed that the use of both co-composted BC and BC mixed with compost increased the soil fungal diversity index and the size and complexity of the fungi correlation network. BC mixed with compost provided plants with the highest amounts of NH_4^+-N, NO_3^--N, and bioavailable K compared to all other variants - they were 1.2 g kg^{-1}, 0.46 g kg^{-1}, and 141.1 mg kg^{-1}, respectively (0.08 g kg^{-1}, 0.2 g kg^{-1}, 101 mg kg^{-1} for control). The soil amendments obtained both by mixing and co-composting also provided over 50% more bioavailable P (about 48 g kg^{-1}) compared to the control (22.1 g kg^{-1}). Thus, the results proved that using both co-composted BC and BC mixed with compost is an alternative method of fertilization, but co-composting is not always required to achieve the intended purpose.

The use of co-composting of organic waste with BCs has created a new type of attractive soil amendment that combines and/or improves the properties of not only compost but also BC. Research shows that the production of functional materials based on BC by using the co-composting process is a good way of soil remediation, while the BC dosage used is important (Luo et al., 2017). As can be seen, various studies also indicate different dependencies of fertilization efficiency on the dose of compost. This is an issue that requires further research and systematization of information.

COMBIs have many advantages in the context of their use as a soil amendment (Fig. 6). They can be used for the remediation of soils contaminated with heavy metals (Mounissamy et al., 2021) as well as for

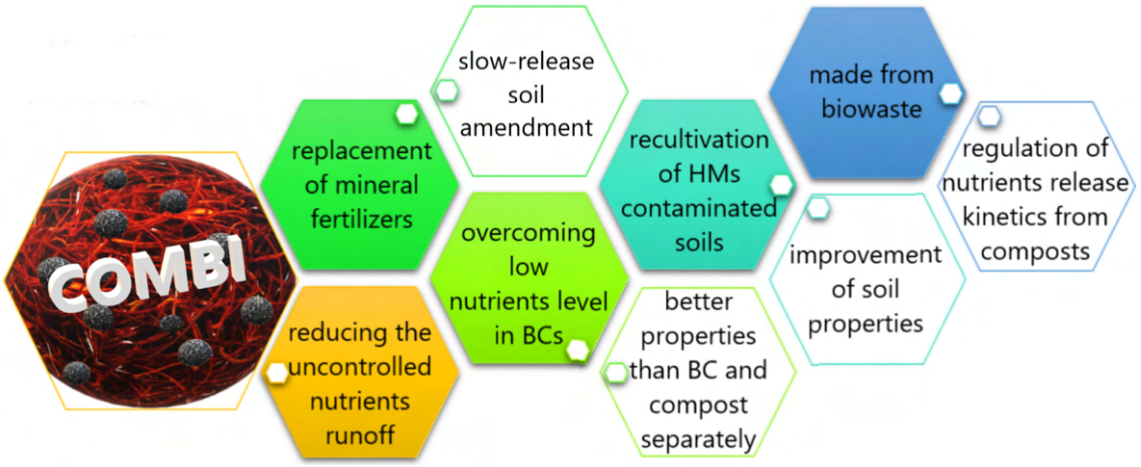

Fig. 6. Advantages of COMBI as a soil amendment.

the improvement of soil properties and fertilization (Luo et al., 2017). Materials of this type are a promising solution that not only overcomes the problem of low nutrient content in BC, but also regulates the kinetics of their release from the compost (Luo et al., 2017). COMBI additionally contributes to reducing the uncontrolled leakage of nutrients into the soil and water environment (Iqbal et al., 2015). Therefore, co-composting with BC seems to be an effective and environmentally friendly method of obtaining soil amendments that provide plants with favorable conditions for growth, often better than in the case of compost or BCs used alone (Wang et al., 2019). In addition, BC and compost raw material are produced from waste, which is in line with the ideas of sustainable development and circular economy, and is economically beneficial. Due to the supply of comparable (or greater) amounts of nutrients by mixtures of BC with compost, this type of natural product may replace mineral fertilizers in the future (Oldfield et al., 2018). COMBI can also be characterized by slow release of nutrients, which makes them particularly environmentally friendly (Haider et al., 2016). These advantages fit in with the requirements set for modern fertilizers by European regulations. In 2019, a new regulation (1009/2019) (Official Journal of the European Union, 2019) was published, which replaces the previous one (2003/2003) from 2003. The EU regulation extends the scope of application and production of fertilizers to new raw materials: bio-based materials and recovered waste materials. The regulation is planned to enter into force in mid-2022, and its primary goal is to open the market for biological fertilizers (NUTRIMAN, 2019). The new regulations will help the policy of sustainable agricultural development thanks to the possibility of replacing inorganic fertilizers with natural ones (e.g. made from waste) characterized by a slow release of nutrients. Moreover, thanks to this legislative revision, the fertilizer market will be thoroughly checked in order to meet safety and quality requirements, which will contribute to the rationalization of the use of fertilizers/soil amendments. It can also reduce the leaching of nutrients into the environment thanks to better legal protection of the approved fertilizers.

Although it has been shown that composting various materials with the addition of BC usually brings greater benefits than mixing finished compost with BC, this does not exclude the attractiveness of the latter. It is not always possible to compost BC with another raw material, e.g. for logistical or economic reasons. In such a situation, an interesting solution is still simply mixing the two components before applying them to the soil. Research shows that soil amendments obtained both by mixing and by co-composting can be effective in fertilizing the soil and improving the quality and efficiency of crops (Oldfield et al., 2018; Varalta and Sorvari, 2020). Which solution is better depends on many factors (composition, duration of the process, dose, type of crops, etc.) and should be selected on a case-by-case basis to suit individual needs. There are research works which have shown that the application of co-composting of organic raw material with BC can lead to the production of a final product (soil amendment) with improved fertilizing properties than in the case of simple mixing (Wang et al., 2019; Zhang and Sun, 2014). However, there are also research results that prove very similar properties of compost mixed with BC and co-composted with BC (Oldfield et al., 2018). The least numerous studies indicate that the use of BC as an additive to compost reduces the value of the obtained compost (Hannet et al., 2021). This is an issue that most certainly requires further research. A separate issue is the fact that the mode of action of COMBI may be the effect of several mechanisms that are still not fully understood (Varalta and Sorvari, 2020) and require additional research.

4. Future outlook and summary

The interest in using BCs for soil fertilization/amendment has been growing for several years. This is shown, for example, by the number of articles published on this topic in recent years (Fig. 7).

The use of BC-based fertilizers or soil amendments is an effective solution, not only a “win-win”, but even a “multi-win” solution, in line with the idea of circular economy and sustainable development. Such solutions include not only the improvement of soil properties (Maikol

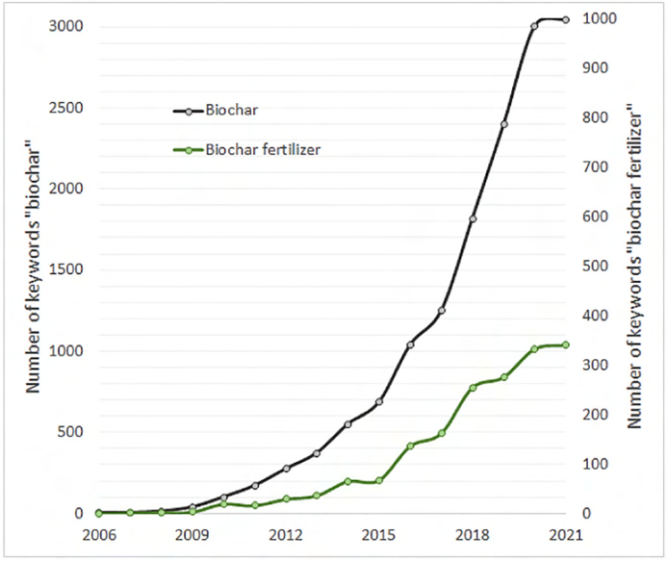

Fig. 7. Number of publications according to SCOPUS with keywords “biochar” and “biochar fertilizer” from 2006 to October 2021.

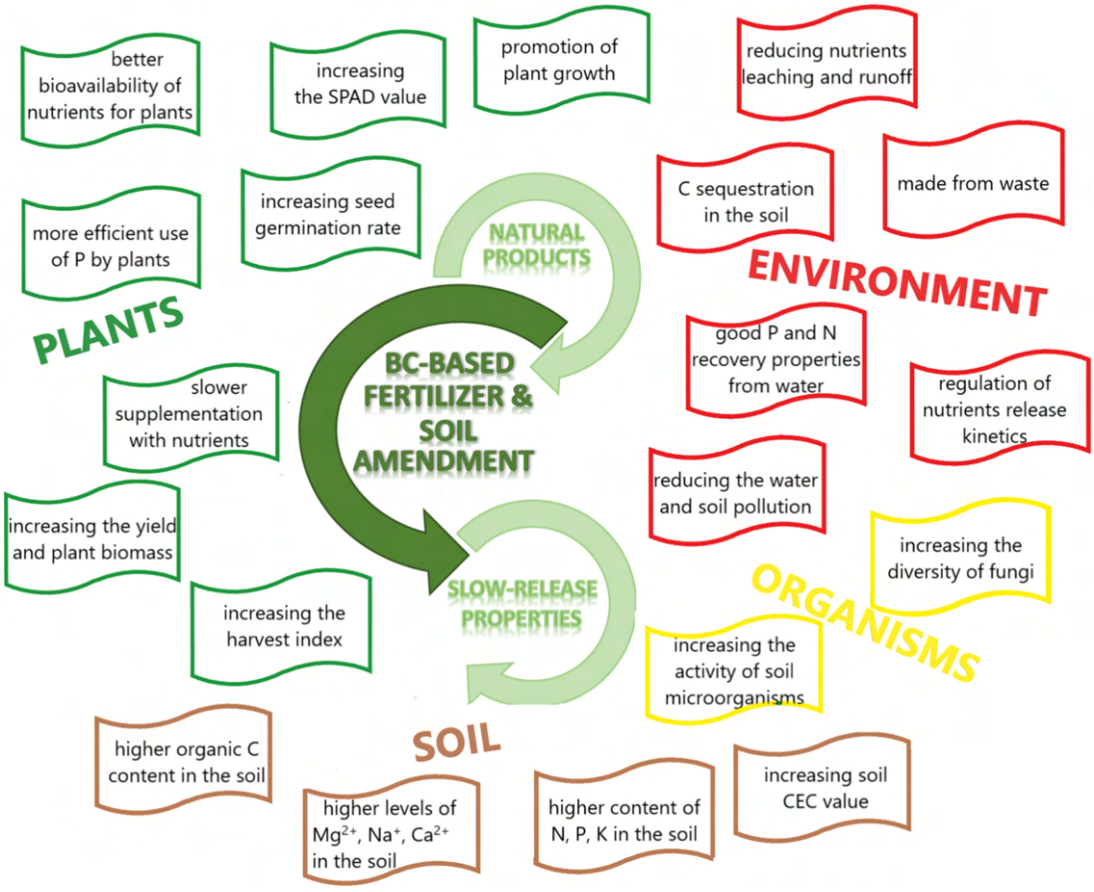

Fig. 8. Environmental benefits of the comprehensive use of BC-based fertilizers and soil amendments.

et al., 2021) and an increase in crop yields, but are also friendly to the climate (Woolf et al., 2010) and the natural environment (Fig. 8).

BC has undoubtedly become an important tool for environmental applications that helps with waste management (Czekała et al., 2019). The literature additionally indicates many methods and techniques of modifying BCs in order to obtain the desired properties (Li et al., 2016; Lu et al., 2018; Sahin et al., 2017). BC as a material for soil remediation has a long history, but now, thanks to the use of the innovative strategies of pyrolysis and modifications, it has opened a new chapter in soil fertilization. It is a material with great potential that should be exploited. However, it should be noted that the commercial use of BC as a fertilizer/soil amendment raises many doubts due to the prejudice that BC is just waste. Therefore, all aspects of using BC and its modifications as an effective fertilizer or soil amendment should be explored. The use of modified BCs for fertilization is a particularly interesting and new issue that requires a lot of research. Below we present points that, in our opinion, remain unresolved in spite of the fact that research on biochar in the context of fertilization has been conducted for years:

- in order to disseminate the idea of using BC-based fertilizers and/or soil amendments in the world, an easier approach to production should be presented, perhaps databases on the types of raw materials and their impact on the properties of the obtained BCs should be created; in addition, such information should be referred to the type/species of plants whose growth is affected by the fertilizer,
- searching for new, better methods of BC modification in order to obtain the simplest, safest, and cheapest procedure that will allow for maximizing the fertilizing properties of these materials,
- it is very important to recognize the mechanisms responsible for the fertilization properties of BCs in order to effectively modify the BC in desired direction and apply BC in patricular ecological tasks,
- conducting long-term pot experiments as well as field experiments in a real environment, which is key to investigating (1) the long-term effect of BCs on the physicochemical properties of the soil and (2) changes in the structure and properties of BCs themselves that take place during their long-term presence in the environment,
- a thorough analysis of the risks associated with the production of BCs from sewage sludge and contaminated biomass (including animal manure) and other controversial types of waste in order to eliminate the potential toxic effects of using this type of fertilizers on the environment,
- the possibility of using and optimizing the process of purifying wastewater and water of important nutrients using BCs and the use of such enriched fertilizers for soil remediation which implements the idea of a circular economy in practice,
- carrying out the extensive research about the BC-based fertilizers/amendments that will comprise the applicable/"real" doses of BC to the soil, taking into account at least two control samples: not only pristine soil but also the soil with an appropriate equivalent of commercial fertilizer nutrients, which unfortunately is not always tested,
- optimization of the effective dose of BC added to composts in the composting process is also an important issue that has not yet been clearly established,
- learning about the mechanism of action of BCs during mixing and co-composting with compost/compost raw material, and indicating which solutions are more favorable for given soils and conditions with a view to creating an effective natural soil amendment.

CRediT authorship contribution statement

Aleksandra Rombel: Writing - original draft, Revision, **Patrycja Krasucka**: Review and editing, Writing - original draft, Revision, **Patryk Oleszczuk**: Conceptualization, Review and editing, Supervision.

Declaration of competing interest

The authors declare no competing interests.

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References

Abideen, Z., Koyro, H.W., Huchzermeyer, B., Gul, B., Khan, M.A., 2020. Impact of a biochar or a biochar-compost mixture on water relation, nutrient uptake and photosynthesis of Phragmites karka. Pedosphere 30, 466–477. https://doi.org/10.1016/S1002-0160(17)60362-X.

Ahmad, A., Chowdhary, P., Khan, N., Chaurasia, D., Varjani, S., Pandey, A., Chaturvedi, P., 2022. Effect of sewage sludge biochar on the soil nutrient, microbial abundance, and plant biomass: a sustainable approach towards mitigation of solid waste. Chemosphere 287, 132112. https://doi.org/10.1016/J.CHEMOSPHERE.2021.132112.

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere https://doi.org/10.1016/j.chemosphere.2013.10.071.

Ahmad, Munir, Usman, A.R.A., Al-Faraj, A.S., Ahmad, Mahtab, Sallam, A., Al-Wabel, M.I., 2018. Phosphorus-loaded biochar changes soil heavy metals availability and uptake potential of maize (Zea mays L.) plants. Chemosphere 194, 327–339. https://doi.org/10.1016/J.CHEMOSPHERE.2017.11.156.

Akdeniz, N., 2019. A systematic review of biochar use in animal waste composting. Waste Manag. https://doi.org/10.1016/j.wasman.2019.03.054.

An, X., Wu, Z., Qin, H., Liu, X., He, Y., Xu, X., Li, T., Yu, B., 2021a. Integrated co-pyrolysis and coating for the synthesis of a new coated biochar-based fertilizer with enhanced slow-release performance. J. Clean. Prod. 283, 124642.

An, X., Wu, Z., Shi, W., Qi, H., Zhang, L., Xu, X., Yu, B., 2021b. Biochar for simultaneously enhancing the slow-release performance of fertilizers and minimizing the pollution of pesticides. J. Hazard. Mater. 407, 124865. https://doi.org/10.1016/J.JHAZMAT.2020.124865.

Antonangelo, J.A., Sun, X., Zhang, H., 2021. The roles of co-composted biochar (COMBI) in improving soil quality, crop productivity, and toxic metal amelioration. J. Environ. Manag. https://doi.org/10.1016/j.jenvman.2020.111443.

Awasthi, M.K., Wang, Q., Chen, H., Wang, M., Ren, X., Zhao, J., Li, J., Guo, D., Li, D., Sheng, Awasthi, S.K., Sun, X., Zhang, Z., 2017. Evaluation of biochar amended biosolids co-composting to improve the nutrient transformation and its correlation as a function for the production of nutrient-rich compost. Bioresour. Technol. 237, 156–166. https://doi.org/10.1016/j.biortech.2017.01.044.

Azeem, B., Kushaari, K., Man, Z.B., Basit, A., Thanh, T.H., 2014. Review on materials & methods to produce controlled release coated urea fertilizer. J. Control. Release https://doi.org/10.1016/j.jconrel.2014.02.020.

Azeem, M., Hale, L., Montgomery, J., Crowley, D., McGiffen, M.E., 2020. Biochar and compost effects on soil microbial communities and nitrogen induced respiration in turfgrass soils. PLoS One 15, e0242209. https://doi.org/10.1371/journal.pone.0242209.

Bashir, A., Rizwan, M., Zia ur Rehman, M., Zubair, M., Riaz, M., Qayyum, M.F., Alharby, H.F., Bamagoos, A.A., Ali, S., 2020. Application of co-composted farm manure and biochar increased the wheat growth and decreased cadmium accumulation in plants under different water regimes. Chemosphere 246. https://doi.org/10.1016/j.chemosphere.2019.125809.

Bedada, W., Karltun, E., Lemenih, M., Tolera, M., 2014. Long-term addition of compost and NP fertilizer increases crop yield and improves soil quality in experiments on smallholder farms. Agric. Ecosyst. Environ. 195, 193–201. https://doi.org/10.1016/j.agee.2014.06.017.

Bello, A., Wang, B., Zhao, Y., Yang, W., Ogundeji, A., Deng, L., Egbeagu, U.U., Yu, S., Zhao, L., Li, D., Xu, X., 2021. Composted biochar affects structural dynamics, function and co-occurrence network patterns of fungi community. Sci. Total Environ. 775, 145672. https://doi.org/10.1016/j.scitotenv.2021.145672.

Benício, L.P.F., Constantino, V.R.L., Pinto, F.G., Vergütz, L., Tronto, J., Da Costa, L.M., 2017. Layered double hydroxides: new Technology in Phosphate Fertilizers Based on nanostructured materials. ACS Sustain. Chem. Eng. 5, 399–409. https://doi.org/10.1021/acssuschemeng.6b01784.

Blouin, G.M., Rindt, D.W., Moore, O.E., 1971. Sulfur-coated fertilizers for controlled release: pilot plant production. J. Agric. Food Chem. 19, 801–808. https://doi.org/10.1021/jf60177a039.

Borges, B.M.M.N., Strauss, M., Camelo, P.A., Sohi, S.P., Franco, H.C.J., 2020. Re-use of sugarcane residue as a novel biochar fertiliser - increased phosphorus use efficiency and plant yield. J. Clean. Prod. 262. https://doi.org/10.1016/j.jclepro.2020.121406.

Chen, Q., Qin, J., Sun, P., Cheng, Z., Shen, G., 2018. Cow dung-derived engineered biochar for reclaiming phosphate from aqueous solution and its validation as slow-release fertilizer in soil-crop system. J. Clean. Prod. 172, 2009–2018. https://doi.org/10.1016/j.jclepro.2017.11.224.

Chen, S., Yang, M., Ba, C., Yu, S., Jiang, Y., Zou, H., Zhang, Y., 2018. Preparation and characterization of slow-release fertilizer encapsulated by biochar-based waterborne copolymers. Sci. Total Environ. 615, 431–437. https://doi.org/10.1016/j.scitotenv.2017.09.209.

Cheng, C.H., Lehmann, J., Engelhard, M.H., 2008. Natural oxidation of black carbon in soils: changes in molecular form and surface charge along a climosequence. Geochim. Cosmochim. Acta 72, 1598–1610. https://doi.org/10.1016/j.gca.2008.01.010.

Chun, Y., Sheng, G., Chiou, G.T., Xing, B., 2004. Compositions and sorptive properties of crop residue-derived chars. Environ. Sci. Technol. 38, 4649–4655. https://doi.org/10.1021/es035034w.

Costa, M.M.E., Cabral-Albuquerque, E.C.M., Alves, T.L.M., Pinto, J.C., Fialho, R.L., 2013. Use of polyhydroxybutyrate and ethyl cellulose for coating of urea granules. J. Agric. Food Chem. 61, 9984–9991. https://doi.org/10.1021/jf401185y.

Ćwieląg-Piasecka, I., Medyńska-Juraszek, A., Jerzykiewicz, M., Dębicka, M., Bekier, J., Jamroz, E., Kawałko, D., 2018. Humic acid and biochar as specific sorbents of pesticides. J. Soils Sediments 18, 2692–2702. https://doi.org/10.1007/s11368-018-1976-5.

Czekała, W., Jezowska, A., Chełkowski, D., 2019. The use of biochar for the production of organic fertilizers. J. Ecol. Eng. 20, 1–8. https://doi.org/10.12911/22998993/93869.

Dahal, R.K., Acharya, B., Farooque, A., 2018. Biochar: a sustainable solution for solid waste management in agro-processing industries. Biofuels 1–9. https://doi.org/10.1080/17597269.2018.1468978.

Diacono, M., Montemurro, F., 2010. Long-term effects of organic amendments on soil fertility. A review. Agron. Sustain. Dev. https://doi.org/10.1051/agro/2009040.

Dias, D.S., Crespi, M.S., Torquato, L.D.M., Kobelnik, M., Ribeiro, C.A., 2017. Torrefied banana tree fiber pellets having embedded urea for agricultural use. J. Therm. Anal. Calorim. 1311 (131), 705–712. https://doi.org/10.1007/S10973-016-6049-7.

Dietrich, C.C., Rahaman, M.A., Robles-Aguilar, A.A., Latif, S., Intani, K., Müller, J., Jablonowski, N.D., 2020. Nutrient loaded biochar doubled biomass production in juvenile maize plants (Zea mays L.). Agronomy 10, 567. https://doi.org/10.3390/agronomy10040567.

Ding, Y., Liu, Y., Liu, S., Li, Z., Tan, X., Huang, X., Zeng, G., Zhou, L., Zheng, B., 2016. Biochar to improve soil fertility. A review. Agron. Sustain. Dev. https://doi.org/10.1007/s13593-016-0372-z.

Dong, D., Wang, C., Van Zwieten, L., Wang, H., Jiang, P., Zhou, M., Wu, W., 2020. An effective biochar-based slow-release fertilizer for reducing nitrogen loss in paddy fields. J. Soils Sediments 20, 3027–3040. https://doi.org/10.1007/s11368-019-02401-8.

Du, C., Shen, Y., Zhou, J., 2013. Application of aqueous silicone–acrylate emulsions in coated controlled release fertilizer. J. Control. Release 172, e18–e19. https://doi.org/10.1016/j.jconrel.2013.08.045.

Fang, L., Li, J.Shan, Donatello, S., Cheeseman, C.R., Poon, C.S., Tsang, D.C.W., 2020. Use of Mg/Ca modified biochars to take up phosphorus from acid-extract of incinerated sewage sludge ash (ISSA) for fertilizer application. J. Clean. Prod. 244, 118853. https://doi.org/10.1016/j.jclepro.2019.118853.

Fang, L., Li, J.Shan, Donatello, S., Cheeseman, C.R., Wang, Q., Poon, C.S., Tsang, D.C.W., 2018. Recovery of phosphorus from incinerated sewage sludge ash by combined two-step extraction and selective precipitation. Chem. Eng. J. 348, 74–83. https://doi.org/10.1016/j.cej.2018.04.201.

Farooque, A.A., Zaman, Q., Abbas, F., Hammad, H.M., Acharya, B., Esau, T., 2020. How can potatoes be smartly cultivated with biochar as a soil nutrient amendment technique in Atlantic Canada? Arab. J. Geosci. https://doi.org/10.1007/s12517-020-05986-4.

Fatima, I., Ahmad, M., Vithanage, M., Iqbal, S., 2021. Abstraction of nitrates and phosphates from water by sawdust- and rice husk-derived biochars: their potential as N- and P-loaded fertilizer for plant productivity in nutrient deficient soil. J. Anal. Appl. Pyrolysis 155. https://doi.org/10.1016/j.jaap.2021.105073.

Finalis, E.R., Sri Djangkung, S.M., Arfiana, Ilhamsyah Noor, Suratno, H., Rosyadi, E., Saputra, H., Noda, R., 2020. Development of carbon based NPK slow release fertilizer using biochar from oil palm empty fruits bunch. Indones. J. Energy 3, 19–24. https://doi.org/10.33116/ije.v3i1.45.

Ginebra, M., Muñoz, C., Calvelo-Pereira, R., Doussoulin, M., Zagal, E., 2022. Biochar impacts on soil chemical properties, greenhouse gas emissions and forage productivity: a field experiment. Sci. Total Environ. 806, 150465. https://doi.org/10.1016/J.SCITOTENV.2021.150465.

Godlewska, P., Oleszczuk, P., 2022. Effect of biomass addition before sewage sludge pyrolysis on the persistence and bioavailability of polycyclic aromatic hydrocarbons in biochar-amended soil. Chem. Eng. J. 429, 132143. https://doi.org/10.1016/J.CEJ.2021.132143.

Godlewska, P., Schmidt, H.P., Ok, Y.S., Oleszczuk, P., 2017. Biochar for composting improvement and contaminants reduction. A review. Bioresour. Technol. https://doi.org/10.1016/j.biortech.2017.07.095.

Goldan, E., Nedeff, V., Sandu, I., Barsan, N., Mosnegutu, E., Panainte, M., 2019. The use of biochar and compost mixtures as potential organic fertilizers. Rev. Chim. 70, 2192–2197. https://doi.org/10.37358/rc.19.6.7303.

Guo, M., 2015. Application of biochar for soil physical improvement. Agricultural & Environmental Applications of Biochar: Advances and Barriers. John Wiley & Sons Ltd, pp. 101–122 https://doi.org/10.2136/sssaspecpub63.2014.0039.5.

Guo, X., Liu, H., Zhang, J., 2020. The role of biochar in organic waste composting and soil improvement: a review. Waste Manag. 102, 884–899. https://doi.org/10.1016/j.wasman.2019.12.003.

Hagemann, N., Kammann, C.I., Schmidt, H.P., Kappler, A., Behrens, S., 2017. Nitrate capture and slow release in biochar amended compost and soil. PLoS One 12. https://doi.org/10.1371/journal.pone.0171214.

Haider, G., Steffens, D., Müller, C., Kammann, C.I., 2016. Standard extraction methods may underestimate nitrate stocks captured by field-aged biochar. J. Environ. Qual. 45, 1196–1204. https://doi.org/10.2134/jeq2015.10.0529.

Hannet, G., Singh, K., Fidelis, C., Farrar, M.B., Muqaddas, B., Bai, S.H., 2021. Effects of biochar, compost, and biochar-compost on soil total nitrogen and available phosphorus concentrations in a corn field in Papua New Guinea. Environ. Sci. Pollut. Res. 1–9. https://doi.org/10.1007/s11356-021-12477-w.

Haygarth, P.M., Jarvis, S.C., 2002. Agriculture, Hydrology and Water Quality.

Hazra, G., 2016. Different types of eco-friendly fertilizers: an overview. Sustain. Environ. 1, 54. https://doi.org/10.22158/se.v1n1p54.

Hoseini, R.Z., Goltapeh, E.M., Modarres-Sanavy, S.A.M., Heidarzadeh, A., 2021. Effect of the bio-fertilizers on the steviol glycosides (SGs) content and biomass in Stevia

rebaudiana (Bert.) Bertoni at vegetative and flowering stages. Sci. Hortic. (Amsterdam) 275, 109658. https://doi.org/10.1016/j.scienta.2020.109658.
Hossain, M.Z., Bahar, M.M., Sarkar, B., Donne, S.W., Ok, Y.S., Palansooriya, K.N., Kirkham, M.B., Chowdhury, S., Bolan, N., 2020. Biochar and its importance on nutrient dynamics in soil and plant. Biochar 2, 379–420. https://doi.org/10.1007/s42773-020-00065-z.
Hua, L., Wu, W., Liu, Y., McBride, M.B., Chen, Y., 2009. Reduction of nitrogen loss and Cu and Zn mobility during sludge composting with bamboo charcoal amendment. Environ. Sci. Pollut. Res. 16, 1–9. https://doi.org/10.1007/s11356-008-0041-0.
Igalavithana, A.D., Ok, Y.S., Usman, A.R.A., Al-Wabel, M.I., Oleszczuk, P., Lee, S.S., 2015. The effects of biochar amendment on soil fertility. Agricultural & Environmental Applications of Biochar: Advances and Barriers, pp. 123–144 https://doi.org/10.2136/sssaspecpub63.2014.0040.
Iqbal, H., Garcia-Perez, M., Flury, M., 2015. Effect of biochar on leaching of organic carbon, nitrogen, and phosphorus from compost in bioretention systems. Sci. Total Environ. 521–522, 37–45. https://doi.org/10.1016/j.scitotenv.2015.03.060.
Jia, Y., Hu, Z., Ba, Y., Qi, W., 2021. Application of biochar-coated urea controlled loss of fertilizer nitrogen and increased nitrogen use efficiency. Chem. Biol. Technol. Agric. 81 (8), 1–11. https://doi.org/10.1186/S40538-020-00205-4.
Jia, Y., Hu, Z., Mu, J., Zhang, W., Xie, Z., Wang, G., 2020. Preparation of biochar as a coating material for biochar-coated urea. Sci. Total Environ. 731, 139063. https://doi.org/10.1016/j.scitotenv.2020.139063.
Jiang, Z., Zheng, H., Xing, B., 2021. Environmental life cycle assessment of wheat production using chemical fertilizer, manure compost, and biochar-amended manure compost strategies. Sci. Total Environ. 760. https://doi.org/10.1016/j.scitotenv.2020.143342.
Jindo, K., Audette, Y., Higashikawa, F.S., Silva, C.A., Akashi, K., Mastrolonardo, G., Sánchez-Monedero, M.A., Mondini, C., 2020. Role of biochar in promoting circular economy in the agriculture sector. Part 1: a review of the biochar roles in soil N, P and K cycles. Chem. Biol. Technol. Agric. https://doi.org/10.1186/s40538-020-00182-8.
Jindo, K., Sonoki, T., Matsumoto, K., Canellas, L., Roig, A., Sanchez-Monedero, M.A., 2016. Influence of biochar addition on the humic substances of composting manures. Waste Manag. 49, 545–552. https://doi.org/10.1016/j.wasman.2016.01.007.
Kammann, C.I., Schmidt, H.P., Messerschmidt, N., Linsel, S., Steffens, D., Müller, C., Koyro, H.W., Conte, P., Stephen, J., 2015. Plant growth improvement mediated by nitrate capture in co-composted biochar. Sci. Rep. 5, 11080. https://doi.org/10.1038/srep11080.
Ketema, M., Bauer, S., 2011. Determinants of manure and fertilizer applications in eastern highlands of Ethiopia. Q. J. Int. Agric. 50, 237.
Khan, M.A., Kim, K.W., Mingzhi, W., Lim, B.K., Lee, W.H., Lee, J.Y., 2008. Nutrient-impregnated charcoal: an environmentally friendly slow-release fertilizer. Environmentalist 28, 231–235. https://doi.org/10.1007/s10669-007-9133-5.
Khan, N., Clark, I., Sánchez-Monedero, M.A., Shea, S., Meier, S., Qi, F., Kookana, R.S., Bolan, N., 2016. Physical and chemical properties of biochars co-composted with biowastes and incubated with a chicken litter compost. Chemosphere 142, 14–23. https://doi.org/10.1016/j.chemosphere.2015.05.065.
Kimetu, J.M., Lehmann, J., 2010. Stability and stabilisation of biochar and green manure in soil with different organic carbon contents. Aust. J. Soil Res., 577–585 https://doi.org/10.1071/SR10036.
Kłapeć, T., Cholewa, A., 2012. Zagrożenia dla zdrowia związane ze stosowaniem nawozów organicznych i organiczno-mineralnych, Medycyna Ogólna i Nauki o Zdrowiu.
Kończak, M., Oleszczuk, P., 2018. Application of biochar to sewage sludge reduces toxicity and improve organisms growth in sewage sludge-amended soil in long term field experiment. Sci. Total Environ. 625, 8–15. https://doi.org/10.1016/j.scitotenv.2017.12.118.
Laird, D., Fleming, P., Wang, B., Horton, R., Karlen, D., 2010. Biochar impact on nutrient leaching from a midwestern agricultural soil. Geoderma 158, 436–442. https://doi.org/10.1016/j.geoderma.2010.05.012.
Lateef, A., Nazir, R., Jamil, N., Alam, S., Shah, R., Khan, M.N., Saleem, M., 2016. Synthesis and characterization of zeolite based nano-composite: an environment friendly slow release fertilizer. Microporous Mesoporous Mater. 232, 174–183. https://doi.org/10.1016/j.micromeso.2016.06.020.
Lateef, A., Nazir, R., Jamil, N., Alam, S., Shah, R., Khan, M.N., Saleem, M., Rehman, S., ur, 2019. Synthesis and characterization of environmental friendly corncob biochar based nano-composite – a potential slow release nano-fertilizer for sustainable agriculture. Environ. Nanotechnol. Monit. Manag. 11, 100212. https://doi.org/10.1016/j.enmm.2019.100212.
Li, J.H., Lv, G.H., Bai, W.B., Liu, Q., Zhang, Y.C., Song, J.Q., 2016. Modification and use of biochar from wheat straw (Triticum aestivum L.) for nitrate and phosphate removal from water. Desalin. Water Treat. 57, 4681–4693. https://doi.org/10.1080/19443994.2014.994104.
Li, R., Wang, Q., Zhang, Z., Zhang, G., Li, Z., Wang, L., Zheng, J., 2015. Nutrient transformation during aerobic composting of pig manure with biochar prepared at different temperatures. Environ. Technol. (United Kingdom) 36, 815–826. https://doi.org/10.1080/09593330.2014.963692.
Liang, J.F., Li, Q.W., Gao, J.Q., Feng, J.G., Zhang, X.Y., Hao, Y.J., Yu, F.H., 2021. Biochar-compost addition benefits Phragmites australis growth and soil property in coastal wetlands. Sci. Total Environ. 769, 145166. https://doi.org/10.1016/j.scitotenv.2021.145166.
Lin, Y., Munroe, P., Joseph, S., Henderson, R., Ziolkowski, A., 2012. Water extractable organic carbon in untreated and chemical treated biochars. Chemosphere 87, 151–157. https://doi.org/10.1016/j.chemosphere.2011.12.007.
Lu, H.P., Li, Z.A., Gascó, G., Méndez, A., Shen, Y., Paz-Ferreiro, J., 2018. Use of magnetic biochars for the immobilization of heavy metals in a multi-contaminated soil. Sci. Total Environ. 622–623, 892–899. https://doi.org/10.1016/j.scitotenv.2017.12.056.
Lucchini, P., Quilliam, R.S., DeLuca, T.H., Vamerali, T., Jones, D.L., 2014. Increased bioavailability of metals in two contrasting agricultural soils treated with waste wood-derived biochar and ash. Environ. Sci. Pollut. Res. 21, 3230–3240. https://doi.org/10.1007/s11356-013-2272-y.
Luo, W., Qian, L., Liu, W., Zhang, X., Wang, Q., Jiang, H., Cheng, B., Ma, H., Wu, Z., 2021. A potential mg-enriched biochar fertilizer: excellent slow-release performance and release mechanism of nutrients. Sci. Total Environ. 768, 144454. https://doi.org/10.1016/J.SCITOTENV.2020.144454.
Luo, X., Liu, G., Xia, Y., Chen, L., Jiang, Z., Zheng, H., Wang, Z., 2017. Use of biochar-compost to improve properties and productivity of the degraded coastal soil in the Yellow River Delta. China. J. Soils Sediments 17, 780–789. https://doi.org/10.1007/s11368-016-1361-1.
Lustosa Filho, J.F., Carneiro, J.S.da S., Barbosa, C.F., de Lima, K.P., Leite, A.do A., Melo, L.C.A., 2020. Aging of biochar-based fertilizers in soil: Effects on phosphorus pools and availability to Urochloa brizantha grass. Sci. Total Environ. 709, 136028. https://doi.org/10.1016/j.scitotenv.2019.136028.
Magrini-Bair, K.A., Czernik, S., Pilath, H.M., Evans, R.J., Maness, C., Leventhal, J., 2009. Biomass derived, carbon sequestering, designed fertilizers. Ann. Environ. Sci. 3, 217–225.
Maikol, N., Haruna, A.O., Maru, A., Asap, A., Medin, S., 2021. Utilization of urea and chicken litter biochar to improve rice production. Sci. Rep. 11, 9955. https://doi.org/10.1038/s41598-021-89332-y.
Masto, R.E., Ansari, M.A., George, J., Selvi, V.A., Ram, L.C., 2013. Co-application of biochar and lignite fly ash on soil nutrients and biological parameters at different crop growth stages of zea mays. Ecol. Eng. 58, 314–322. https://doi.org/10.1016/j.ecoleng.2013.07.011.
Mikos-Szymańska, M., Schab, S., Rusek, P., Borowik, K., Bogusz, P., Wyzińska, M., 2019. Preliminary study of a method for obtaining brown coal and biochar based granular compound fertilizer. Waste Biomass Valoriz. 10, 3673–3685. https://doi.org/10.1007/s12649-019-00655-4.
Mizuta, K., Matsumoto, T., Hatate, Y., Nishihara, K., Nakanishi, T., 2004. Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. Bioresour. Technol. 95, 255–257. https://doi.org/10.1016/j.biortech.2004.02.015.
Mounissamy, V.C., Parihar, R.S., Dwivedi, A.K., Saha, J.K., Rajendiran, S., Lakaria, B.L., Patra, A.K., 2021. Effects of co-composting of municipal solid waste and pigeon pea biochar on heavy metal mobility in soil and translocation to leafy vegetable spinach. Bull. Environ. Contam. Toxicol. 106, 536–544. https://doi.org/10.1007/s00128-020-03096-1.
Mukherjee, A., Zimmerman, A.R., 2013. Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar-soil mixtures. Geoderma 193–194, 122–130. https://doi.org/10.1016/j.geoderma.2012.10.002.
Nardis, B.O., Da Silva, Santana, Carneiro, J., Souza, I.M.G.De, Barros, R.G.De, Azevedo Melo, L.C., 2020. Phosphorus recovery using magnesium-enriched biochar and its potential use as fertilizer. Arch. Agron. Soil Sci. 1–17. https://doi.org/10.1080/03650340.2020.1771699.
Naz, M.Y., Sulaiman, S.A., 2016. Slow release coating remedy for nitrogen loss from conventional urea: a review. J. Control. Release https://doi.org/10.1016/j.jconrel.2016.01.037.
NUTRIMAN, 2021. Final Conference Presentations [WWW Document]. https://nutriman.net/sites/default/files/2021-09/Final_conference_WP2_20210916.pdf.
Nutriman, 2019. The new fertiliser regulation – consequences for farmers [WWW Document]. https://nutriman.net/news/new-fertiliser-regulation-consequences-farmers. (Accessed 12 April 2021).
Official Journal of the European Union, 2019. Regulation (EU) 2019/1009 of the European Parliament and of the Council. Official Journal of the European Union 1–114 PE/76/2018/REV/1.
Oldfield, T.L., Sikirica, N., Mondini, C., López, G., Kuikman, P.J., Holden, N.M., 2018. Biochar, compost and biochar-compost blend as options to recover nutrients and sequester carbon. J. Environ. Manag. 218, 465–476. https://doi.org/10.1016/j.jenvman.2018.04.061.
Pandit, N.R., Schmidt, H.P., Mulder, J., Hale, S.E., Husson, O., Cornelissen, G., 2020. Nutrient effect of various composting methods with and without biochar on soil fertility and maize growth. Arch. Agron. Soil Sci. 66, 250–265. https://doi.org/10.1080/03650340.2019.1610168.
Peng, X., Ye, L.L., Wang, C.H., Zhou, H., Sun, B., 2011. Temperature- and duration-dependent rice straw-derived biochar: characteristics and its effects on soil properties of an ultisol in southern China. Soil Tillage Res. 112, 159–166. https://doi.org/10.1016/j.still.2011.01.002.
Petrus, H.T.B.M., Putera, A.D.P., Wangi, I.P., Ramadhian, M.A., Setiawan, H., Prasetya, A., 2020. Characterization of nitrogen release in modified controlled-release-fertilizer using Rice husk biochar. Int. J. Technol. 11, 774. https://doi.org/10.14716/ijtech.v11i4.3520.
Pogorzelski, D., Filho, J.F.L., Matias, P.C., Santos, W.O., Vergütz, L., Melo, L.C.A., 2020. Biochar as composite of phosphate fertilizer: characterization and agronomic effectiveness. Sci. Total Environ. 743, 140604. https://doi.org/10.1016/j.scitotenv.2020.140604.
Qayyum, M.F., Liaquat, F., Rehman, R.A., Gul, M., ul Hye, M.Z., Rizwan, M., Rehaman, M.Z. ur, 2017. Effects of co-composting of farm manure and biochar on plant growth and carbon mineralization in an alkaline soil. Environ. Sci. Pollut. Res. 24, 26060–26068. https://doi.org/10.1007/s11356-017-0227-4.
Radin, R., Abu Bakar, R., Ishak, C.F., Ahmad, S.H., Tsong, L.C., 2018. Biochar-compost mixture as amendment for improvement of polybag-growing media and oil palm seedlings at main nursery stage. Int. J. Recycl. Org. Waste Agric. 7, 11–23. https://doi.org/10.1007/s40093-017-0185-3.
Rahman, M.M., Salleh, M.A.M., Rashid, U., Ahsan, A., Hossain, M.M., Ra, C.S., 2014. Production of slow release crystal fertilizer from wastewaters through struvite crystallization - a review. Arab. J. Chem. 7, 139–155. https://doi.org/10.1016/j.arabjc.2013.10.007.
Rasool, M., Akhter, A., Soja, G., Haider, M.S., 2021. Role of biochar, compost and plant growth promoting rhizobacteria in the management of tomato early blight disease. Sci. Rep. 11, 1–16. https://doi.org/10.1038/s41598-021-85633-4.

Sahin, O., Taskin, M.B., Kaya, E.C., Atakol, O., Emir, E., Inal, A., Gunes, A., 2017. Effect of acid modification of biochar on nutrient availability and maize growth in a calcareous soil. Soil Use Manag. 33, 447–456. https://doi.org/10.1111/sum.12360.
Sajjadi, B., Broome, J.W., Chen, W.Y., Mattern, D.L., Egiebor, N.O., Hammer, N., Smith, C.L., 2019. Urea functionalization of ultrasound-treated biochar: a feasible strategy for enhancing heavy metal adsorption capacity. Ultrason. Sonochem. 51, 20–30. https://doi.org/10.1016/j.ultsonch.2018.09.015.
Saleh, K., Steinmetz, D., Hemati, M., 2003. Experimental study and modeling of fluidized bed coating and agglomeration. Powder Technology. Elsevier, pp. 116–123 https://doi.org/10.1016/S0032-5910(02)00254-1.
Sanchez-Monedero, M.A., Cayuela, M.L., Roig, A., Jindo, K., Mondini, C., Bolan, N., 2018. Role of biochar as an additive in organic waste composting. Bioresour. Technol. https://doi.org/10.1016/j.biortech.2017.09.193.
Shang, L., Xu, H., Huang, S., Zhang, Y., 2018. Adsorption of ammonium in aqueous solutions by the modified biochar and its application as an effective N-fertilizer. Water Air Soil Pollut. 229, 1–15. https://doi.org/10.1007/s11270-018-3956-1.
Shaviv, A., 2001. Advances in controlled-release fertilizers. Adv. Agron. https://doi.org/10.1016/s0065-2113(01)71011-5.
Shi, W., Ju, Y., Bian, R., Li, L., Joseph, S., Mitchell, D.R.G., Munroe, P., Taherymoosavi, S., Pan, G., 2020. Biochar bound urea boosts plant growth and reduces nitrogen leaching. Sci. Total Environ. 701, 134424. https://doi.org/10.1016/j.scitotenv.2019.134424.
Si, L., Xie, Y., Ma, Q., Wu, L., 2018. The short-term effects of Rice straw biochar, nitrogen and phosphorus fertilizer on rice yield and soil properties in a cold waterlogged paddy field. Sustainability 10, 537. https://doi.org/10.3390/su10020537.
Sim, D.H.H., Tan, I.A.W., Lim, L.L.P., Hameed, B.H., 2021. Encapsulated biochar-based sustained release fertilizer for precision agriculture: a review. J. Clean. Prod. 303, 127018. https://doi.org/10.1016/J.JCLEPRO.2021.127018.
Smith, S.R., 2009. A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge. Environ. Int. https://doi.org/10.1016/j.envint.2008.06.009.
Sohi, E., Lopez-Capel, E., Krull, E., Bol, R., 2009. Biochar, climate change and soil: a review to guide future research. CSIRO L. Water Sci Rep. (ISSN: 1834-6618) 64 pp.
Stefaniuk, M., Oleszczuk, P., 2016. Addition of biochar to sewage sludge decreases freely dissolved PAHs content and toxicity of sewage sludge-amended soil. Environ. Pollut. 218, 242–251. https://doi.org/10.1016/j.envpol.2016.06.063.
Stefaniuk, M., Tsang, D.C.W., Ok, Y.S., Oleszczuk, P., 2018. A field study of bioavailable polycyclic aromatic hydrocarbons (PAHs) in sewage sludge and biochar amended soils. J. Hazard. Mater. 349, 27–34. https://doi.org/10.1016/j.jhazmat.2018.01.045.
Tang, Y., Alam, M.S., Konhauser, K.O., Alessi, D.S., Xu, S., Tian, W.J., Liu, Y., 2019. Influence of pyrolysis temperature on production of digested sludge biochar and its application for ammonium removal from municipal wastewater. J. Clean. Prod. 209, 927–936. https://doi.org/10.1016/j.jclepro.2018.10.268.
Tomczyk, B., Siatecka, A., Gao, Y., Ok, Y.S., Bogusz, A., Oleszczuk, P., 2020. The convertion of sewage sludge to biochar as a sustainable tool of PAHs exposure reduction during agricultural utilization of sewage sludges. J. Hazard. Mater. 392, 122416. https://doi.org/10.1016/j.jhazmat.2020.122416.
Varalta, F., Sorvari, J., 2020. Biochar-compost mixtures as a promising solution to organic waste management within a circular holistic approach. Organic Waste Composting through Nexus Thinking. Springer International Publishing, pp. 213–232 https://doi.org/10.1007/978-3-030-36283-6_10.
Vendra Singh, S., Chaturvedi, S., Dhyani, V.C., Kasivelu, G., 2020. Pyrolysis temperature influences the characteristics of rice straw and husk biochar and sorption/desorption behaviour of their biourea composite. Bioresour. Technol. 314, 123674. https://doi.org/10.1016/J.BIORTECH.2020.123674.
Wang, B., Gao, B., Fang, J., 2017. Recent advances in engineered biochar productions and applications. Crit. Rev. Environ. Sci. Technol. 47, 2158–2207. https://doi.org/10.1080/10643389.2017.1418580.
Wang, M., Xiang, A., Gao, Z., Zhang, K., Ren, Y., Hu, Z., 2021. Study on the nitrogen-releasing characteristics and mechanism of biochar-based urea infiltration fertilizer. Biomass Convers. Biorefinery 2021 (1), 1–11. https://doi.org/10.1007/S13399-021-01848-5.
Wang, X., Lü, S., Gao, C., Xu, X., Wei, Y., Bai, X., Feng, C., Gao, N., Liu, M., Wu, L., 2014. Biomass-based multifunctional fertilizer system featuring controlled-release nutrient, water-retention and amelioration of soil. RSC Adv. 4, 18382–18390. https://doi.org/10.1039/c4ra00207e.
Wang, Y., Villamil, M.B., Davidson, P.C., Akdeniz, N., 2019. A quantitative understanding of the role of co-composted biochar in plant growth using meta-analysis. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2019.06.244.
Wei, L., Shutao, W., Jin, Z., Tong, X., 2014. Biochar influences the microbial community structure during tomato stalk composting with chicken manure. Bioresour. Technol. 154, 148–154. https://doi.org/10.1016/j.biortech.2013.12.022.
Wei, Y., Wang, J., Chang, R., Zhan, Y., Wei, D., Zhang, L., Chen, Q., 2021. Composting with biochar or woody peat addition reduces phosphorus bioavailability. Sci. Total Environ. 764, 142841. https://doi.org/10.1016/j.scitotenv.2020.142841.
Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J., Joseph, S., 2010. Sustainable biochar to mitigate global climate change. Nat. Commun. 1, 1–9. https://doi.org/10.1038/ncomms1053.
Wu, W., Yan, B., Sun, Y., Zhong, L., Lu, W., Chen, G., 2021. Potential of yak dung-derived hydrochar as fertilizer: mechanism and model of controlled release of nitrogen. Sci. Total Environ. 781, 146665. https://doi.org/10.1016/J.SCITOTENV.2021.146665.
Xiang, A., Qi, R., Wang, M., Zhang, K., Jiang, E., Ren, Y., Hu, Z., 2020. Study on the infiltration mechanism of molten urea and biochar for a novel fertilizer preparation. Ind. Crop. Prod. 153, 112558. https://doi.org/10.1016/j.indcrop.2020.112558.
Xiang, W., Zhang, X., Chen, J., Zou, W., He, F., Hu, X., Tsang, D.C.W., Ok, Y.S., Gao, B., 2020. Biochar technology in wastewater treatment: a critical review. Chemosphere https://doi.org/10.1016/j.chemosphere.2020.126539.
Xiao, Y., Raheem, A., Ding, L., Chen, W.H., Chen, X., Wang, F., Lin, S.L., 2022. Pretreatment, modification and applications of sewage sludge-derived biochar for resource recovery- a review. Chemosphere 287, 131969. https://doi.org/10.1016/J.CHEMOSPHERE.2021.131969.
Xie, T., Reddy, K.R., Wang, C., Yargicoglu, E., Spokas, K., 2015. Characteristics and applications of biochar for environmental remediation: a review. Crit. Rev. Environ. Sci. Technol. 45, 939–969. https://doi.org/10.1080/10643389.2014.924180.
Yang, Yang, Liu, B., Ni, X., Tao, L., Yu, L., Yang, Ye, Feng, M., Zhong, W., Wu, Y., 2021. Rice productivity and profitability with slow-release urea containing organic-inorganic matrix materials. Pedosphere 31, 511–520. https://doi.org/10.1016/S1002-0160(21)60001-2.
Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L., 2011. Biochar derived from anaerobically digested sugar beet tailings: characterization and phosphate removal potential. Bioresour. Technol. 102, 6273–6278. https://doi.org/10.1016/j.biortech.2011.03.006.
Ye, Z., Zhang, L., Huang, Q., Tan, Z., 2019. Development of a carbon-based slow release fertilizer treated by bio-oil coating and study on its feedback effect on farmland application. J. Clean. Prod. 239, 118085. https://doi.org/10.1016/j.jclepro.2019.118085.
Yousaf, B., Liu, G., Wang, R., Zia-ur-Rehman, M., Rizwan, M.S., Imtiaz, M., Murtaza, G., Shakoor, A., 2016. Investigating the potential influence of biochar and traditional organic amendments on the bioavailability and transfer of Cd in the soil–plant system. Environ. Earth Sci. 75, 1–10. https://doi.org/10.1007/s12665-016-5285-2.
Zahra, M.B., Aftab, Z.E.H., Akhter, A., Haider, M.S., 2021. Cumulative effect of biochar and compost on nutritional profile of soil and maize productivity. J. Plant Nutr. https://doi.org/10.1080/01904167.2021.1871743.
Zalewski, A., Piwowar, A., 2018. Światowy rynek nawozów mineralnych z uwzględnieniem zmian cen bezpośrednich nośników energii oraz surowców. Instytut Ekonomiki Rolnictwa i Gospodarki Żywnościowej - Państwowy Instytut Badawczy.
Zhang, J., Lü, F., Shao, L., He, P., 2014. The use of biochar-amended composting to improve the humification and degradation of sewage sludge. Bioresour. Technol. 168, 252–258. https://doi.org/10.1016/j.biortech.2014.02.080.
Zhang, L., Sun, X., 2014. Changes in physical, chemical, and microbiological properties during the two-stage co-composting of green waste with spent mushroom compost and biochar. Bioresour. Technol. 171, 274–284. https://doi.org/10.1016/j.biortech.2014.08.079.
Zhang, X., You, S., Tian, Y., Li, J., 2019. Comparison of plastic film, biodegradable paper and bio-based film mulching for summer tomato production: soil properties, plant growth, fruit yield and fruit quality. Sci. Hortic. (Amsterdam) 249, 38–48. https://doi.org/10.1016/j.scienta.2019.01.037.
Zhao, F., Zou, G., Shan, Y., Ding, Z., Dai, M., He, Z., 2019. Coconut shell derived biochar to enhance water spinach (Ipomoea aquatica Forsk) growth and decrease nitrogen loss under tropical conditions. Sci. Rep. 9, 20291. https://doi.org/10.1038/s41598-019-56663-w.
Zhao, L., Cao, X., Zheng, W., Scott, J.W., Sharma, B.K., Chen, X., 2016. Copyrolysis of biomass with phosphate fertilizers to improve biochar carbon retention, slow nutrient release, and stabilize heavy metals in soil. ACS Sustain. Chem. Eng. 4, 1630–1636. https://doi.org/10.1021/acssuschemeng.5b01570.
Zheng, Jufeng, Han, J., Liu, Z., Xia, W., Zhang, X., Li, L., Liu, X., Bian, R., Cheng, K., Zheng, Jinwei, Pan, G., 2017. Biochar compound fertilizer increases nitrogen productivity and economic benefits but decreases carbon emission of maize production. Agric. Ecosyst. Environ. 241, 70–78. https://doi.org/10.1016/j.agee.2017.02.03.

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The high dose of biochar reduces polycyclic aromatic hydrocarbons losses during co-composting of sewage sludge and wheat straw

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Research article

The high dose of biochar reduces polycyclic aromatic hydrocarbons losses during co-composting of sewage sludge and wheat straw

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ABSTRACT

The aim of the study was to investigate the effect of the biochar (BC) dose on solvent extractable (C_{tot}) and freely dissolved (C_{free}) polycyclic aromatic hydrocarbons (PAHs) content during co-composting. A significantly better reduction of Σ16 C_{tot} PAHs after 98 days occurred during composting with BC (for 1% of BC – 44% and for 5% of BC – 23%) than in the control (15%). Despite the relatively high reduction of C_{tot} PAHs in the experiment with 5% BC rate, the content of the PAHs was still the highest compared to other variants. Regarding C_{free} PAHs, 5% rate of BC resulted in the best reduction of PAHs, while the 1% BC dose resulted in a lower reduction of C_{free} than the control. For 1% BC, PAHs losses was more effective, and sequestration processes played a less significant role than in the experiment with 5% dose of BC. The total and dissolved organic carbon, and ash were predominantly responsible for C_{tot} and C_{free} losses, and additionally pH for C_{free}. The results of the experiment indicate that BC performs a crucial role in composting, affecting the C_{tot} and C_{free} PAHs in the compost but the final effect strictly depends on the BC dose.

1. Introduction

Sewage sludge (SL) is a by-product of the wastewater treatment that has been a problematic biowaste for many years. Worldwide production of SL is estimated to be 45 million tonnes annually (dry sludge) (Guo et al., 2023). There have been directives (i.e. Sewage Sludge Directive 86/278/EEC) encouraging the use of SL in agriculture, while regulating their application in order to prevent potentially negative effects on soil, vegetation or living organisms. SL is a source of organic matter, nitrogen, phosphorus, calcium, magnesium, and other macro- and microelements necessary for plants growth and development (Tomczyk et al., 2020). However, it is still forbidden to use raw SL directly as soil fertilizer, due to the fact that SL may also contain many hazardous substances (Galey et al., 2022; Gao et al., 2020). Among many hazardous substances that can be found in SL, polycyclic aromatic hydrocarbons (PAHs) are a group that in recent years has been the subject of interest (Premnath et al., 2021; Stańczyk-Mazanek et al., 2019). PAHs are persistent organic pollutants that pose a threat to various types of organisms, due to the fact that these compounds can be found in soil, water, crops, and air. PAHs are carcinogenic, teratogenic, mutagenic, and toxic (Haritash and Kaushik, 2009; Lee and Lee, 2010).

Composting has been proposed as the approach which may solve the problem of PAHs contamination in SL. Composting is based on the natural process of biological decomposition and stabilization of organic matter (Hettiarachchi et al., 2020). Research shows (Yañez et al., 2009) that biosolids composting (including SL) improves the properties of raw biosolid, what promotes plant growth, improves soil moisture retention, and increases the amount of stable organic matter in the soil. At the same time, during the composting of SL, level of organic contaminants is reduced including PAHs (Hua et al., 2008; Oleszczuk, 2007a). This solution allows for the effective management of the inconvenient biowaste, but also limits the release of toxic substances into the environment, which are decomposed during the composting (Sayara and Sánchez, 2020).

Currently, great emphasis is placed on the role of biochar (BC) as an effective and environmentally friendly substrate added during composting (Das et al., 2020; Nguyen et al., 2022). BC may contribute to a more effective composting (mainly promoting degradation and humic acids formation) and additionally reduction of greenhouse gas emissions compared to conventional composting without these additives (Chen et al., 2022). Recent work (Verma et al., 2023) has showed that BC also influences bacterial composition, richness, and dynamics. Furthermore,

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BC increases microbial activity and accelerates maturation of compost (Sánchez-García et al., 2015). However, PAHs can be found in BCs which concentration depends on the type of feedstock and pyrolysis conditions (Zielińska and Oleszczuk, 2015a) and may range from 1 to 100 mg/kg (Chen et al., 2022). Nevertheless, PAHs contained in BCs are much less available than those present in SL (Oleszczuk, 2006).

There are many studies where BC was used during SL composting, but these studies were mainly focused on heavy metals immobilization and phytoavailability, reducing greenhouse gases emissions, supporting microbial structures and activity, and effects that BC implements on the SL composting in general (Chen et al., 2020; Du et al., 2019; Zhang et al., 2014; Zhou et al., 2023). There is only one paper where the PAHs content was studied during co-composting BC with SL (Kopeć et al., 2017) and no studies where bioavailability of these contaminants was investigated. It should be evoked that the study on the bioavailability of pollutants is a key issue, because the bioavailable content indicates properly the possible physical, chemical, and biological interactions of pollutants in the soil or sediments (Ehlers and Luthy, 2003) and allows to evaluate the real environmental risk related with their presence in the particular matrix (Rončević et al., 2016).

The aim of the present study was to evaluate the effect of the BC's dose on the persistence (based on organic solvent extractable content, C_{tot}) and bioavailability (based on freely dissolved content, C_{free}) of PAHs during composting of a the mixture of SL and wheat straw (WS). The influence of selected physicochemical properties of BC and composted material on the range of PAHs losses depending on the composting phase was also investigated to explain the possible mechanisms responsible for PAHs bioavailability and losses during composting.

2. Materials and methods

2.1. Composting feedstock

Sewage sludge (SL) and wheat straw (WS) with or without BC were used as a feedstock for composting. Detailed information about particular feedstocks is presented in Supporting Information (SI). SL and WS were mixed in a 1:1 mass ratio (dry mass), then 0 (control), 1% and 5% (w/w) of BC was added to the SL/WS and mixed gently to obtain homogenous mixture. To improve the composting process, the mixture was sprayed using bicompost microbiological agent (Organika-Agrarius Sp. z o.o., Przemyśl, Poland). The composting material was placed in bioreactors (BKB-100, ROTAMETR, Gliwice, Poland) with a volume of 100 L with electronic controlling system of temperature and aeration (in the range from 0 to 180 L/h). The material was co-composted in bioreactors for 5 weeks and then transferred to a plastic barrel for maturation and stored for 2 months. To set the appropriate moisture content (which was estimated on 60–70%), deionized water (DI) was added to the bioreactors periodically. Initial aeration in bioreactors was set at 30 L/h. After three days of composting, the aeration was increased to 95 L/h and keep on this level to the end of composing in bioreactors. To measure the concentration of particular gases (O_2, CO_2, CO, NO, CH_4 and N_2) released during composting, the OPTIMA7 Biogas Analyzer (MRU GmbH, Germany) was used. Compost samples (approximately 100 g of dry mass) were collected at various stages of the composting process - at the beginning and after 3, 7, 14, 21, 28, 35, 70, and 98 days. After sampling the representative sample from the bioreactor, it was evenly distributed on filter paper and air-dried for 48 h in a fume hood to prevent contamination with other substances. Next, the samples were grounded using a laboratory knife grinder (TESTCHEM, Radlin, Poland), and stored at 4 °C in a plastic zip-bag before analysis.

2.2. Physico-chemical characterization of samples

The total organic carbon (TOC) and dissolved organic carbon (DOC) were analyzed using TOC-L Analyzer equipped with SSM5000 furnace (Shimadzu, Kioto, Japan). TOC was determined from a solid sample. DOC and pH were determined in solutions after extraction. Extracts were prepared by shaking (10 rpm/min) 1 g of material with 10 mL of Milli Q water for 24 h at room temperature (22 ± 2 °C) (Laboratory shaker, Type 358A, ELPIN+, Katowice, Poland). Then, extracts were filtered in a glass funnel on a qualitative paper filter (Munktell Filter AB, Germany). The pH values were determined using a HQ430D universal laboratory multi-parameter meter (HACH, Loveland, Colorado, USA). The ash content was calculated on the basis of the mass difference (loss) during the residence of 1 g of the material in the furnace (Magma Therm, Istanbul, Turkey) at 760 °C for 6 h. To determine the moisture content in a freshly collected compost sample approximately 10 g of a representative sample was weighed into a Petri dish and then dried in a laboratory dryer (POL-EKO, Wodzisław Śląski, Poland) at 105 °C for 6 h until a constant mass of the material was established. Moisture was calculated from the weight difference.

2.3. Total (C_{tot}) PAHs concentration

Polycyclic aromatic hydrocarbons (PAHs) (C_{tot}) extraction and extract purification was carried out using an accelerated solvent extraction (ASE) system (Dionex ASE 350 Accelerated Solvent Extractor, ThermoFisher Scientific, Waltham, Massachusetts, USA) according to protocol previously described by (Hilber et al., 2012; Kim et al., 2003). Briefly, the composted material or final compost (1 g) was mixed with 6 g of activated silica gel, 0.1 g of copper, and 0.1 g of EDTA and added to a extraction cell. Activated silica gel was used for absorbing potentially present water, copper to bind inorganic ions (e.g. phosphates), and EDTA to bind metal ions. Extracts were filtered by cellulose filters (Thermo Scientific, Waltham, Massachusetts, USA) placed on the bottom of the cell. Extraction was carried out with approximately 30 mL of hexane at 150 °C and under the pressure of 14 MPa. The samples were then concentrated using a rotary vacuum concentrator RVC 2-25CD (Martin Christ, Osterode am Harz, Germany). The samples were then subjected to qualitative and quantitative analysis using a Trace 1300 gas chromatograph (ThermoFisher Scientific, Waltham, Massachusetts, USA), equipped with a Rxi-5 ms column (length 30 m, id 0.25 mm, and 0.25 μm film thickness, Restek, Glastron, France) (Zielińska and Oleszczuk, 2016).

2.4. Freely dissolved (C_{free}) PAHs concentration

Freely dissolved PAHs (C_{free}) content in investigating samples was determined using the method described previously (Oleszczuk et al., 2016). Dry and ground samples of the composting material or final compost (1 g) were placed into a 50 mL Erlenmeyer flask with 2 stripes of polyoxymethylene polymer (POM) and 40 mL of 200 mg/L sodium azide aqueous solution. The flasks were shaken on a rotary shaker (Rotax 6.8. VELP, Usmate Velate, Italy) for 28 days, then the POM stripes were removed, cleaned with Milli Q water and dried. Dry POM stripes were extracted using the mixture of heptane and acetone (4:1, v/v) for 48 h. The extract was concentrated and analyzed by GC-MS as described before.

3. Results and discussion

3.1. Composting parameters and compost samples characterization

Based on temperature changes during composting four typical phases were observed which indicate that the process was proceeding correctly (Fig. S1). No significant differences ($P > 0.05$) were found between the control and the treatments with BC. Mesophilic phase I lasted about 3 days, but its extension (to 4 days) was observed for the material with 1% BC addition (Fig. S1). During mesophilic phase I, the pH decreased in the case of all treatments (Fig. 1C, Table S2), which resulted from the transformation of nitrogen and carbon compounds into organic acids (Guo et al., 2020a,b). The highest decrease in pH was

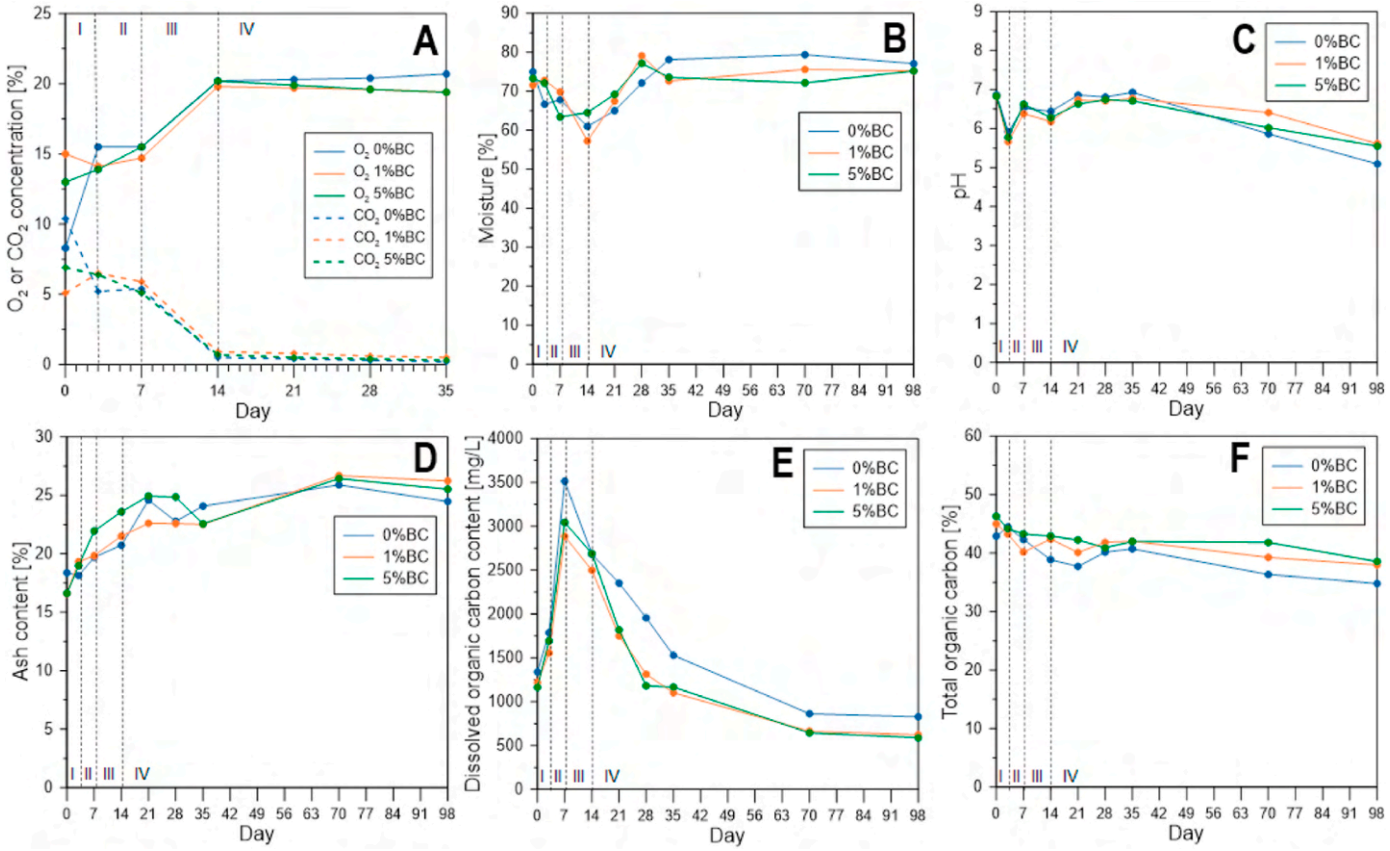

Fig. 1. Changes of physico-chemical properties of compost depending on the composting phase (I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation). A – oxygen or carbon dioxide concentration [%], B – moisture [%], C – pH, D – ash (mineral) content [%], E – dissolved organic carbon content [mg/L], F – total organic carbon [%]. The values are the average of triplicates.

noted for the treatment with 1% BC (Fig. 1C, Table S2). At this stage, increased nitrogen (II) oxide emission was also detected, which confirms the above findings (Table S1). Moreover, during this phase the highest oxygen consumption was observed among all the composting phases (Fig. 1A, Table S1). The addition of BC (regardless of its rate) increased the amount of CO_2 produced during mesophilic phase I (by 24% more compared to the control) (Fig. 1A, Table S1), which is evidence of enhanced microbial activity in the presence of BC (Meng et al., 2018).

In the thermophilic phase, the maximum temperature was obtained for 1% BC addition (Fig. S1). The achieved temperature and its persistence time were sufficient for effective sanitization of SL (Petric et al., 2012). This is confirmed by an earlier study (X. Guo et al., 2020a,b) in which BC also increased the thermophilic phase temperature. This effect was however found to be determined by the BC rate. An increase in the percentage of BC to 5% did not contribute to a rise in temperature during the thermophilic phase. This could have been associated with the reduced availability of some ingredients of the compost (as a result of their being bound by BC), necessary for effective activity of thermophilic bacteria. In the course of the thermophilic phase, there was an increase in pH (to 6.38–6.62) (Fig. 1C, Table S2), which could have been caused by the breakdown of proteins (transformation of organic nitrogen into NH_3) (Meena et al., 2021) and by the transformation of organic acids as a result of organic matter degradation (Oleszczuk, 2007b). The larger was the BC addition before composting, the higher was the increase of pH. During this phase, dissolved organic carbon (DOC) was also found to increase and its content was higher for the control than for the treatments with BC (by 14% and 20% for the lower and higher rate of BC, respectively) (Fig. 1E, Table S2). An increase in DOC during composting may result from the solubilization (increasing the solubility of substances using the so-called dissolution mediators) of unstable compounds contained in the organic matter of the matrix through, among others, microbial degradation (Said-Pullicino et al., 2007). A lower content of DOC observed in the treatments with BC may be related to the binding of DOC by BC, as indicated by an earlier study (Kończak et al., 2021).

During mesophilic phase II, the pH was found to fall and its range was dependent on the experimental treatment (Fig. 1C, Table S2). A decrease in DOC ranging from 12 to 24% relative to the thermophilic phase was also observed in this phase (Fig. 1E, Table S2). A reduction in DOC during composting may occur as a result of mineralization of organic soluble compounds contained in the matrix as well as due to repolymerization and/or condensation reactions. This leads to the formation of complex organic substances with a high molecular mass and lower water solubility (Said-Pullicino et al., 2007). Substances of this type may undergo flocculation or adsorption into the organic matter contained in the solid phase of the composted material. This effect can also be enhanced in the treatment with BC as a result of adsorption of DOC by BC (Kończak et al., 2021).

At the initial stage of the maturation phase (between the 14th and 35th day of composting), there was an increase in pH to 6.71–6.93, whereas during the second stage (between the 35th and 98th day) the pH in each of the treatments significantly declined, reaching a level from 5.09 to 5.61 (Fig. 1C, Table S2). The highest pH values were noted for the treatment with BC. No significant differences ($P > 0.05$) were found between the BC rates used. The decline in pH was caused by the formation of fulvic and humic acids (Meena et al., 2021). Similarly to the previous phase of composting, the DOC level gradually decreased from the beginning of maturation, reaching the lowest level for 5% BC addition (589 mg/L), followed by the treatment with 1% BC addition (622 mg/L), while the highest level was found for the control (830

mg/L) (Fig. 1E, Table S2), which would confirm the earlier suppositions about the binding of DOC by BC (Kończak et al., 2021).

In the course of composting, TOC was also found to decrease in the range from 7.1 to 8.0%, with a simultaneous increase in the mineral fraction from 6.1 to 9.6% compared to the feedstock before composting (Fig. 1F, Table S2). This is a regular phenomenon in which microbial decomposition (mineralization) of organic matter occurs, which translates into a reduced organic carbon content (Kopeć et al., 2017; Siebielska, 2014). At the same time, the inorganic (mineral) fraction present in the compost material becomes more concentrated (Fig. 1D, Table S2).

3.2. C_{tot} and C_{free} PAHs in sewage sludge and biochar

The Σ16 C_{tot} PAHs content in the SL was 1751 ± 122 μg/kg, which is much lower than the typical values for municipal SL from areas with similar anthropo-pressure (Oleszczuk et al., 2014; Stefaniuk and Oleszczuk, 2016). The 4-ring PAHs (42%) were predominant, followed by 3- and 5-ring compounds (25% and 24.0%, respectively) (Fig. 2A). PHE, FLA, BaP, and PYR were predominant PAHs in SL (Fig. S2A, Table S3). The SL used in the experiment do not exceed the maximum limits recommended by Council of the European Community (Σ9 PAHs <6 mg/kg dry mass) (CEC, 2000).

Th Σ16 C_{free} PAHs in the SL was 144.4 ± 3.9 ng/L. The groups of 2-4-ring PAHs accounted the majority of the C_{free} PAHs (Fig. 2A). The predominant was 2-ring PAH consisted 50% (Fig. S2A, Table S3) of the Σ16 C_{free} PAHs. The 5- and 6-ring PAHs accounted less than 0.25% (Fig. 2A), which is typical value for SL (Oleszczuk et al., 2014).

The Σ16 C_{tot} PAHs content in the BC used in the experiment was 7163 ± 480 μg/kg. The content of Σ16 C_{tot} PAHs is a standard value (often even much lower) compared to other BCs obtained from wood biomass (Hilber et al., 2012; Keiluweit et al., 2012). The 2-ring and 3-ring PAHs were predominant in the BC, accounting 34% and 47%, respectively (Fig. 2B). Regards to the individual C_{tot} PAHs, the highest contribution showed NAP (34%) and PHE (20%) (Fig. S2B). The Σ16 C_{tot} PAHs in BC used in the experiment does not exceed the limits established by the Swiss Chemical Risk Reduction Act for basic grade material (EBC, 2015).

The Σ16 C_{free} PAHs content in the BC was 324.2 ± 12.5 ng/L and was approximately 2 times higher than in SL. The distribution of the particular groups of PAHs regards to rings number in Σ16 C_{free} PAHs was similar to that of Σ16 C_{tot} PAHs (Fig. 2B).

3.3. C_{tot} PAHs changes during composting

Due to a significantly higher content of Σ16 C_{tot} PAHs in BC than in SL (more than 4 times), the addition of BC to the composted mixture caused a 19% and 48% increase in Σ16 C_{tot} PAHs in the treatments with 1% and 5% BC addition, respectively (Fig. 3A, Table S4). The changes in Σ16 C_{tot} PAHs throughout the entire composting period were clearly

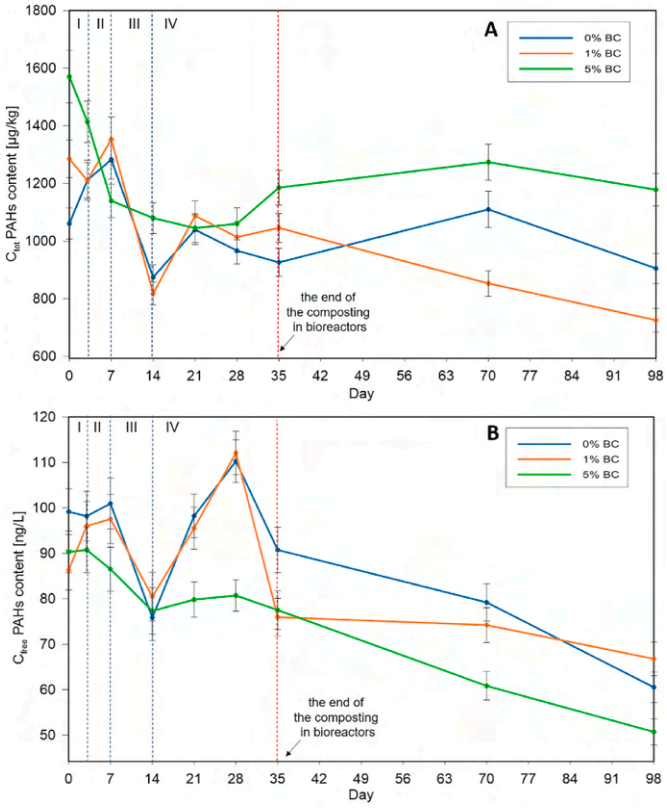

Fig. 3. Change of solvent extractable (A) and freely dissolved (B) Σ16 PAHs content during composting. Composting phases: I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation. Error bars means standard deviation error (in triplicate).

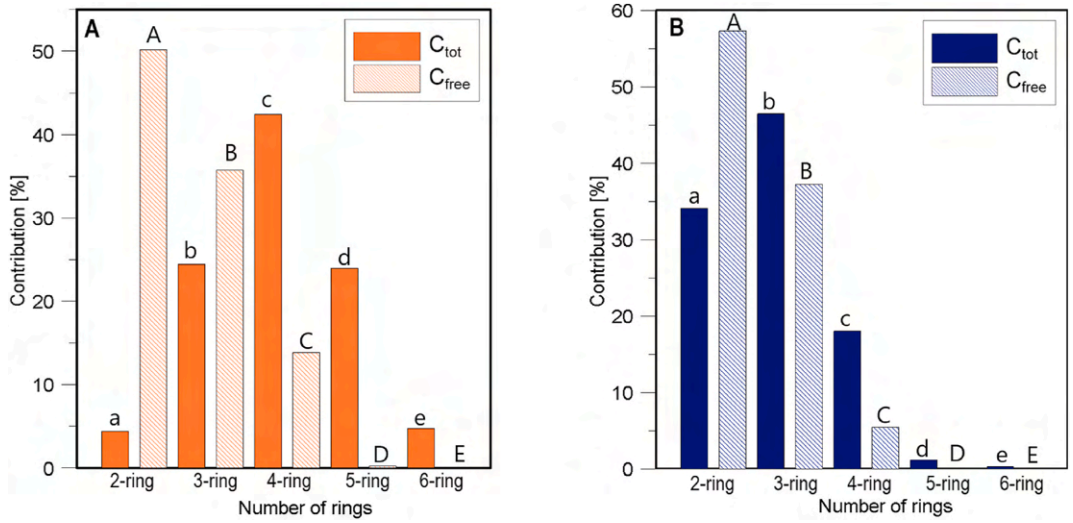

Fig. 2. Contribution of particular PAHs groups in the sewage sludge (A) and biochar (B) regarding number of rings in the solvent extractable (C_{tot}) and freely dissolved (C_{free}) PAHs content. Different letters on bars indicate a significant difference in PAHs groups ($p < 0.05$) according to the HSD Tukey test for $\alpha = 0.05$ (a-e – differences between groups for C_{tot}, A-E – differences between groups for C_{free}).

dependent on the experimental treatment (Fig. 3A). In the control treatment, the content of Σ16 C_{tot} PAHs significantly increased (by 21%) during the first 7 days of composting (in the mesophilic and thermophilic phases), while subsequently an rapid drop (by 18%) was observed to a level lower than that observed at the beginning of the experiment. This is in contradiction with earlier data (Amir et al., 2005) that showed that the highest decrease in PAH content is observed in the thermophilic phase, which is associated with high temperature and microbial activity. The observed differences are attributable to the different type of SL as well as to the different contents of contaminants and the form in which they occur in SL. The compost maturation period (from the 14th to the 98th day), on the other hand, was characterized by variations in Σ16 C_{tot} PAHs, while ultimately, after 98 days of compositing, it reached a level lower by 15% than that observed at the beginning of the experiment (Fig. 3A).

In the experiment with the 1% BC rate, the content of Σ16 C_{tot} PAHs was very similar to that observed for the control treatment. There were differences only at the beginning of the study (mesophilic phase I) and during compost maturation (Fig. 3A). A significant decrease (by 44%) in Σ16 C_{tot} PAHs was noted relative to the beginning of the experiment. Contrary to that, in the treatment with 5% BC addition the level of Σ16 C_{tot} PAHs abruptly dropped during the first 14 days (by 31%) and maintained at a constant level over the next 14 days, which confirms the earlier theory about a rapid decline in PAHs during the first phases of composting (Amir et al., 2005). After 35 days of compositing, there was an increase in Σ16 C_{tot} PAHs to a value around 1200 μg/kg for the compost with 5% BC addition, which persisted until the end of the maturation stage (a 25% lower content than at the beginning of the experiment) (Fig. 3A, Table S4).

Despite that BC may be a factor increasing the PAH content in the composted feedstock, a relatively better reduction in Σ16 C_{tot} PAHs was found for the treatments with BC than for the compost without BC. This can be related to the fact that BC provides favorable conditions for the development of microorganisms by attaching them to its porous surface and protecting them, which prolongs the longevity of microbes. Such conditions contribute to an increased level of PAH degradation (Anyika et al., 2015; Kończak et al., 2023). With the appropriately chosen rate (1%), the PAH content was ultimately lower by 20% than in the control treatment. Kopeć et al. (2017) observed a similar relationship during composting of SL with maize straw with 8% BC addition (based on a dry mass ratio). In spite of a relatively high reduction in C_{tot} PAHs in the treatment with the 5% BC rate, the content of the investigated compounds was still the highest in this treatment in comparison to the control and the 1% BC rate (by 30% and 62%, respectively, Fig. 3A). This indicates that a too high addition of BC had a negative effect on the final PAH content in the mature compost compared to the compost both without BC addition and with the lower rate of BC. A possible cause is the incorporation of a too large amount of PAHs at the higher BC rate and thus preventing their effective degradation by microorganisms. An increased rate of BC may also limit the availability of PAHs to organisms, which substantially reduces degradation efficiency. Reduction in the total content of PAHs during composting may result both from the degradation of these compounds by microorganisms and from their strong adsorption by the matrix components (Oleszczuk, 2007a). Additionally, a part of PAHs can be bound (sequestered) in difficult-to-reach sites of the matrix and these compounds can be incorporated into bound residues (Antizar-Ladislao et al., 2004). These processes lead to a reduced degree of leaching of PAHs by organic solvents, which contributes to their low penetration into soils and the low availability of these compounds to organisms (Oleszczuk, 2007a). The observed decline in the content of PAHs may be associated with their volatilization, but a significant effect is found almost exclusively for the most volatile NAP (Wong et al., 2002).

Fig. 4A shows the profile of the individual PAH groups at the beginning of the experiment and in the ready-made compost (after the maturation process). Distinct differences were observed mainly for the 4- and 5-ring PAHs. Regardless of the experimental treatment, composting resulted in a substantial decrease in the percentage of 5-ring C_{tot} PAHs (Fig. 4A, Table S4), with a simultaneous increase in the percentage of 4-ring PAHs. In the case of BC addition (at both rates), there was a more substantial increase in the percentage of the sum of 2- and 3-ring PAHs relative to the sum of 4-6-ring PAHs, which are more toxic and harmful to the environment (Marcińczyk et al., 2022). At the same time, the reduction in 4-6-ring PAHs was more effective in the BC-containing composts in comparison to the control (the sum of these PAHs remained almost unchanged in the control) (Fig. 4A, Table S4). As far as the highly toxic BaP is concerned, 1% BC addition contributed to the highest (73%) reduction of this compound in the compost after the completion of composting relative to the other two treatments (control – 68%, treatment with 5% BC addition – 45%).

Fig. 5A shows an increase/decrease in C_{tot} for the individual PAH groups depending on the number of rings in comparison with the beginning of the experiment. The profile of the C_{tot} changes in the individual PAH groups during composting is presented in Fig. S3. BC

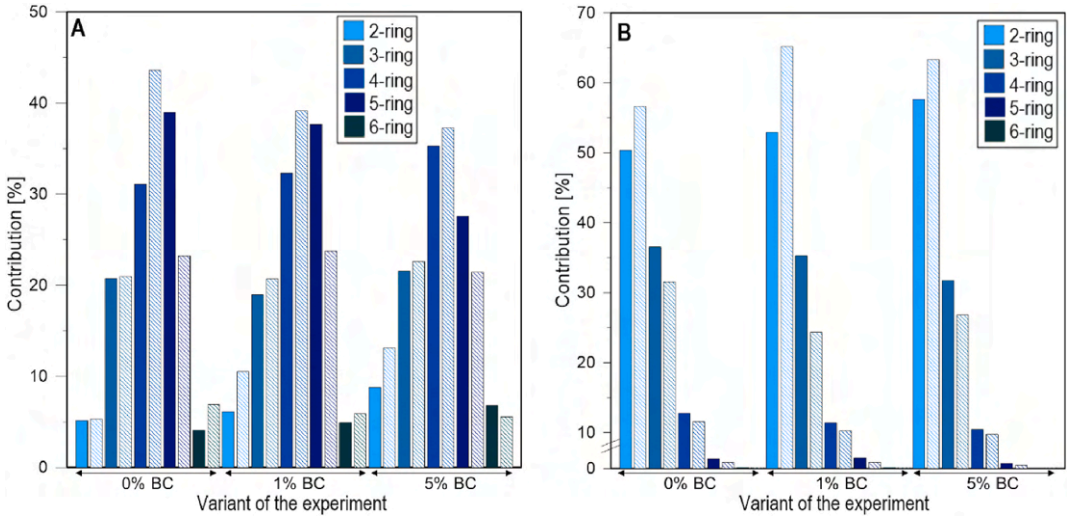

Fig. 4. Solvent extractable (A) and freely dissolved (B) Σ16 PAHs number of rings contribution in compost with various doses of biochar at the beginning (solid color) and at the end (striped color) of the experiment. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

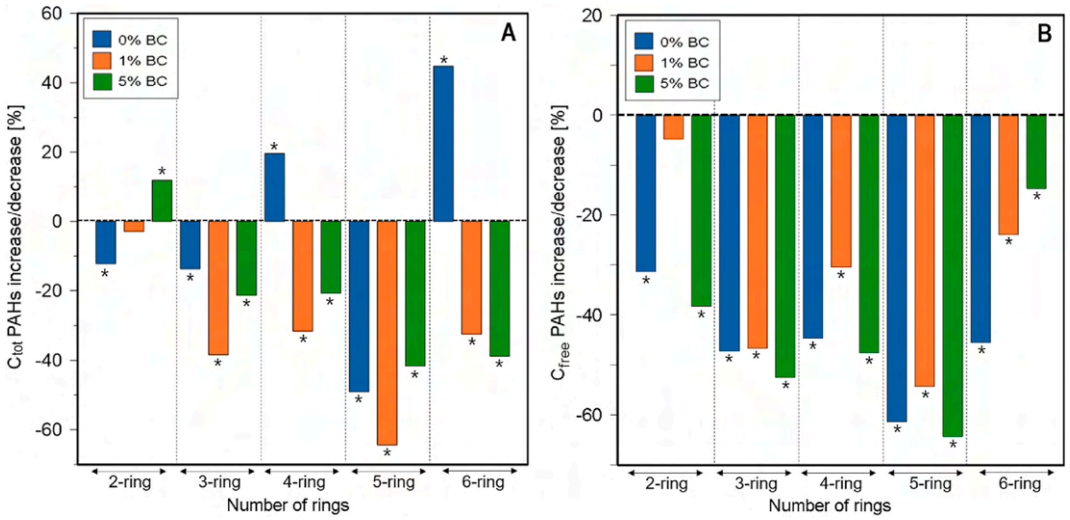

Fig. 5. The increase/decrease (%) for the individual PAH groups (depending on the number of rings) in solvent extractable (A) and freely dissolved (B) Σ16 PAHs content in comparison with the beginning of the experiment in composts with various doses of biochar. * - means statistically significant difference ($P \leq 0.05$) compared to the beginning of the experiment.

addition was observed to contribute to decreasing the content of ≥ 3-ring PAHs and this decrease is not proportionate to the BC rate (a higher level of reduction in the percentage of PAHs at the lower BC rate, apart from 6-ring PAHs). The lower BC addition resulted in the most effective reduction in 3-5-ring PAHs relative to the beginning of the experiment (Fig. 5A). Regardless of the experimental treatment, the highest reduction was obtained for the 5-ring PAHs. The observed differences in the level of the PAH groups in the composts may be related to the different interactions of the compounds with the matrix (Oleszczuk, 2007a), but the influence of BC is visible since it is responsible for a decrease in the percentage of ≥ 3-ring PAHs during composting.

In comparing the results of the reduction in the total PAH content (from 15% to 44% for the Σ16 PAHs) to studies dealing with composting SL alone (or with other additions than BC) (Cai et al., 2007; Y. Guo et al., 2020a,b; Poluszyńska et al., 2017), it should be stated that these results were lower than those reported in the literature. For example, Guo et al. (Y. Guo et al., 2020a,b) composted SL with green forest waste at different weight ratios over a period of 50 days, achieving removal efficiency of Σ16 PAHs in the range from 62% to 75%. Poluszyńska et al. (2017) composted SL with an addition of sawdust for 30 days, achieving a reduction in Σ16 PAHs at a level of as much as 85%. After 56-day composting of a mixture of SL and rice straw, Cai et al. (2007) obtained removal efficiency of Σ16 PAHs at a level of 64–94%. The observed differences in comparison with the earlier studies can be due to the different composting process conditions, but also the different interactions of the PAHs with the matrix of the composted material and the different contents of the individual PAH groups. Furthermore, the PAH content in the above cited studies was much higher than in this experiment, which may determine the greater efficiency in removing compounds of this type, as demonstrated previously (Lü et al., 2021).

The studies dealing with BC addition to composting of organic wastes other than sewage sludge in the context of PAH content are equally scarce. Chen et al. (2022) composted fruit and vegetable waste with BC (2, 5, and 10%). The greatest PAH removal efficiency was achieved for the highest BC rate. The differences in PAH removal efficiency are undoubtedly related to the different feedstock used during composting.

3.4. C_{free} PAHs changes during composting

The content of Σ16 C_{free} PAHs before the composting process was the highest in the control treatment (99.2 ng/L, Table S5). The BC addition to SL/WS reduced Σ16 C_{free} PAHs by 13% and 9% for the treatment with the 1% and 5% BC rates, respectively (Fig. 3B). This decrease is associated with the greater affinity of PAHs for BC than for SL, which was confirmed in a previous study (Zielińska and Oleszczuk, 2015b). During the first phase of composting (mesophilic phase I), the Σ16 C_{free} PAHs maintained a constant level in the control treatment and in the treatment with 5% BC addition, whereas in the treatment with 1% BC addition the Σ16 C_{free} PAHs were found to increase (by 11% relative to the beginning of the experiment) (Fig. 3B, Table S5). This was predominantly attributable to an increased content of BaA (a 51% higher value than at the beginning of composting) (Table S5). The thermophilic phase did not affect significantly the Σ16 C_{free} PAH content (Fig. 3B). In spite of the differences in the content of Σ16 C_{free} PAHs in the initial composting period, after the end of mesophilic phase II (day 14) the content of Σ16 C_{free} PAHs became equal in all experimental treatments (Fig. 3B, Table S5). During compost maturation, the content of Σ16 C_{free} PAHs was characterized by different dynamics depending on the experimental treatment. The obtained results demonstrate that between the 14th and 28th day of composting (the first stage of maturation), the interactions of PAHs with the matrix became weaker, which resulted in release of PAHs (an increase in C_{free} content) in the control and in the treatment with 1% BC addition. No similar effect was found for the 5% BC rate (a plateau content of C_{free} from the 14th to 35th day, Fig. 3B). The subsequent stages of compost maturation were characterized by a decline in Σ16 C_{free} PAHs. Ultimately, on the 98th day of composting, it was found that the greatest effectiveness in reducing Σ16 C_{free} PAHs was achieved for the treatment with 5% BC addition (44%), followed by the control (39%), whereas the experiment with the 1% BC rate was characterized by the weakest effectiveness in reducing Σ16 C_{free} PAH (23%).

Fig. 4B illustrates the profile of the individual C_{free} PAH groups at the beginning of the experiment and in the ready-made compost (after the maturation process). During composting, the profile of the PAHs underwent changes, which can particularly be seen in the case of 2-4-ring PAHs. The percentage of ≥ 3-ring PAHs was observed to decrease at the expense of 2-ring PAHs, but it was not proportionate to the BC rate. This effect was the most evident in the case of the 1% BC rate (Fig. 4B).

Fig. 5B shows an increase/decrease in C_{free} for the individual PAH groups depending on the number of rings compared to the beginning of the experiment. The changes in C_{free} for the individual PAH groups with a breakdown into the composting phases are displayed in Fig. S4. It was observed that the higher BC addition contributed to a greater decrease in the content of most of the PAH groups (from 38% to 64%) in comparison with the 1% BC rate and the control. However, BC addition does not

have a beneficial effect on the content of 6-ring PAHs during composting. Similar observations were also made by Oleszczuk et al. (2014), which was explained by the fact that 6-ring PAHs are bound to the SL matrix sufficiently strongly so that in such a system BC ceases to perform a significant role in reducing their bioavailability.

3.5. Comparison of C_{tot} and C_{free} profiles

In comparing the profile of the changes in Σ16 C_{tot} PAHs versus Σ16 C_{free} PAHs during the process for the different compost treatments, information can be obtained whether the observed changes for C_{free} were related to a decrease/increase in C_{tot} or they resulted from the changes associated with weakened/strengthened interactions between the PAHs and the composted material. Fig. 6 shows the changes in the content of C_{tot} and C_{free} during the entire composting process depending on the experimental treatment.

Based on the presented relationships, it can be inferred that C_{free} is related to C_{tot} only during the initial period of composting (until the 35th day) and that the influence diminishes with the increasing BC rate (Fig. 6). In the case of the control treatment, the profile of the changes in C_{free} and C_{tot} until the 35th day of composting is very similar and therefore the C_{free} content is determined by an increase/decrease in total PAH concentration (Fig. 6A). This change can be noticed during the late maturation period (day 35–70) where in spite of an increase in C_{tot}, a continuous linear decline in C_{free} was observed until the end of the study period. This suggests strengthened interactions between the PAHs and the composted material with compost maturation. A similar relationship in the final period of the study was observed for the higher BC rate (Fig. 6C). Nevertheless, the profile of C_{free} relative to C_{tot} for the treatments with BC shows greater variations and fewer relationships than for the control. Some similarities (mainly between the 7th and 21st day) were noted for the treatment with 1% BC addition, which indicates the dependence of C_{free} on C_{tot} during the duration of mesophilic phase II and at the beginning of maturation (Fig. 6B). Worth noting is the fact that during maturation of the material in the experiment with 1% BC, C_{tot} decreased, whereas C_{free} stabilized at a constant level and did not change.

3.6. Log K_{oc} coefficient values

The log K_{oc} coefficient informs how strongly individual PAHs are bound to the matrix (SL, BC, or finally the ready-made compost) (Hawthorne et al., 2006). Indirectly, the log K_{oc} coefficient may also provide information on the potential mobility of a compound in the soil, whereas an analysis of changes in log K_{oc} during composting allows to determine the affinity of PAHs to the composted material over time (Oleszczuk, 2007b). The higher the value of log K_{oc}, the greater affinity for the matrix is exhibited by the particular compound. Log K_{oc} values increase with increasing molecular mass of PAHs (Oleszczuk, 2007b). The more rings there are in the PAH molecule, the more hydrophobic and more susceptible to phenomena reducing its mobility and bioavailability it is (Oleszczuk, 2007b).

Throughout the entire composting period, the affinity of the individual PAHs for the compost underwent certain changes, which is indicated by the changing value of log K_{oc} (Fig. 7). To present the changes undergoing in the affinity for the matrix, four PAHs representing compounds with different properties were selected (NAP, PHE, FLA, and BaP) (Fig. 7). Regardless of the type of PAH, log K_{oc} had the highest values for the treatment with 5% BC addition, which may explain the reduced degradation of C_{tot} PAHs during composting compared both to the 1% BC rate and the control treatment. At the same time, this explains the highest removal efficiency of C_{free} PAHs in the case of this treatment. As regards both the control and the treatment with 1% BC addition, the log K_{oc} values were dependent on both the type of compound and the composting stage. Nevertheless, in most cases (except for BaP) and during most of the composting process, higher log K_{oc} values were recorded for the treatment with the 1% BC rate than for the control. Fig. 7 also demonstrates that the affinity of the individual PAHs for the composted material exhibited some variations throughout the entire composting period. Irrespective of the experimental treatment, the initial period of composting (until the 35th day) was characterized by the greatest dynamics of changes. During the maturation

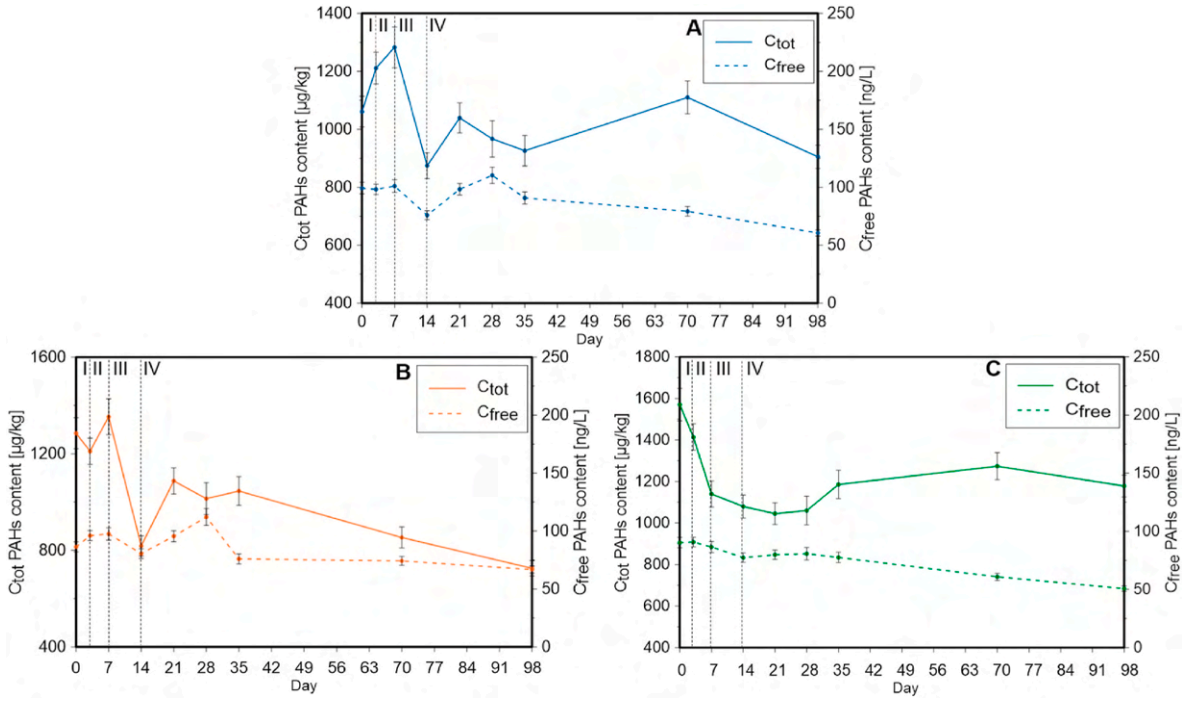

Fig. 6. The profile of solvent extractable Σ16 PAHs (C_{tot}) and freely dissolved Σ16 PAHs (C_{free}) content changes during composting. A – compost without BC, B – compost with 1% BC, C – compost with 5% BC. Composting phases: I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation. Error bars means standard deviation error (in triplicate).

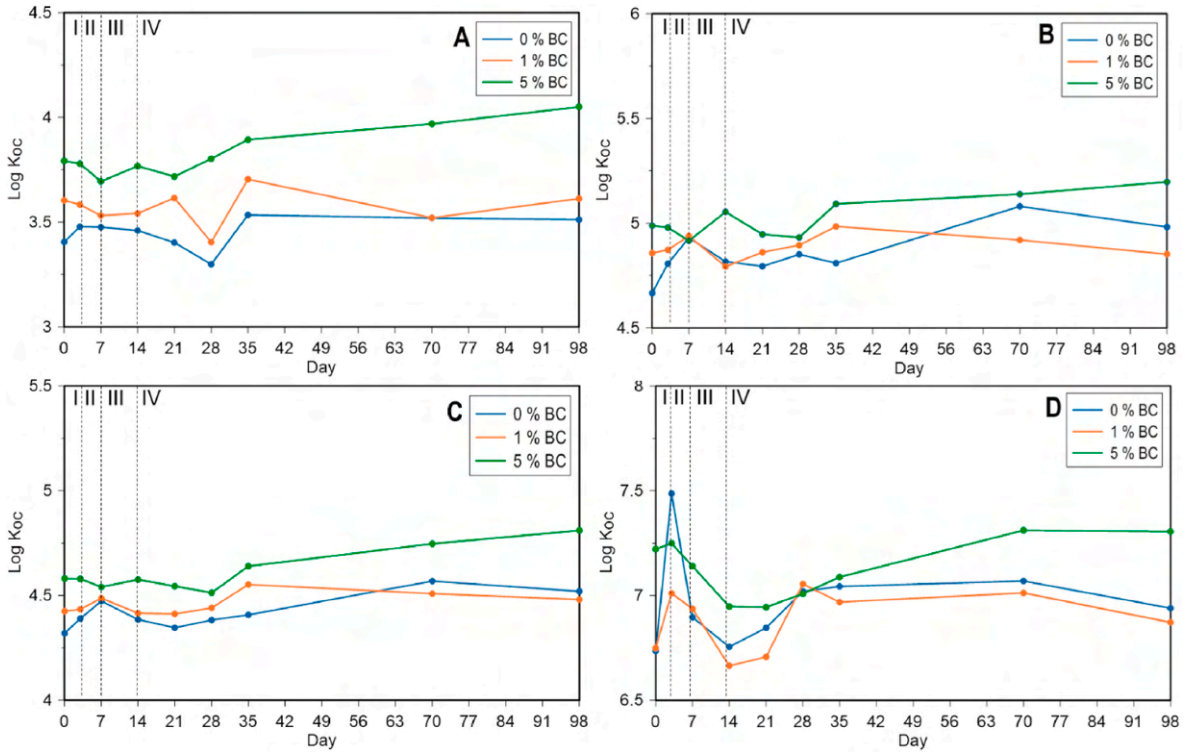

Fig. 7. Log organic carbon – water partitioning coefficients (K_{oc}) values for four chosen PAHs: A – naphthalene (NAP), B – phenanthrene (PHE), C – fluoranthene (FLA), D – benzo(a)pyrene (BaP) during composting. Composting phases: I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation.

period, an increase in log K_{oc} was observed only in the case of the treatment with the 5% BC rate, whereas in the other cases log K_{oc} was found to increase up to a certain moment, while subsequently there was a decrease (PHE and FLA for the control treatment) or there were no changes and a decrease (the other PAHs). A comparison of the log K_{oc} values obtained in this experiment (based on measurements made on the last day of the experiment) with guideline-recommended values is shown in Fig. S5.

3.7. Correlation between PAHs content and physico-chemical properties of composts

To determine the effect of the physicochemical properties of the composted material on the content of C_{tot} and C_{free} PAHs, a statistical analysis based on correlation analysis was performed. The evaluation of correlations between C_{tot} PAHs and the physicochemical properties of the composted feedstock reveals sporadic statistically significant relationships ($P \leq 0.05$), predominantly between TOC, DOC, and the inorganic fraction (mineral fraction, ash) (Table S6). The frequency of relationships for the individual PAHs increased with the increasing percentage of BC in the compost, which indicates its leading role in C_{tot} PAH losses in the experimental systems studied. The most frequent correlations of C_{tot} were found with ash content (mineral fraction). With the increasing percentage of the inorganic fraction in the compost, the content of C_{tot} PAHs was observed to decline. Studies (Sun et al., 2013; Tan et al., 2015; Xu et al., 2017) reveal that the mineral fraction of BC reduces its adsorption capacity due to the blocking of pores by ash. However, it is indicated that the inorganic fraction may also exhibit adsorption properties towards some organic contaminants (Kończak et al., 2023) or it may have catalytic activity promoting their breakdown. Furthermore, the presence of some minerals may support the processes of hydrolysis and reduction of hydrophobic organic contaminants, whereas the products formed may have greater affinity for the BC surface and bind to it in a permanent way (Xu et al., 2017). PAHs or their derivatives may bind to inorganic components incorporated with BC and then diffuse into less accessible sites of the matrix, which prevents their extraction (Ma et al., 2012). This confirms that the adsorption/sequestration/reduction processes are primarily responsible for the PAH losses observed in the case of the treatment with the higher BC rate, while the biological degradation of these compounds is responsible to a lesser extent. With the decreasing BC rate, the frequency of correlations between C_{tot} and ash declined, which may suggest that the above-mentioned processes ceased to dominate in PAH losses during composting and that the main role in PAH losses was taken over by microorganisms.

Research reveals that an increasing level of TOC is a factor reducing biodegradation of PAHs and intensifying their binding (sequestration/adsorption) (Kończak et al., 2023). A positive correlation ($p < 0.05$) between C_{tot} PAHs and TOC (Table S6) observed in the present study related only to some of the PAHs in the treatment with 5% BC addition. As suggested earlier, this confirms that in the treatment with the higher BC rate biological degradation of PAHs performed a less important role and that the observed losses of PAHs were primarily associated with their adsorption or chemical degradation.

The statistical analysis also demonstrated infrequent relationships between C_{tot} and DOC for some of the PAHs (Table S6). At the higher BC rate, negative correlations were observed between DOC and 2- and 3-ring C_{tot} PAHs, whereas at the lower BC rate positive correlations were shown to occur for some of the 5- and 6-ring PAHs (Table S6). A study by Wang et al. (2021) found that the level of DOC is positively correlated to the degree of degradation of total PAHs, affecting their desorption and subsequent biodegradation in the soil. This finds confirmation in the present study, notably in the occurrence of negative relationships between C_{tot} and DOC at the 5% BC rate (the higher the DOC content, the lower the content of C_{tot} PAHs, i.e. the higher the degree of their losses). Studies reveal that DOC, apart from its tendency to bind to PAHs and being leached with them into the aqueous phase (which has a greater influence on the bioavailable concentration of PAHs) (Mukherjee and Zimmerman, 2013), may impact the binding of PAHs to dissolved colloidal material (King et al., 2004), thus indirectly

affecting the total concentration of PAHs.

Similarly as for C_{tot}, in the case of C_{free} PAHs the correlations also related to TOC, DOC, and ash (Table S7). Moreover, positive correlations were noted between C_{free} and pH (mainly for the control treatment). This demonstrates that in BC-containing systems it is the carbon material that is responsible for the lower bioavailability of PAHs (like in the case of C_{tot}). In the control treatment, on the other hand, processes probably associated with the activity of microorganisms, which are determined by changes in pH, play an important role in C_{free} PAH losses. The positive correlation between pH and C_{free} PAHs may be associated with the higher extractability of PAHs from the material with increasing pH (Yu et al., 2018). It should be emphasized that pH, apart from microbial activity, regulates many processes that may indirectly influence the persistence of PAHs (e.g. the availability of nutrients to PAH-degrading microorganisms (Pawar, 2015)).

The observed strong correlations between C_{free} PAHs and the TOC content in the compost (Table S7) result from the strong affinity of TOC for PAHs, which impacts their immobilization by binding them in the matrix (in this case, most probably by BC which was characterized by a 85% TOC content). As in the case of C_{tot}, the most frequent correlations with TOC were found for the compost with the higher BC addition. A high TOC content in the material promotes reduced bioavailability of the investigated compounds over the composting period, which are permanently sequestered in the matrix and are not easily extracted into the environment (Oleszczuk, 2007a).

As regards DOC, positive correlations were found with some of the 4-6-ring PAHs for the treatments with BC (Table S7). Studies (Kobayashi et al., 2008; Mukherjee and Zimmerman, 2013) demonstrate that DOC exhibits high affinity for PAHs, which potentially increases their solubility and extractability. Additionally, interactions with DOC are related to the hydrophobicity of a given compound (the more hydrophobic it is, the stronger they are) (King et al., 2004). Therefore, by achieving a lower DOC content than in the control treatment (Fig. 1E), composting with BC addition resulted in a lower degree of leaching of PAHs with DOC, and this translated into a lower content of C_{free} PAHs than for the control (this effect was evident to a greater degree for the higher BC rate).

Similarly as in the case of C_{tot} PAHs, negative correlations were noted between C_{free} PAHs and ash, but they occurred primarily for the low molecular weight PAHs (Table S7) and were found more frequently for the treatments with BC. The effect of ash on C_{free} was most probably attributable to the occurrence of the same processes as in the case of C_{tot} PAHs. The larger amount of the mineral fraction incorporated with the higher dose of BC caused the binding of the PAHs and hence the lowest C_{free} content was obtained for the 5% BC rate among the treatments studied.

4. Conclusions

The addition of BC to SL affected both C_{tot} and C_{free} PAHs at different composting stages. In the treatments with BC, a relatively better reduction of Σ16 C_{tot} PAHs occurred than for the control treatment. This may be associated with the fact that BC provides favorable conditions for the development of microorganisms and thereby the level of PAH degradation increases. 1% BC addition proved to be more effective in reducing the content of Σ16 C_{tot} PAHs than the treatment with the 5% BC rate. A too large addition of BC had a negative effect on the final PAH content in the mature compost. On the one hand, it could have been associated with the incorporation of a too large amount of PAHs with the higher dose of BC and with prevention of their effective degradation. A too high rate of BC also inhibited the processes related to effective degradation PAHs as a result of their being bound by BC. Based on the analysis of the changes in the K_{oc} coefficient, it was found that during compost maturation interactions between PAHs and the composted material are strengthened. Log K_{oc} had the highest values for the compost mixture with 5% BC addition, which may explain the reduced degradation of C_{tot} PAHs during composting compared to the lower BC rate and the control treatment. In the case of the higher BC addition, PAHs showed a limited degree of degradation, but they were strongly bound to the matrix through adsorption/sequestration, which reduced their leaching. Based on the evaluation of the correlations between the changes in PAH content and the physicochemical properties of the material during composting, it was found that TOC, DOC, and ash are predominantly responsible for PAH losses during the process in the case of C_{tot} and additionally pH in the case of C_{free} PAHs.

Statements and declarations

Ethical approval

Not applicable.

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CRediT authorship contribution statement

Aleksandra Rombel: Conceptualization, Methodology, Investigation, Writing - original draft. **Krzysztof Różyło:** Investigation, Methodology. **Patryk Oleszczuk:** Conceptualization, Writing - review & editing, Supervision.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.119628.

References

Amir, S., Hafidi, M., Merlina, G., Hamdi, H., Revel, J.C., 2005. Fate of polycyclic aromatic hydrocarbons during composting of lagooning sewage sludge. Chemosphere 58, 449–458. https://doi.org/10.1016/J.CHEMOSPHERE.2004.09.039.

Antizar-Ladislao, B., Lopez-Real, J.M., Beck, A.J., 2004. Bioremediation of polycyclic aromatic hydrocarbon (PAH)-contaminated waste using composting approaches. Crit. Rev. Environ. Sci. Technol. 34, 249–289. https://doi.org/10.1080/10643380490434119.

Anyika, C., Abdul Majid, Z., Ibrahim, Z., Zakaria, M.P., Yahya, A., 2015. The impact of biochars on sorption and biodegradation of polycyclic aromatic hydrocarbons in soils—a review. Environ. Sci. Pollut. Res. 22, 3314–3341. https://doi.org/10.1007/S11356-014-3719-5.

Cai, Q.Y., Mo, C.H., Wu, Q.T., Zeng, Q.Y., Katsoyiannis, A., Férard, J.F., 2007. Bioremediation of polycyclic aromatic hydrocarbons (PAHs)-contaminated sewage sludge by different composting processes. J. Hazard Mater. 142, 535–542. https://doi.org/10.1016/J.JHAZMAT.2006.08.062.

CEC, 2000. Working Document on Sludge, 3rd draft. Council of the European Community, Brussels.

Chen, H., Awasthi, S.K., Liu, T., Duan, Y., Zhang, Z., Awasthi, M.K., 2020. Compost biochar application to contaminated soil reduces the (im)mobilization and phytoavailability of lead and copper. J. Chem. Technol. Biotechnol. 95, 408–417. https://doi.org/10.1002/JCTB.5986.

Chen, P., Shen, G., Liang, J., 2022. Dissipation and risk assessment of polycyclic aromatic hydrocarbons in industrial-scale biochar composting. J. Soils Sediments 22, 1976–1986.

Das, S.K., Ghosh, G.K., Avasthe, R., 2020. Application of biochar in agriculture and environment, and its safety issues. Biomass Convers. Biorefinery 13, 1359–1369. https://doi.org/10.1007/S13399-020-01013-4.

Du, J., Zhang, Y., Qu, M., Yin, Y., Fan, K., Hu, B., Zhang, H., Wei, M., Ma, C., 2019. Effects of biochar on the microbial activity and community structure during sewage sludge composting. Bioresour. Technol. 272, 171–179. https://doi.org/10.1016/J.BIORTECH.2018.10.020.

EBC, 2015. European Biochar Certificate - Guidelines for a Sustainable Production of Biochar. European Biochar Foundation (EBC). https://doi.org/10.13140/RG.2.1.4658.7043.

Ehlers, L.J., Luthy, R.G., 2003. Peer reviewed: contaminant bioavailability in soil and sediment. Environ. Sci. Technol. 37, 295A–302A. https://doi.org/10.1021/ES032524F.

Galey, B., Gautier, M., Kim, B., Blanc, D., Chatain, V., Ducom, G., Dumont, N., Gourdon, R., 2022. Trace metal elements vaporization and phosphorus recovery during sewage sludge thermochemical treatment – a review. J. Hazard Mater. 424, 127360 https://doi.org/10.1016/J.JHAZMAT.2021.127360.

Gao, N., Kamran, K., Quan, C., Williams, P.T., 2020. Thermochemical conversion of sewage sludge: a critical review. Prog. Energy Combust. Sci. 79, 100843 https://doi.org/10.1016/J.PECS.2020.100843.

Guo, S., Dong, R., Chang, Z., Xie, Y., Chen, G., Long, G., 2023. Performance and microstructure of sustainable cementitious materials mixed by municipal sewage sludge ash, slag, and fly ash. Construct. Build. Mater. 367, 130028 https://doi.org/10.1016/J.CONBUILDMAT.2022.130028.

Guo, X., Liu, H., Zhang, J., 2020a. The role of biochar in organic waste composting and soil improvement: a review. Waste Manag. 102, 884–899. https://doi.org/10.1016/j.wasman.2019.12.003.

Guo, Y., Rene, E.R., Wang, J., Ma, W., 2020b. Biodegradation of polyaromatic hydrocarbons and the influence of environmental factors during the co-composting of sewage sludge and green forest waste. Bioresour. Technol. 297, 122434 https://doi.org/10.1016/J.BIORTECH.2019.122434.

Haritash, A.K., Kaushik, C.P., 2009. Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. J. Hazard Mater. 169, 1–15. https://doi.org/10.1016/j.jhazmat.2009.03.137.

Hawthorne, S.B., Grabanski, C.B., Miller, D.J., 2006. Measured partitioning coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: Part 1. KOC values. Environ. Toxicol. Chem. 25, 2901–2911. https://doi.org/10.1897/06-115R.1.

Hettiarachchi, H., Bouma, J., Caucci, S., Zhang, L., 2020. Organic waste composting through Nexus Thinking: linking soil and waste as a substantial contribution to sustainable development. In: Organic Waste Composting through Nexus Thinking. Springer International Publishing, pp. 1–15. https://doi.org/10.1007/978-3-030-36283-6_1.

Hilber, I., Blum, F., Leifeld, J., Schmidt, H.P., Bucheli, T.D., 2012. Quantitative determination of PAHs in biochar: a prerequisite to ensure its quality and safe application. J. Agric. Food Chem. 60, 3042–3050. https://doi.org/10.1021/JF205278V.

Hua, L., Wu, W., Liu, Y., Chen, Y., McBride, M.B., 2008. Effect of composting on polycyclic aromatic hydrocarbons removal in sewage sludge. Water Air Soil Pollut. 193, 259–267. https://doi.org/10.1007/S11270-008-9687-Y.

Keiluweit, M., Kleber, M., Sparrow, M.A., Simoneit, B.R.T., Prahl, F.G., 2012. Solvent-extractable polycyclic aromatic hydrocarbons in biochar: influence of pyrolysis temperature and feedstock. Environ. Sci. Technol. 46, 9333–9341. https://doi.org/10.1021/ES302125K.

Kim, J.H., Moon, J.K., Li, Q.X., Cho, J.Y., 2003. One-step pressurized liquid extraction method for the analysis of polycyclic aromatic hydrocarbons. Anal. Chim. Acta 498, 55–60. https://doi.org/10.1016/J.ACA.2003.08.049.

King, A.J., Readman, J.W., Zhou, J.L., 2004. Determination of polycyclic aromatic hydrocarbons in water by solid-phase microextraction–gas chromatography–mass spectrometry. Anal. Chim. Acta 523, 259–267. https://doi.org/10.1016/J.ACA.2004.07.050.

Kobayashi, T., Navarro, R.R., Tatsumi, K., Iimura, Y., 2008. Influence of compost amendment on pyrene availability from artificially spiked soil to two subspecies of Cucurbita pepo. Sci. Total Environ. 404, 1–9. https://doi.org/10.1016/J.SCITOTENV.2008.06.011.

Kończak, M., Godlewska, P., Wiśniewska, M., Oleszczuk, P., 2023. Chemical properties of soil determine the persistence and bioavailability of polycyclic aromatic hydrocarbons in sewage sludge- or sewage sludge/biomass-derived biochar-amended soils. Environ. Pollut. 319, 120909 https://doi.org/10.1016/J.ENVPOL.2022.120909.

Kończak, M., Siatecka, A., Nazarkovsky, M.A., Czech, B., Oleszczuk, P., 2021. Sewage sludge and solid residues from biogas production derived biochar as an effective bio-waste adsorbent of fulvic acids from water or wastewater. Chemosphere 278, 130447. https://doi.org/10.1016/J.CHEMOSPHERE.2021.130447.

Kopeć, M., Smreczak, B., Ukalska-Jaruga, A., Mierzwa-Hersztek, M., Gondek, K., 2017. Changes of PAHs and C humic fractions in composts with sewage sludge and biochar amendment. Desalination Water Treat. 97, 234–243. https://doi.org/10.5004/dwt.2017.21629.

Lee, B.-K., Lee, B.-K., 2010. Sources, distribution and toxicity of polyaromatic hydrocarbons (PAHs) in particulate matter. In: Air Pollution. IntechOpen. https://doi.org/10.5772/10045.

Lü, H., Chen, X.H., Mo, C.H., Huang, Y.H., He, M.Y., Li, Y.W., Feng, N.X., Katsoyiannis, A., Cai, Q.Y., 2021. Occurrence and dissipation mechanism of organic pollutants during the composting of sewage sludge: a critical review. Bioresour. Technol. 328, 124847 https://doi.org/10.1016/J.BIORTECH.2021.124847.

Ma, L., Zhang, J., Han, L., Li, W., Xu, L., Hu, F., Li, H., 2012. The effects of aging time on the fraction distribution and bioavailability of PAH. Chemosphere 86, 1072–1078. https://doi.org/10.1016/J.CHEMOSPHERE.2011.11.065.

Marcińczyk, M., Krasucka, P., Duan, W., Pan, B., Siatecka, A., Oleszczuk, P., 2022. Ecotoxicological characterization of engineered biochars produced from different feedstock and temperatures. Sci. Total Environ. 861, 160640 https://doi.org/10.1016/J.SCITOTENV.2022.160640.

Meena, A.L., Karwal, M., Dutta, D., Mishra, R.P., 2021. Composting: phases and factors responsible for efficient and improved composting consortium research platform on conservation agriculture view project Network project on organic farming view project. Agric. Food E-Newsletter 3, 85–90. https://doi.org/10.13140/RG.2.2.13546.95689.

Meng, L., Zhang, S., Gong, H., Zhang, X., Wu, C., Li, W., 2018. Improving sewage sludge composting by addition of spent mushroom substrate and sucrose. Bioresour. Technol. 253, 197–203. https://doi.org/10.1016/J.BIORTECH.2018.01.015.

Mukherjee, A., Zimmerman, A.R., 2013. Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar–soil mixtures. Geoderma 193–194, 122–130. https://doi.org/10.1016/J.GEODERMA.2012.10.002.

Nguyen, M.K., Lin, C., Hoang, H.G., Sanderson, P., Dang, B.T., Bui, X.T., Nguyen, N.S.H., Vo, D.V.N., Tran, H.T., 2022. Evaluate the role of biochar during the organic waste composting process: a critical review. Chemosphere 299, 134488. https://doi.org/10.1016/J.CHEMOSPHERE.2022.134488.

Oleszczuk, P., 2007a. Changes of polycyclic aromatic hydrocarbons during composting of sewage sludges with chosen physico-chemical properties and PAHs content. Chemosphere 67, 582–591. https://doi.org/10.1016/J.CHEMOSPHERE.2006.09.067.

Oleszczuk, P., 2007b. Investigation of potentially bioavailable and sequestrated forms of polycyclic aromatic hydrocarbons during sewage sludge composting. Chemosphere 70, 288–297. https://doi.org/10.1016/J.CHEMOSPHERE.2007.06.011.

Oleszczuk, P., 2006. Persistence of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge-amended soil. Chemosphere 65, 1616–1626. https://doi.org/10.1016/J.CHEMOSPHERE.2006.03.007.

Oleszczuk, P., Kuśmierz, M., Godlewska, P., Kraska, P., Pałys, E., 2016. The concentration and changes in freely dissolved polycyclic aromatic hydrocarbons in biochar-amended soil. Environ. Pollut. 214, 748–755. https://doi.org/10.1016/J.ENVPOL.2016.04.064.

Oleszczuk, P., Zielińska, A., Cornelissen, G., 2014. Stabilization of sewage sludge by different biochars towards reducing freely dissolved polycyclic aromatic hydrocarbons (PAHs) content. Bioresour. Technol. 156, 139–145. https://doi.org/10.1016/J.BIORTECH.2014.01.003.

Pawar, R.M., 2015. The effect of soil pH on bioremediation of polycyclic aromatic hydrocarbons (PAHs). J. Biorem. Biodegrad. 6, 1–14. https://doi.org/10.4172/2155-6199.1000291.

Petric, I., Helić, A., Avdić, E.A., 2012. Evolution of process parameters and determination of kinetics for co-composting of organic fraction of municipal solid waste with poultry manure. Bioresour. Technol. 117, 107–116. https://doi.org/10.1016/J.BIORTECH.2012.04.046.

Poluszyńska, J., Jarosz-Krzemińska, E., Helios-Rybicka, E., 2017. Studying the effects of two various methods of composting on the degradation levels of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. Water Air Soil Pollut. 228, 1–10. https://doi.org/10.1007/S11270-017-3481-7.

Premnath, N., Mohanrasu, K., Guru Raj Rao, R., Dinesh, G.H., Prakash, G.S., Ananthi, V., Ponnuchamy, K., Muthusamy, G., Arun, A., 2021. A crucial review on polycyclic aromatic Hydrocarbons - environmental occurrence and strategies for microbial degradation. Chemosphere 280, 130608. https://doi.org/10.1016/J.CHEMOSPHERE.2021.130608.

Rončević, S., Spasojević, J., Maletić, S., Jazić, J.M., Isakovski, M.K., Agbaba, J., Grgić, M., Dalmacija, B., 2016. Assessment of the bioavailability and phytotoxicity of sediment spiked with polycyclic aromatic hydrocarbons. Environ. Sci. Pollut. Res. 23, 3239–3246. https://doi.org/10.1007/s11356-015-5566-4.

Said-Pullicino, D., Erriquens, F.G., Gigliotti, G., 2007. Changes in the chemical characteristics of water-extractable organic matter during composting and their influence on compost stability and maturity. Bioresour. Technol. 98, 1822–1831. https://doi.org/10.1016/J.BIORTECH.2006.06.018.

Sánchez-García, M., Alburquerque, J.A., Sánchez-Monedero, M.A., Roig, A., Cayuela, M. L., 2015. Biochar accelerates organic matter degradation and enhances N mineralisation during composting of poultry manure without a relevant impact on gas emissions. Bioresour. Technol. 192, 272–279. https://doi.org/10.1016/j.biortech.2015.05.003.

Sayara, T., Sánchez, A., 2020. Bioremediation of PAH-contaminated soils: process enhancement through composting/compost. Appl. Sci. 10, 3684. https://doi.org/10.3390/APP10113684.

Siebielska, I., 2014. Comparison of changes in selected polycyclic aromatic hydrocarbons concentrations during the composting and anaerobic digestion processes of municipal waste and sewage sludge mixtures. Water Sci. Technol. 70, 1617–1624. https://doi.org/10.2166/WST.2014.417.

Stańczyk-Mazanek, E., Stępniak, L., Kępa, U., 2019. Analysis of migration of polycyclic aromatic hydrocarbons from sewage sludge used for fertilization to soils, surface waters, and plants. Water 11, 1270. https://doi.org/10.3390/W11061270, 2019.

Stefaniuk, M., Oleszczuk, P., 2016. Addition of biochar to sewage sludge decreases freely dissolved PAHs content and toxicity of sewage sludge-amended soil. Environ. Pollut. 218, 242–251. https://doi.org/10.1016/j.envpol.2016.06.063.

Sun, K., Kang, M., Zhang, Z., Jin, J., Wang, Z., Pan, Z., Xu, D., Wu, F., Xing, B., 2013. Impact of deashing treatment on biochar structural properties and potential sorption mechanisms of phenanthrene. Environ. Sci. Technol. 47, 11473–11481. https://doi.org/10.1021/es4026744.

Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere 125, 70–85. https://doi.org/10.1016/j.chemosphere.2014.12.058.

Tomczyk, B., Siatecka, A., Gao, Y., Ok, Y.S., Bogusz, A., Oleszczuk, P., 2020. The convertion of sewage sludge to biochar as a sustainable tool of PAHs exposure reduction during agricultural utilization of sewage sludges. J. Hazard Mater. 392, 122416 https://doi.org/10.1016/j.jhazmat.2020.122416.

Verma, S., Kumar Awasthi, M., Liu, T., Kumar Awasthi, S., Yadav, V., Ravindran, B., Syed, A., Eswaramoorthy, R., Zhang, Z., 2023. Biochar as smart organic catalyst to regulate bacterial dynamics during food waste composting. Bioresour. Technol. 373, 128745 https://doi.org/10.1016/J.BIORTECH.2023.128745.

Wang, J., Bao, H., Pan, G., Zhang, H., Li, Jia, Li, Jiao, Cai, J., Wu, F., 2021. Combined application of rhamnolipid and agricultural wastes enhances PAHs degradation via increasing their bioavailability and changing microbial community in contaminated soil. J. Environ. Manag. 294 https://doi.org/10.1016/J.JENVMAN.2021.112998.

Wong, J.W.C., Wan, C.K., Fang, M., 2002. Pig manure as a co-composting material for biodegradation of PAH-contaminated soil. Environ. Technol. 23, 15–26. https://doi.org/10.1080/09593332508618438.

Xu, X., Zhao, Y., Sima, J., Zhao, L., Mašek, O., Cao, X., 2017. Indispensable role of biochar-inherent mineral constituents in its environmental applications: a review. Bioresour. Technol. 241, 887–899. https://doi.org/10.1016/J.BIORTECH.2017.06.023.

Yañez, R., Alonso, J.L., Díaz, M.J., 2009. Influence of bulking agent on sewage sludge composting process. Bioresour. Technol. 100, 5827–5833. https://doi.org/10.1016/J.BIORTECH.2009.05.073.

Yu, L., Duan, L., Naidu, R., Semple, K.T., 2018. Abiotic factors controlling bioavailability and bioaccessibility of polycyclic aromatic hydrocarbons in soil: putting together a bigger picture. Sci. Total Environ. 613–614, 1140–1153. https://doi.org/10.1016/J.SCITOTENV.2017.09.025.

Zhang, J., Lü, F., Shao, L., He, P., 2014. The use of biochar-amended composting to improve the humification and degradation of sewage sludge. Bioresour. Technol. 168, 252–258. https://doi.org/10.1016/j.biortech.2014.02.080.

Zhou, Q., Liu, G., Hu, Z., Zheng, Y., Lin, Z., Li, P., 2023. Impact of different structures of biochar on decreasing methane emissions from sewage sludge composting. Waste Manag. Res. 41 https://doi.org/10.1177/0734242X221122586.

Zielińska, A., Oleszczuk, P., 2016. Effect of pyrolysis temperatures on freely dissolved polycyclic aromatic hydrocarbon (PAH) concentrations in sewage sludge-derived biochars. Chemosphere 153, 68–74. https://doi.org/10.1016/J.CHEMOSPHERE.2016.02.118.

Zielińska, A., Oleszczuk, P., 2015a. The conversion of sewage sludge into biochar reduces polycyclic aromatic hydrocarbon content and ecotoxicity but increases trace metal content. Biomass Bioenergy 75, 235–244. https://doi.org/10.1016/J.BIOMBIOE.2015.02.019.

Zielińska, A., Oleszczuk, P., 2015b. Evaluation of sewage sludge and slow pyrolyzed sewage sludge-derived biochar for adsorption of phenanthrene and pyrene. Bioresour. Technol. 192, 618–626. https://doi.org/10.1016/J.BIORTECH.2015.06.032.

Supporting information

The high dose of biochar reduces polycyclic aromatic hydrocarbons losses during co-composting of sewage sludge and wheat straw

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1. Materials and methods

1.1. Chemicals

Silica (SiO_2) was purchased from Macherey-Nagel GmbH & Co. KG (Germany). Sodium azide (grade ≥ 99%) and ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA) were provided by Sigma-Aldrich (Germany). The n-heptane (grade ≥ 99%), hexane (grade ≥ 95%) solvents, and copper (Cu) were all supplied by Merck (Germany). Acetone (grade ≥ 99.5%) was purchased from POCH (Poland). Isooctane (for GC analysis, grade ≥ 99.5%) was supplied by Chempur (Poland). Polyoxymethylene (POM) was provided by C.S. Hyde Co. (USA). Milli Q water with electrical conductivity below 0.05 μS cm^{-1} was used to prepare all solutions.

1.2. Composting feedstock

SL was collected from the Municipal Sewage Treatment Plant in Zamość (50°44'9.39" N, 23°14'14.92" E, Poland). SL used in the experiment was obtained as a result of anaerobic digestion and was mechanically pre-dehydrated on a belt press (20% dry mass (DM)). The moisture of raw SL was about 80%, the content of TOC = 34%, N = 4.5%, H = 4.9%, pH = 6.81, EC = 5.84 mS/cm, ash content = 2.4%, and DOC = 630 mg/L. WS was obtained from a conventional farm specializing in crop production in Liśnik Mały (50°53′25.13″N, 22°05′36.77″E, Poland). WS was shredded during standard harvesting of wheat yield. The moisture of WS was 12%, content of TOC = 53%, N = 0.69%, H = 6.78%, and ash = 4.2%. The BC used for the experiment was obtained commercially by pyrolysis of wood chips (deciduous-coniferous) at a temperature of 650 °C (Fluid S.A., Sędziszów, Poland). The pH was 6.65, EC = 0.56 mS/cm, ash content = 37%, TOC = 85%, and DOC = 448.5 mg/L. In order to introduce beneficial microorganisms isolated from the soil, which are responsible for the proper course of composting, the bicompost microbiological preparation was used (Organika-Agrarius Sp. z o.o., Przemyśl, Poland). It contains mixture of various strains of *Bacillus* sp. bacteria in the amount of not less than $1 \cdot 10^9$ JTK in 1 g of the product. A solution was prepared by dissolving of 20 g in 10 L of DI water and 1 L of the solution was added per bioreactor (100 L of mixed material).

1.3. GC-MS quantification

The GC-MS was used under the selected ion monitoring mode and equipped with a single quadrupole. A Rxi®-5ms crossbond® 5% diphenyl and 95% dimethyl polysiloxane fused capillary column (length 30 m, id 0.25 mm, and 0.25 μm film thickness) from Restek (Glastron, France) was used. As the carrier gas helium at a constant flow rate of 1.5 mL/min was used.

The GC oven temperature was programmed to ramp from 75°C (hold time – 30 sec) to 245°C at 25°C/min, subsequently to 300°C at 4°C/min (hold time – 60 sec). The injector temperature was set to 310°C. Mass spectra were acquired at the electron ionization mode, while selected ion monitoring (SIM) mode was performed using the molecular ions selective for individual PAHs. The recovery (%) for individual PAHs ranged from 87.1 to 94.5 %.

1.4. K_{oc} coefficient

For the evaluation of individual PAH bioavailability and general behavior in the environment, the PAH partitioning coefficient between organic carbon and water (K_{oc}) was used[1]. The following equations were implemented to calculate above mentioned coefficient:

$$K_d = \frac{\Sigma 16\ C_{tot}\ PAHs}{\Sigma 16\ C_{free}\ PAHs} \qquad (1)$$

$$K_{oc} = \frac{K_d}{TOC} \cdot 100\% \qquad (2)$$

where: Σ16 C_{tot} PAHs is solvent extractable content of Σ16 PAHs given in µg/kg, Σ16 C_{free} PAHs is freely dissolved content of Σ16 PAHs given in µg/L, and TOC is total organic carbon given in %.

2. Results and discussion

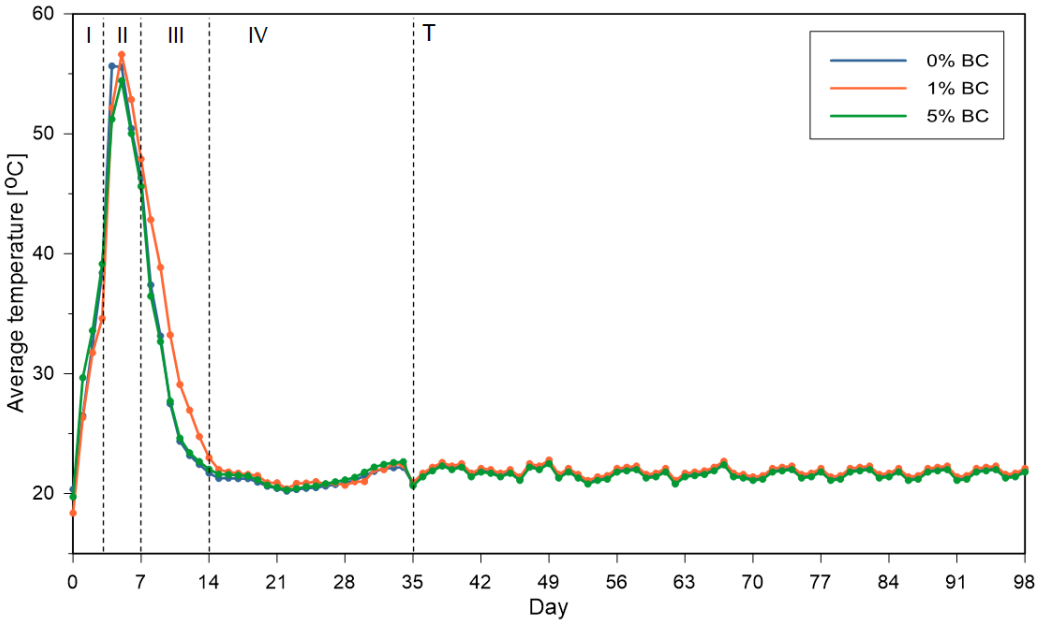

Fig. S1. Average temperature changes in the compost pile during composting. Composting phases: I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation. T – transfer to a plastic barrel. The values are the average of four measurements per day.

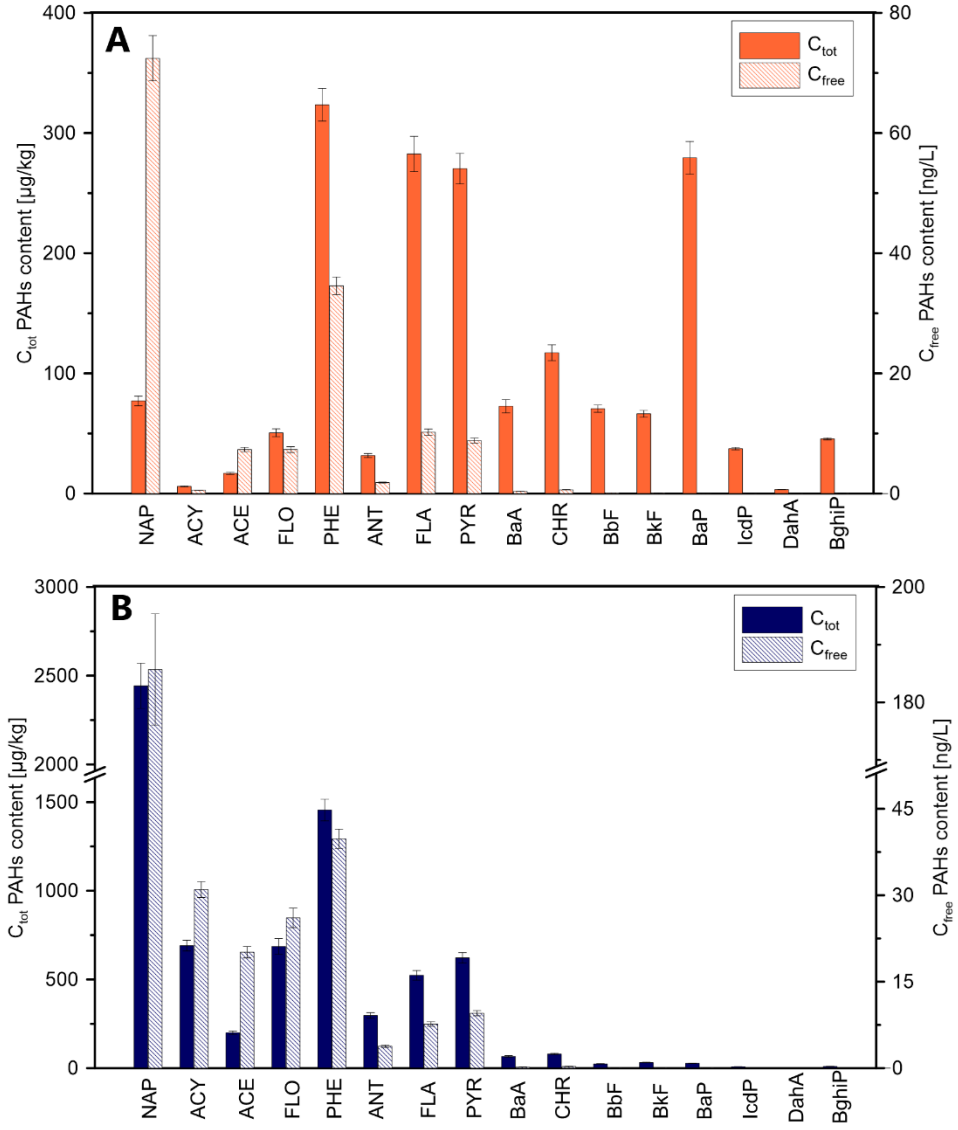

Fig. S2. The solvent extractable (C_{tot}, µg/kg) and freely dissolved (C_{free}, ng/L) content of individual PAHs in the sewage sludge (A) and biochar (B). Error bars represent standard deviation (SD, n = 3). PAHs: NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene).

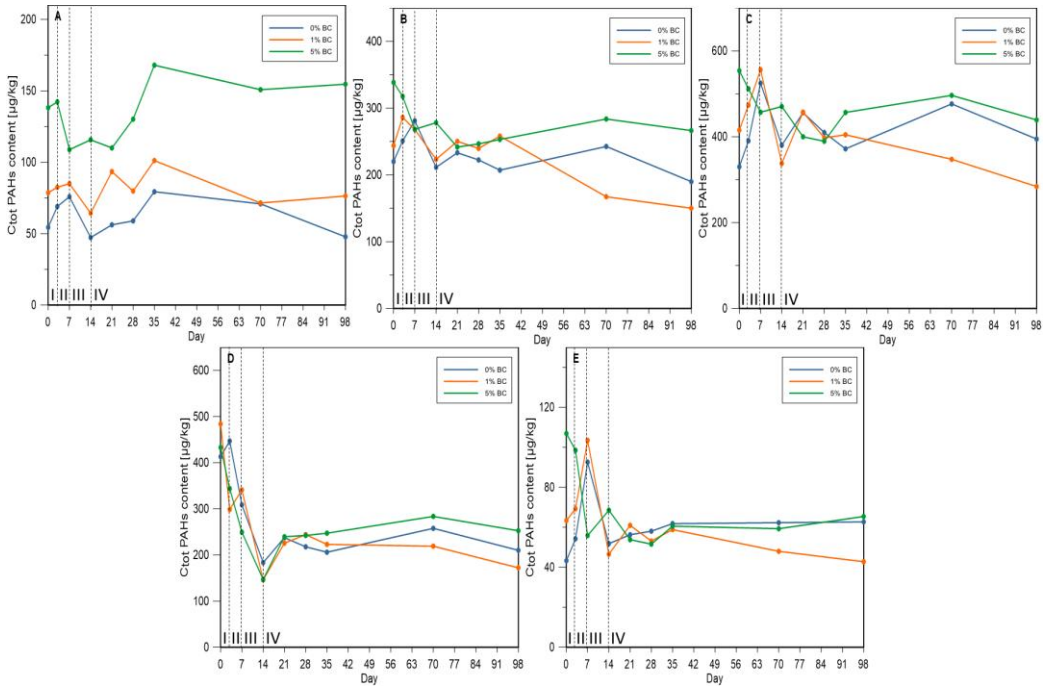

Fig. S3. Change of solvent extractable Σ16 PAHs (C_{tot}) content, depending on the number of rings, during composting (A – 2-ring, B – 3-ring, C – 4-ring, D – 5-ring, E – 6-ring PAHs). Composting phases: I – mesophilic I, II – thermophilic, III – mesophilic II, IV – maturation.

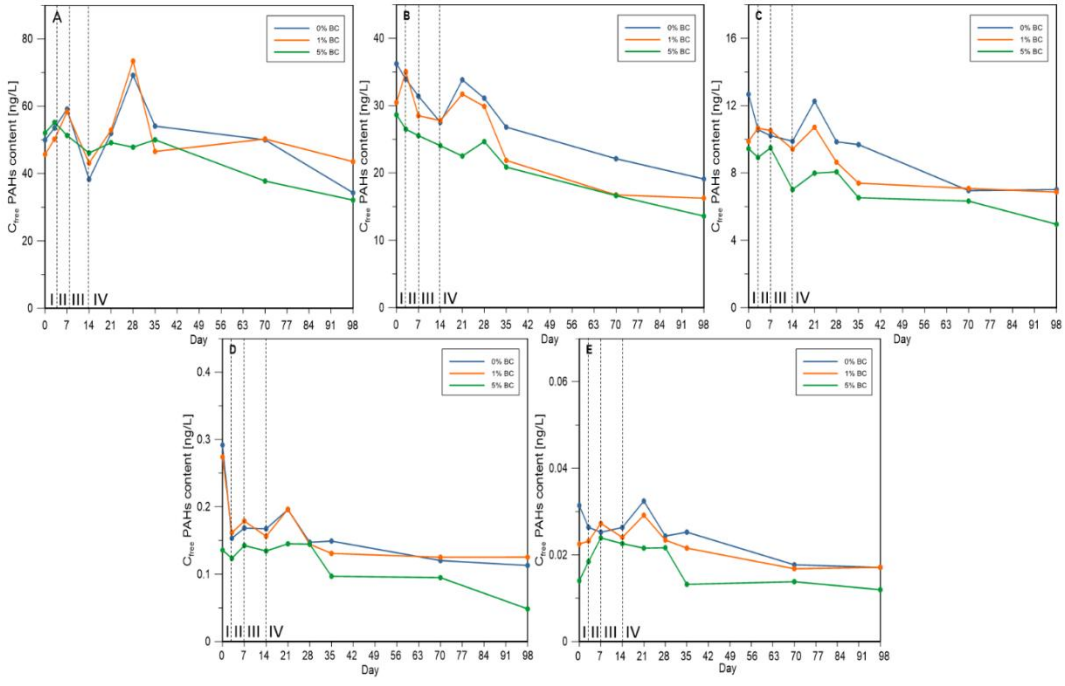

Fig. S4. Change of freely dissolved Σ16 PAHs (C_{free}) content, depending on the number of rings, during composting (A – 2-ring, B – 3-ring, C – 4-ring, D – 5-ring, E – 6-ring PAHs). Composting phases: I – mesophilic I, II – thermophilic, III – mesophilic II, IV – maturation.

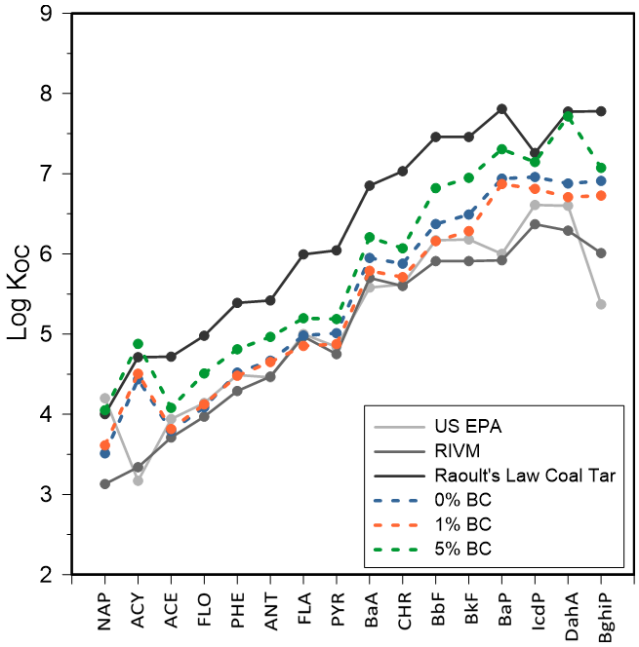

Fig. S5. Log K_{oc} values [L/kg] for individual PAHs in the end of the present experiment compared to recommended values from RIVM for soils[2], US EPA for sediments[3], and Raoult's Law Coal Tar sorption model[4]. PAHs: NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene).

The course of dependence for the control and the lower dose of BC is very similar to the values recommended by the US EPA[3] for sediments (small differences were observed for NAP, ACY, BaP and BghiP). A similar course of dependence can also be observed for low molecular weight PAHs in the context of the values recommended by RIVM[2] for soils. Importantly, for 5- and 6-ring PAHs, the log K_{oc} values clearly exceed the previously mentioned values, which shows that the composts obtained in this experiment should not have a negative impact on the environment, because of strong bonding of high molecular weight PAHs to the matrix. Log K_{oc} for most PAHs and in all experimental variants are lower than those resulting from Raoult's Law Coal Tar sorption model[4], which is better suited to describe the adsorption of PAHs in soil than in sludge or compost[1].

Table S1. Temperature of the compost pile and various gases concentration in the exhaust gas mixture during composting. Composting phases: I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation. Nd – not detected.

Day	Composting phase	Average temperature [°C]	O_2 [%]	CO_2 [%]	CO [ppm]	NO [ppm]	CH_4 [ppm]	N_2 [%]
0% BC								
0	I	20.4	8.3	10.4	10	2	1340	81.1
3	I	38.4	15.5	5.2	2	11	120	79.4
7	II	46.3	15.5	5.4	1	1	350	79.1
14	III	21.7	20.2	0.5	nd	5	nd	79.4
21	IV	20.4	20.3	0.4	nd	4	nd	79.2
28	IV	20.9	20.4	0.3	nd	3	nd	79.2
35	IV	20.8	20.7	0.2	nd	1	nd	79.2
1% BC								
0	I	18.4	15.0	5.1	3	3	nd	79.9
3	I	34.6	14.1	6.5	3	54	nd	79.4
7	II	47.9	14.7	5.9	6	1	700	79.3
14	III	23.0	19.8	0.9	1	1	nd	79.3
21	IV	20.9	19.7	0.8	nd	1	nd	79.1
28	IV	20.7	19.6	0.6	nd	1	nd	79.2
35	IV	20.9	19.4	0.5	nd	nd	nd	79.2
5% BC								
0	I	19.7	13.0	6.9	6	2	260	80.1
3	I	39.2	13.9	6.4	5	60	nd	79.7
7	II	45.6	15.5	5.1	3	nd	580	79.4
14	III	22.0	20.2	0.7	1	1	nd	79.2
21	IV	20.5	19.9	0.5	1	1	nd	79.3
28	IV	21.1	19.6	0.4	1	1	nd	79.2
35	IV	20.7	19.4	0.3	1	nd	nd	79.1

Table S2. Physico-chemical properties of compost depending on the composting phase (I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation).

Day	Composting phase	Moisture [%]	pH	Ash [%]	TOC [%]	DOC [mg/L]
0% BC						
0	I	75.0	6.87	18.4	42.9	1339
3	I	66.7	5.92	18.2	44.5	1786
7	II	67.8	6.53	19.7	42.3	3513
14	III	61.0	6.44	20.7	38.9	2683
21	IV	65.0	6.86	24.6	37.7	2353
28	IV	72.1	6.81	22.8	40.2	1956
35	IV	78.1	6.93	24.1	40.7	1528
70	IV	79.4	5.86	25.9	36.3	863.1
98	IV	77.1	5.09	24.5	34.8	829.5
1% BC						
0	I	71.6	6.83	16.6	45.0	1218
3	I	72.8	5.66	19.3	43.2	1554
7	II	69.8	6.38	19.8	40.2	2884
14	III	57.2	6.18	21.5	42.4	2498
21	IV	67.5	6.73	22.6	40.1	1750
28	IV	79.1	6.71	22.6	41.8	1313
35	IV	72.6	6.77	22.5	42.0	1102
70	IV	75.6	6.41	26.7	39.3	663.2
98	IV	75.2	5.61	26.2	38.0	621.7
5% BC						
0	I	73.3	6.83	16.6	46.3	1164
3	I	72.1	5.77	19.0	44.2	1693
7	II	63.4	6.62	21.9	43.3	3044
14	III	64.5	6.28	23.6	42.9	2688
21	IV	69.2	6.63	24.9	42.2	1818
28	IV	77.2	6.74	24.9	40.9	1181
35	IV	73.6	6.71	22.6	42.0	1167
70	IV	72.2	6.02	26.4	41.8	645.7
98	IV	75.2	5.55	25.5	38.6	589.1

Table S3. Solvent extractable (C_{tot}) [µg/kg] and freely dissolved (C_{free}) [ng/L] PAHs content in sewage sludge and biochar.

Compound	Sewage sludge		Biochar	
	C_{tot} [µg/kg]	C_{free} [ng/L]	C_{tot} [µg/kg]	C_{free} [ng/L]
NAP	77.1±4.58	72.4±3.44	2443±112	185.7±13.0
ACY	5.96±0.30	0.56±0.03	690.8±61.7	31.0±2.72
ACE	16.8±1.10	7.32±0.39	199.6±17.2	20.1±0.94
FLO	50.5±2.57	7.31±0.59	686.1±41.9	26.1±2.15
PHE	323.5±25.9	34.6±3.19	1455±155.5	39.8±2.62
ANT	31.6±2.64	1.82±0.12	296.8±18.7	3.81±0.26
FLA	282.6±19.2	10.2±0.67	523.4±35.4	7.65±0.49
PYR	270±19.7	8.82±0.63	622.1±47.1	9.54±0.86
BaA	72.7±4.82	0.343±0.03	66.0±5.03	0.2±0.02
CHR	117.2±10.4	0.613±0.04	79.7±7.62	0.29±0.02
BbF	70.6±6.3	0.129±0.01	23.9±1.65	0.035±0.003
BkF	66.4±5.71	0.105±0.01	31.7±2.46	0.038±0.003
BaP	279.4±22.6	0.078±0.005	27.2±1.70	0.041±0.003
IcdP	37.4±2.60	0.022±0.002	8.11±0.70	0.005±0.0005
DahA	3.33±0.28	0.003±0.0003	0.39±0.03	0.0003±0.00003
BghiP	45.5±3.76	0.023±0.002	9.17±0.60	0.0056±0.0004

Where: NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene).

Table S4. Solvent extractable (C_{tot}) PAHs content [µg/kg] in material during composting (the values are the average of three solvent extractions).

	Day of experiment																									
	0			3			7			14			21			28			35			70			98		
Variant (% BC)	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**
NAP	54.4	78.6	138.2	69.0	82.5	142.2	75.8	85.0	108.8	47.3	64.4	115.7	56.2	93.5	110.0	59.0	79.8	130.1	79.3	101.2	167.9	70.86	71.5	150.8	47.8	76.4	154.6
ACY	3.29	5.41	15.0	5.45	6.91	13.4	6.47	7.491	9.51	3.43	3.88	8.41	4.20	5.92	8.45	3.69	5.05	10.5	5.61	10.3	3.82	4.63	4.68	12.7	3.58	5.00	12.0
ACE	13.4	16.0	19.0	15.5	18.5	18.5	17.3	16.2	17.1	11.2	12.7	15.5	14.0	16.43	16.6	14.5	16.8	17.7	14.0	17.1	16.6	16.8	11.8	18.6	11.5	11.7	18.6
FLO	27.0	33.2	53.0	32.9	40.1	51.6	42.0	36.5	39.3	27.8	28.3	39.1	31.4	33.59	35.0	29.6	32.8	37.9	26.1	38.4	30.8	31.7	19.5	42.1	20.4	17.4	37.4
PHE	160.0	168.6	218.6	177.1	196.5	203.7	189.9	183.2	180.0	151.3	161.7	191.8	163.8	174.4	162.2	157.7	167.7	159.9	144.1	171.6	182.4	170.2	117.6	185.1	139.0	104.0	174.9
ANT	16.3	20.6	32.9	19.9	24.2	30.4	25.4	24.5	22.4	17.7	16.8	23.4	19.8	19.9	19.4	16.9	17.4	20.4	17.2	20.8	19.4	19.3	13.7	25.2	15.4	12.0	23.5
FLA	131.5	155.8	201.7	148.5	174.0	184.4	189.1	198.7	167.4	141.0	124.2	171.2	163.8	167.0	148.4	150.8	144.4	144.4	134.6	150.8	168.4	176.3	124.2	180.4	141.8	102.9	159.6
PYR	119.7	147.2	186.4	139.4	168.1	175.6	184.1	195.4	167.1	139.4	127.4	169.6	169.1	166.4	147.6	150.5	142.9	143.0	135.0	148.9	163.6	175.3	127.3	178.7	142.7	101.3	156.4
BaA	30.4	43.0	62.6	38.4	50.0	56.1	57.5	64.3	46.9	38.4	33.7	51.3	46.2	48.3	41.1	42.3	44.3	40.8	39.9	40.0	48.3	48.2	37.0	52.5	42.2	30.4	49.0
CHR	48.3	69.5	103.2	64.1	81.4	95.5	94.0	97.7	75.9	61.6	52.4	78.3	77.0	75.6	62.8	66.2	65.8	61.3	62.3	65.0	76.3	76.8	58.9	84.9	68.0	49.5	74.0
BbF	31.0	44.4	72.6	39.3	51.2	65.1	66.0	72.9	45.8	40.6	35.9	23.4	49.1	53.2	41.4	45.1	44.4	39.8	37.2	42.5	48.7	49.1	37.1	50.3	45.2	32.0	51.2
BkF	30.6	43.3	91.5	40.5	54.6	74.7	81.9	84.3	49.3	42.6	36.2	29.6	52.7	52.6	43.9	44.5	44.3	42.8	39.3	44.5	47.9	50.5	36.7	55.0	48.9	32.4	52.5
BaP	349.5	392.0	254.0	356.5	187.1	192.5	147.9	169.8	152.1	99.1	73.3	91.4	124.5	115.4	146.5	125.8	152.2	155.4	125.9	133.3	145.5	154.8	142.0	172.8	111.2	104.6	140.8
IcdP	20.8	30.7	55.7	26.0	35.5	53.2	51.5	56.6	25.7	24.4	21.8	32.2	31.8	31.0	27.2	27.0	24.3	23.7	32.6	25.6	28.8	29.4	21.9	32.6	29.1	20.4	31.1
DahA	1.97	4.12	14.9	10.6	5.77	11.4	12.7	14.0	2.34	1.28	0.779	2.56	11.4	4.44	7.7	2.35	3.21	4.43	3.71	2.61	5.10	3.32	3.25	5.40	4.84	3.30	8.12
BghiP	22.5	32.7	51.2	28.2	33.8	45.3	41.1	46.9	30.1	27.5	24.7	36.3	24.5	29.9	26.6	31.1	28.8	27.9	29.2	33.2	31.8	32.9	26.1	26.70	33.7	22.4	34.4

Where: NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene).

Table S5. Freely dissolved (C_{free}) PAHs content [ng/L] in material during composting (the values are the average of three POM extraction).

	Day of experiment																										
	0			3			7			14			21			28			35			70			98		
Variant (% BC)	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**	**0%**	**1%**	**5%**
NAP	49.9	45.7	52.0	53.5	50.2	55.2	59.1	58.3	51.3	38.3	43.1	46.1	51.9	52.9	49.2	69.2	73.4	47.8	54.1	46.5	50.0	50.0	50.3	37.8	34.3	43.5	32.1
ACY	0.620	0.646	1.077	0.694	0.768	0.865	0.614	0.593	0.703	0.395	0.395	0.534	0.517	0.508	0.515	0.514	0.538	0.577	0.389	0.400	0.514	0.307	0.346	0.438	0.306	0.361	0.371
ACE	7.33	6.31	5.92	6.85	7.37	5.64	6.46	5.74	5.69	4.58	5.25	5.10	6.19	7.04	5.23	6.64	6.98	5.95	5.69	4.59	4.94	5.05	3.85	4.04	4.32	4.18	3.61
FLO	8.57	7.30	6.89	7.99	8.38	6.26	7.80	6.80	5.99	6.76	6.50	5.60	7.81	7.16	5.14	7.47	7.05	5.67	6.30	4.78	4.79	5.11	3.26	3.59	3.90	3.05	2.70
PHE	17.9	14.8	13.4	16.9	16.9	12.5	14.9	14.0	12.1	14.6	14.5	11.9	17.3	15.8	10.8	15.3	14.2	11.5	13.2	11.2	9.76	10.7	8.5	7.74	9.80	8.03	6.31
ANT	1.79	1.40	1.35	1.52	1.59	1.20	1.61	1.41	1.06	1.23	1.12	0.919	2.03	1.22	0.82	1.21	1.09	1.00	1.25	0.872	0.870	0.924	0.780	0.830	0.772	0.626	0.593
FLA	6.61	5.05	4.84	5.40	5.44	4.51	5.18	5.34	4.74	5.02	4.67	3.53	6.14	5.36	3.92	4.96	4.29	3.94	4.87	3.65	3.18	3.42	3.49	3.06	3.45	3.38	2.36
PYR	5.55	4.42	4.21	4.70	4.72	4.02	4.57	4.73	4.35	4.41	4.33	3.12	5.54	4.84	3.71	4.44	3.94	3.74	4.37	3.42	3.06	3.19	3.24	2.99	3.24	3.15	2.37
BaA	0.163	0.117	0.141	0.151	0.177	0.134	0.166	0.140	0.127	0.163	0.149	0.128	0.193	0.177	0.123	0.150	0.140	0.133	0.142	0.092	0.102	0.117	0.117	0.092	0.110	0.115	0.071
CHR	0.343	0.279	0.259	0.316	0.321	0.258	0.297	0.309	0.271	0.287	0.268	0.238	0.376	0.335	0.238	0.295	0.269	0.251	0.296	0.238	0.193	0.224	0.239	0.191	0.210	0.225	0.147
BbF	0.076	0.060	0.054	0.067	0.067	0.055	0.067	0.072	0.063	0.071	0.065	0.059	0.083	0.078	0.057	0.065	0.061	0.062	0.065	0.052	0.047	0.050	0.050	0.041	0.045	0.052	0.018
BkF	0.061	0.048	0.043	0.057	0.050	0.041	0.055	0.058	0.052	0.054	0.052	0.049	0.068	0.063	0.047	0.053	0.050	0.046	0.055	0.043	0.022	0.038	0.041	0.033	0.037	0.039	0.014
BaP	0.150	0.163	0.036	0.027	0.043	0.025	0.044	0.046	0.026	0.041	0.037	0.024	0.041	0.053	0.039	0.028	0.031	0.036	0.027	0.033	0.028	0.031	0.032	0.020	0.030	0.033	0.016
IcdP	0.015	0.011	0.009	0.013	0.011	0.009	0.012	0.013	0.011	0.013	0.011	0.011	0.015	0.014	0.010	0.011	0.011	0.010	0.012	0.010	0.004	0.007	0.007	0.006	0.007	0.007	0.005
DahA	0.005	0.003	0.002	0.001	0.002	0.002	0.003	0.003	0.003	0.002	0.002	0.002	0.004	0.003	0.002	0.001	0.002	0.001	0.002	0.002	0.001	0.001	0.002	0.001	0.001	0.002	0.000
BghiP	0.016	0.012	0.005	0.013	0.013	0.010	0.013	0.014	0.013	0.014	0.013	0.012	0.017	0.016	0.011	0.013	0.013	0.012	0.014	0.012	0.010	0.010	0.009	0.008	0.010	0.010	0.007

Where: NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene).

147 **Table S6.** Pearson correlation coefficients for the relation between C_{tot} of individual PAHs and
148 Σ16 C_{tot} PAHs and physico-chemical characteristics of composts.

PAH	0% BC			1% BC			5% BC		
	Ash	TOC	DOC	Ash	TOC	DOC	Ash	TOC	DOC
NAP	0.187	0.199	-0.087	-0.134	0.027	-0.044	-0.001	-0.263	**-0.788***
ACY	-0.124	0.423	0.400	-0.210	0.131	0.053	-0.346	0.293	-0.292
ACE	-0.059	0.361	0.220	-0.654	0.569	0.254	-0.270	0.073	**-0.669***
FLO	-0.340	0.479	**0.719***	**-0.743***	0.641	0.483	**-0.727***	**0.691***	-0.038
PHE	-0.432	0.513	0.528	**-0.791***	0.662	0.624	**-0.818***	**0.763***	0.030
ANT	-0.252	0.345	**0.724***	**-0.789***	0.546	0.592	**-0.748***	0.660	-0.135
FLA	0.174	-0.102	0.446	**-0.669***	0.340	0.608	**-0.727***	**0.731***	-0.065
PYR	0.374	-0.282	0.413	-0.607	0.280	0.651	-0.612	**0.682***	0.015
BaA	0.314	-0.225	0.481	-0.536	0.146	0.627	**-0.719***	0.645	-0.147
CHR	0.264	-0.193	0.510	-0.572	0.187	0.577	**-0.769***	**0.707***	-0.103
BbF	0.180	-0.176	0.566	-0.504	0.074	**0.681***	**-0.674***	0.454	-0.438
BkF	0.071	-0.084	0.624	-0.464	0.024	**0.695***	**-0.775***	0.610	-0.335
BaP	**-0.714***	**0.709***	-0.197	**-0.705***	0.665	-0.1278	**-0.694***	0.612	-0.370
IcdP	0.0447	0.074	0.608	-0.539	0.079	**0.680***	**-0.822***	**0.702***	-0.150
DahA	-0.187	0.271	0.508	-0.339	-0.141	0.546	-0.663	0.472	-0.432
BghiP	0.134	-0.134	0.293	-0.589	0.221	0.597	**-0.889***	**0.671***	-0.014
Σ16 C_{tot} PAHs	-0.440	0.541	0.348	**-0.820***	0.537	0.451	**-0.781***	0.657	-0.309

Where: ash – mineral content [%]; TOC – total organic carbon [%], DOC – dissolved organic carbon [mg/L]; NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene); * indicates statistically significant correlation ($p < 0.05$).

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Table S7. Pearson correlation coefficients for the relation between C_{free} of individual PAHs and Σ16 C_{free} PAHs and physico-chemical characteristics of composts.

PAH	0% BC				1% BC				5% BC			
	pH	Ash	TOC	DOC	pH	Ash	TOC	DOC	pH	Ash	TOC	DOC
NAP	0.533	-0.127	0.513	0.314	0.336	-0.017	-0.033	0.152	0.576	**-0.712***	**0.769***	0.528
ACY	0.323	**-0.817***	**0.877***	0.469	-0.049	**-0.807***	0.622	0.318	0.335	**-0.953***	**0.892***	0.207
ACE	0.542	-0.601	**0.812***	0.243	0.150	-0.647	0.531	0.366	**0.679***	-0.635	**0.691***	0.502
FLO	**0.684***	**-0.704***	**0.818***	0.565	0.177	**-0.828***	**0.697***	0.590	0.592	**-0.777***	**0.853***	0.552
PHE	**0.667***	**-0.667***	**0.732***	0.470	0.178	**-0.791***	**0.672***	0.613	0.573	**-0.740***	**0.834***	0.610
ANT	0.6165	-0.464	0.557	0.519	0.072	**-0.875***	0.661	0.610	0.426	**-0.882***	**0.907***	0.281
FLA	**0.723***	-0.614	**0.667***	0.434	0.088	**-0.781***	0.487	**0.703***	0.517	**-0.744***	**0.836***	0.539
PYR	**0.740***	-0.537	0.613	0.453	0.120	**-0.752***	0.464	**0.746***	0.552	-0.661	**0.764***	0.520
BaA	**0.688***	-0.403	0.450	**0.719***	-0.249	-0.256	0.087	0.494	0.586	-0.633	**0.773***	0.556
CHR	**0.760***	-0.435	0.578	0.465	0.0847	-0.584	0.289	0.611	0.549	-0.579	**0.748***	0.665
BbF	**0.790***	-0.455	0.540	0.565	0.099	-0.487	0.152	**0.756***	**0.680***	-0.361	0.629	**0.688***
BkF	**0.770***	-0.451	0.594	0.539	0.281	-0.472	0.155	**0.783***	0.509	-0.268	0.588	**0.727***
BaP	0.3457	-0.500	0.351	-0.096	0.383	**-0.694***	0.638	-0.040	**0.799***	-0.309	0.440	0.151
IcdP	**0.713***	-0.603	0.647	0.546	0.429	-0.627	0.336	**0.750***	0.338	-0.236	0.436	**0.762***
DahA	0.500	-0.314	0.298	0.127	**0.712***	-0.597	0.349	0.514	0.283	-0.541	**0.762***	**0.741***
BghiP	**0.810***	-0.346	0.455	0.361	0.283	-0.478	0.192	**0.799***	0.267	0.328	-0.126	**0.721***
Σ16 C_{free} PAHs	**0.693***	-0.409	**0.715***	0.441	0.046	-0.512	0.412	0.381	0.594	**-0.750***	**0.821***	0.554

Where: ash – mineral content [%]; TOC – total organic carbon [%], DOC – dissolved organic carbon [mg/L]; NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene); * indicates statistically significant correlation ($p < 0.05$).

References

1. Arp HPH, Lundstedt S, Josefsson S, et al. Native oxy-PAHs, N-PACs, and PAHs in historically contaminated soils from Sweden, Belgium, and France: Their soil-porewater partitioning behavior, bioaccumulation in Enchytraeus crypticus, and bioavailability. *Environ Sci Technol*. 2014;48(19):11187-11195. doi:doi.org/10.1021/es5034469

2. Verbruggen EM. Environmental risk limits for polycyclic aromatic hydrocarbons (PAHs): For direct aquatic, benthic, and terrestrial toxicity. *RIVM Rep*. 2012;607711007:339.

3. US EPA. *Equilibrium Partitioning Sediment Guidelines (ESBs) for the Protection of Benthic Organisms: PAH Mixtures*. U.S. Environmental Protection Agency; 2003.

4. Arp HPH, Breedveld GD, Cornelissen G. Estimating the in situ sediment-porewater distribution of PAHs and chlorinated aromatic hydrocarbons in anthropogenic impacted sediments. *Environ Sci Technol*. 2009;43(15):5576-5585. doi:10.1021/ES9012905

D3

Aleksandra Rombel, Monika Raczkiewicz, Patryk Oleszczuk

Reducing metal mobility and associated ecological and human health risks in sewage sludge compost via biochar addition

Biomass Conversion and Biorefinery

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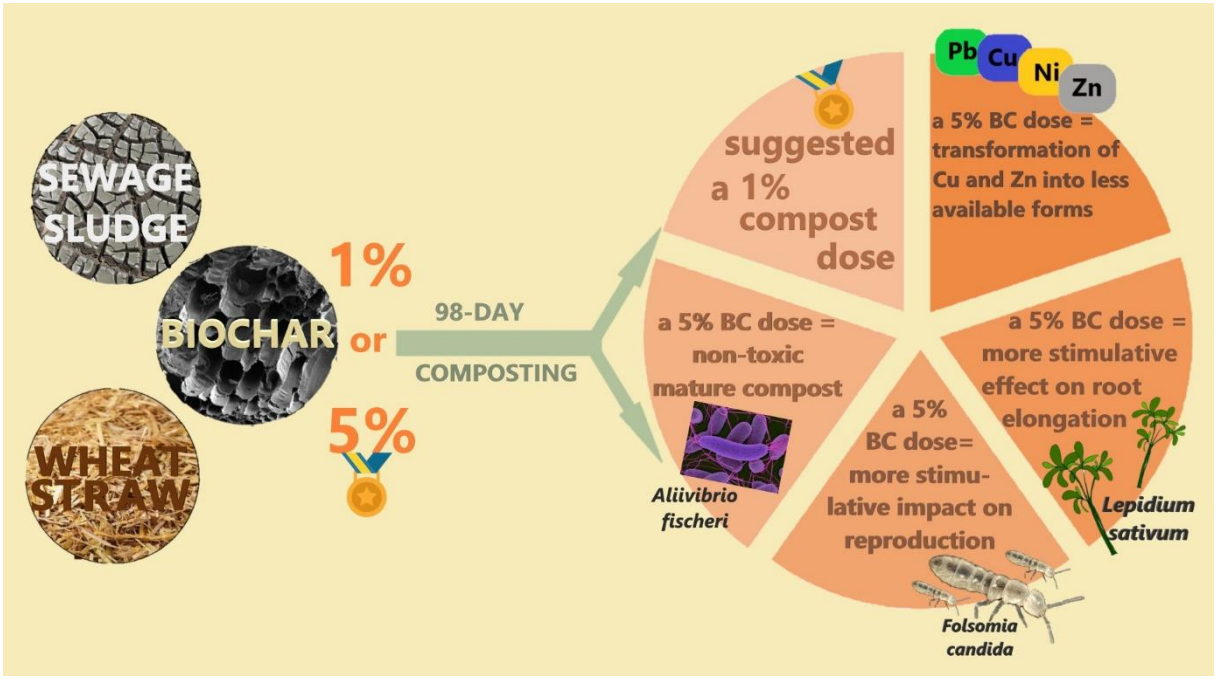
SEWAGE SLUDGE
BIOCHAR
WHEAT STRAW
1%
or
5%
98-DAY
COMPOSTING
suggested a 1% compost dose
Pb
Cu
Ni
Zn
a 5% BC dose = transformation of Cu and Zn into less available forms
a 5% BC dose = more stimulative effect on root elongation
Lepidium sativum
a 5% BC dose= more stimu-lative impact on reproduction
Folsomia candida
a 5% BC dose = non-toxic mature compost
Aliivibrio fischeri

Highlights

- Dose-dependent effects of biochar on metal speciation during sludge composting
- Integrated chemical speciation and multi-trophic ecotoxicity assessment
- 1% biochar most effective for Ni immobilization; 5% for Cu and Zn stabilization
- Biochar reduced bacterial toxicity and enhanced plant and invertebrate responses
- Findings guide optimal biochar use for safer, sustainable sludge valorization

Reducing metal mobility and associated ecological and human health risks in sewage sludge compost via biochar addition

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Abstract

This study examined the impact of biochar (BC) dose (1% and 5%) on the mobility of potentially toxic elements (Zn, Cu, Ni, Pb) and the ecotoxicity of composted sewage sludge–wheat straw feedstock in various stages of composting. Metal speciation was assessed using the sequential extraction, and toxicity was evaluated with bioassays across multiple trophic levels (bacteria, plant, and invertebrate). Results showed that BC altered metal speciation in a dose- and metal-specific manner: 1% BC effectively immobilized Ni, while 5% BC enhanced Cu and Zn stabilization. Pb remained largely immobile throughout composting. The mechanism behind the beneficial effect of BC on the metals during composting resulted mainly from the BC's extended specific surface, functional groups, and BC ability to enhance microbial activity during composting. Ecotoxicological tests confirmed that 5% BC reduced bacterial and plant toxicity and stimulated invertebrate reproduction, although excessive soil amendment (5% compost dose) negatively affected springtails. These findings demonstrate that BC addition during sewage sludge composting improves environmental safety, but optimal doses depend on both the targeted metal and the intended soil application rate.

Keywords: waste management; carbon; sludge; metals; sustainability

1. INTRODUCTION

Every year, millions of tons of various types of waste are generated globally [1]. Among the most interesting types is sewage sludge (SL), a complex material that is both promising and problematic. On the one hand, it contains valuable nutrients like nitrogen, phosphorus, calcium, and magnesium [2]. On the other hand, it accumulates various hazardous pollutants, from toxic organic and inorganic compounds to dangerous bacteria and parasite eggs [2]. One notable group of pollutants in SL is potentially toxic elements (PTEs). These elements largely determine how SL can be safely used in the environment, mainly because they are toxic, persistent, and non-biodegradable [3].

Consequently, it is crucial to employ treatment methods that, although do not eliminate PTEs, can alter the speciation and limit their mobility and bioavailability. Composting is one of the methods used to manage waste (including SL) and generate a valuable product [1]. However, composting alone is most frequently insufficient for the PTEs removal from the final product [4]. Nevertheless, there are numerous mechanisms governing passivation and/or immobilization of PTEs over the composting period.

During composting, an increase of the total PTEs is often observed [1]. The total PTEs content in compost is typically at least 20% higher than in the initial material, and in some cases, it can even double [5]. During composting, approximately half of the organic material (carbohydrates, lipids, lignin, and proteins) is transformed to carbon dioxide and evaporated, while the remainder is ultimately converted into stable compounds [5]. This results in significant reduction in the volume of the material after composting and thus results in a densification of nondegradable PTEs. Numerous organizations have established comprehensive guidelines that define permissible concentrations thresholds for PTEs in composting products and soil amendments (**Table S1**). Contemporary research has demonstrated that the mobility and bioavailability of PTEs is predominantly determined by their chemical speciation and

complexation states, rather than their total content [6]. Consequently, modern composting techniques focus not on the complete elimination of PTEs, but rather on facilitating chemical transformation that minimize their bioavailability and potential ecological impact [1]. To determine the availability of PTEs in various matrices, several methods have been proposed, such as the Tessier sequential method, and extraction proposed by the Community Bureau of Reference (BCR). The BCR method is the most commonly used, as it determines various PTEs fractions (the exchangeable (F1), the reducible (F2), the oxidizable (F3) and the residual (F4)). Moreover the BCR method is verified, simple, and not time consuming [7].

Recently, biochar (BC) has emerged as a promising bulking agent in composting applications [5], though its use in composting of SL remains understudied [4, 8, 9] despite its known benefits in reducing PTE bioavailability and mobility during composting other matrices [10]. Research by Zhao et al. (2024) demonstrated that animal-derived BC reduced Pb and Cd bioavailability by 30% and 12%, respectively, while plant-derived BC decreased Cu and Zn bioavailability by 50% and 39%, respectively. This effect stems from the formation of stable organometallic complexes (e.g. PTEs ions with phosphorus), and also new functional groups during humification. Awasthi et al. (2016) reported that BC with lime amendment achieved the most significant reduction in PTEs bioavailability (35 – 88%) compared to control and lime only treatments in SL and wheat straw composting.

Extensive research has been conducted on the addition of BC during the composting of organic feedstocks, such as various manures [11] and agricultural wastes [12]. These studies showed that BC incorporation positively influences PTEs passivation through multiple mechanisms [1]. BC addition enhances microbial activity, promotes humic acid formation which directly contributes to PTE immobilization [1]. When tested against other additives (calcium magnesium phosphate fertilizer and mushroom residue), BC demonstrated superior Cu passivation rates [13]. The efficacy of PTE immobilization often showed a positive

correlation with BC loading rates, as observed with rice husk-, peanut shell-, and wheat straw-derived BCs in swine manure composting [14]. Nevertheless, Liu et al. (2017) found optimal PTEs passivation at 1% BC dose, with higher concentration showing diminishing returns. At a 2% application rate, BC significantly altered bacterial communities and achieved greater reduction in DTPA-extractable PTEs compared to non-BC composting treatments [15].

Although BC has been extensively tested as a compost additive for agricultural wastes and manures, there is a clear research gap in its application to SL. Previous works have shown BC enhances metal immobilization and reduces ecotoxicity [16], but dose-dependent effects during SL composting remain underexplored. Moreover, few studies link chemical speciation of PTEs with ecotoxicological outcomes across multiple trophic levels.

The aim of this study was to address both gaps, providing new insight into how BC dose shapes the environmental safety of compost products derived from SL. By connecting chemical speciation with ecotoxicological outcomes, our research offers a novel perspective on understanding the environmental safety of composted materials.

2. MATERIALS AND METHODS

2.1. Composting feedstock

Sewage sludge (SL) and wheat straw were used as feedstock (1:1 dry mass). Biochar (BC) was added at concentrations of 1% or 5% (w/w). Detailed specification of the feedstocks and BC is presented in the previous paper [17]. BC was a commercially produced deciduous-coniferous material. The experiment with no BC was used as a control. Details about composting process (temperature, exhaust gas concentration, physico-chemical properties) is presented in the previous research [17]. Approximately 100 g of compost samples were collected at predetermined intervals throughout the composting duration – specifically at the initiation (day 0, T0) and subsequently on days 3, 14, and 98 (T1, T2, T3), which were

correlated with the early thermophilic phase (T1), late mesophilic *II* phase (T2), and maturation completion (T3). These sampling intervals were selected based on characteristic temperature fluctuation that distinct composting phases. The samples underwent air-drying, grinding with a laboratory knife grinder (TESTCHEM, Radlin, Poland), and were stored at 4 °C in a plastic zip-lock bags pending further analysis.

2.2. Physico-chemical characterization of samples

Detailed information regarding physico-chemical characterization of samples are presented in the supplementary information (SI). Briefly, dissolved organic carbon (DOC) and total organic carbon (TOC) were quantified using a TOC-L Analyzer equipped with SSM5000 furnace (Shimadzu, Kioto, Japan). DOC and pH values were measured in solutions after extraction. pH was determined using an HQ430D universal laboratory multi-parameter meter (HACH, Loveland, Colorado, USA). Ash content was calculated based on the mass difference after incineration in a furnace (Magma Therm, Istanbul, Turkey) at 760 °C for 6 h. Moisture content was determined by drying in a laboratory dryer (POL-EKO, Wodzisław Śląski, Poland) at 105 °C for 6 h until a constant mass was achieved.

2.3. Metal speciation analysis

Metal fractions (Zn, Cu, Ni, Pb) were sequentially extracted using a modified BCR procedure through four steps [18]. In F1, samples were mixed with acetic acid solution (0.11 mol/L) (POCH, Poland), shaken for 16 h at 22 °C (ELPIN+, Type 358A, Katowice, Poland), centrifuged (Centrifuge MPW-352, Poland), and the supernatant was collected, with residue washed using Milli Q water. For F2, the residue was treated with hydroxylammonium chloride solution (0.5 mol/L) (CHEMPUR, Poland) at pH 2, following the same separation process. F3 involved a two-stage hydrogen peroxide (8.8 mol/L) (POCH, Poland) digestion of the residue

126 (85 °C for 2h, then 100 °C for 3h), followed by ammonium acetate extraction (1 mol/L)
127 (CHEMPUR, Poland). The final F4 step consisted of aqua regia (HCl: HNO_3 3:1 v/v) digestion
128 of remaining residue using microwave treatment (120 °C, 1.5 h) (StartD, Microwave Digestion
129 System, Milestone, Italy). F1 – F3 extracts were filtered through PTFE filters and F4 through
130 paper filters, with metals quantified by ICP-OES (iCAP 7400 Duo model, Thermo Scientific)
131 using six-point calibration (0.02 – 5 mg/L). Solutions for the calibration curve were prepared
132 by diluting the multi-element standard (Merck, Germany) (concentration of metals 1 g/L) with
133 Milli Q water and acidified using HNO_3. The whole procedure was described in detail in SI.

134 ## 2.4. Bioassays

135 The ecotoxicological assessment was conducted across four critical temporal points
136 during the composting process (T0 – T3). Three ecotoxicological bioassays were selected, each
137 targeting a different trophic level: a phytotoxicity assessment using *Lepidium sativum*
138 (Phytotoxkit® test), a bacteria luminescence inhibition test employing *Aliivibrio fischeri*
139 (Microtox® test), and an invertebrate mortality/reproduction test utilizing *Folsomia candida*
140 (Collembolan test).

141 The selection of ecotoxicological tests was justified by the intention to present the
142 impact on various trophic levels of organisms. *F. candida* represents soil fauna that plays a key
143 role in nutrient cycling and organic matter decomposition [19]. The Microtox® test provides a
144 rapid and sensitive indicator of leachates' general toxicity. The Phytotoxkit® test evaluates
145 phytotoxic effects, represents primary producers, and is the most frequently used toxicity assay,
146 allowing for easier comparison with other studies. In combination, these three bioassays provide
147 a holistic assessment of compost safety.

148 The Phytotoxkit® bioassay evaluated material toxicity by measuring *L. sativum* seed
149 germination and root growth inhibition after 3-day exposure [20]. Test plates contained OECD

reference soil mixed with 1% and 5% (w/w) test material at 100% water holding capacity (WHC). Ten seeds were placed 1 cm apart on filter paper overlaying the soil mixture. Plates were incubated vertically at 25 °C for 3 days (POL-EKO dryer, Wodzisław Śląski, Poland). Root lengths were measured via Image Tool 3.0 software (UTHSCSA, San Antonio, USA) from photographs taken post-incubation.

A. fischeri luminescence inhibition was assessed at 15 min following established protocol [21]. Aqueous extracts were prepared by agitating 1 g material in 10 mL Milli Q water (24 h, 22 ± 2 °C, 150 rpm) using an ELPIN+ 358A horizontal shaker (Katowice, Poland). Extracts were filtered through qualitative paper (Munktell, Germany) and pH-adjusted using 0.01 mol/L NaOH/HCl. Analysis was performed via Microtox® M500 with MicrotoxOmni software (JJS Technical Services, Schaumburg, Illinois, USA).

Ecotoxicological test with *F. candida* was performed according to the standard method [22]. OECD soil mixed with 1 and 5% of the tested material (w/w) was placed in Petri dish, Milli Q water was added until reaching 50% WHC, and the mixture was thoroughly homogenized. Then ten adult *F. candida* were placed in each dish, and the dish was weighed. Each dish was fed weekly with yeast and watered with Milli Q water until reaching the recorded mass. After 28 days in the constant temperature (20 °C) and light conditions (16 h light/8 h dark) adults and juveniles were counted in each dish. The calculations were conducted manually using the ImageJ 1.54 software (ImageJ 1.54, Java, USA).

To ensure statistical robustness and reproducibility, all bioassays were carried out in triplicate, and statistical analyses were performed using one-way ANOVA with Tukey's post-hoc test ($p \leq 0.05$). Results are reported as mean ± SD.

3. RESULTS AND DISCUSSION

3.1. Changes in PTEs fraction distribution during composting

Throughout the composting process (in control and BC-enriched variants), Ni, Cu, and Pb were predominantly present (ranging from 52% to 100%) in the F3 fraction (associated with organic matter and sulphides) (**Fig. 1, Table S2**). While Zn also showed a dominant presence in this fraction (from 35% to 52%), its F1 and F2 fractions contributed significantly to the element's total content, indicating that Zn was the most mobile among the studied elements (**Fig. 1, Table S2**). Based on bioavailability (contribution in F1 and F2 fractions), the analyzed PTEs can be arranged in the following sequence: Zn > Ni > Cu > Pb. The presence of analyzed PTEs in F3 fraction is typical and was also observed in previous research [2].

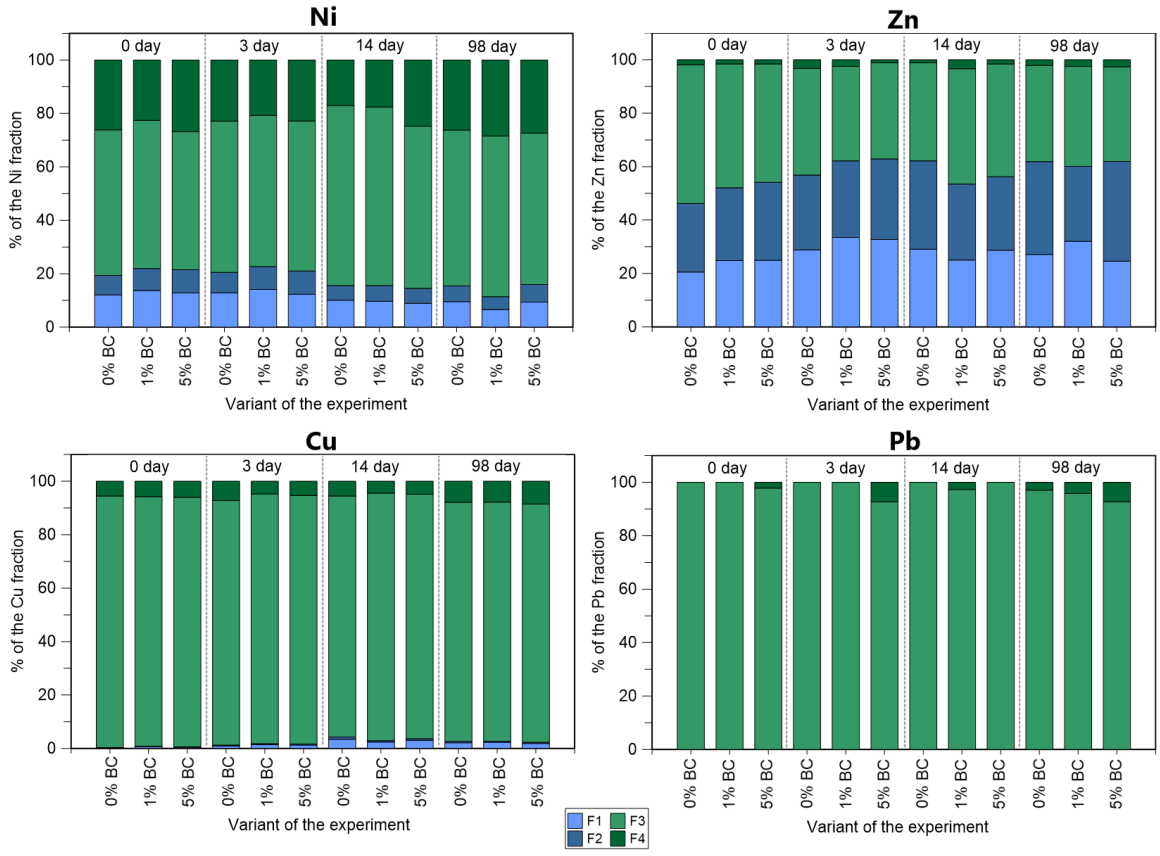


Fig. 1. Distribution of different fractions (F1, F2, F3, F4) of PTEs in materials with various biochar (BC) doses during composting.

185

186 The materials at distinct stages of composting differed slightly in the contribution of
187 individual PTE fractions (F1 – F4) (**Fig. 1 and S1**). At the beginning of composting (0 day), all
188 four PTEs tested presented a different profile of fractions F1 – F4, and differences were also
189 observed for BC-enriched variants compared to the control (**Fig. 1**). For the control, the F1 and
190 F2 contributions were observed only for Ni and Zn (12.1 and 7.3% for Ni and 20.6 and 25.6%
191 for Zn, respectively). The contribution of fraction F3 was the highest for Pb (100%), slightly
192 lower for Cu (94.1%), then similar for Ni (54.5%) and Zn (52.0%). For fraction F4, the highest
193 contribution was to Ni (26.1%), with much lower contributions to Cu (5.5%) and Zn (1.9%).
194 The addition of BC to the composted material caused differences in the percentage distribution
195 of fractions only for Zn, while the fraction distribution profile for Ni, Cu, and Pb remained
196 almost unchanged (**Fig. 1**). The differences became more pronounced with higher BC addition
197 to the composting process. For Zn, the contribution of fractions F1 – F3 increased in variants
198 enriched with BC while F4 showed a corresponding decrease.

199 The distribution patterns of PTE fractions during composting varied by PTE type, with
200 BC contribution showing no significant influence (**Fig. 1**). For Ni, fractions F1 and F2 exhibited
201 a declining through day 14 for control and day 98 for BC-enriched variants (**Fig. 1**). The F4
202 fraction initially decreased (observed on days 3 and 14 for control and 1% BC dose,
203 respectively) before returning to baseline levels by the end of the composting period (**Fig. 1**).
204 These changes in Ni fraction distribution remained consistent across experimental conditions,
205 with BC addition generally showing minimal impact on the overall patterns.

206 Changes with time for Zn were completely different from those for Ni. The readily
207 available fractions F1 and F2 showed progressive increases throughout the composting period,
208 while the moderately available fraction F3 consistently decreased across all experimental

variants (**Fig. 1**). The residual fraction F4 showed irregular variations with no discernible pattern.

Cu demonstrated more complex dynamics. F1 and F2 fractions initially increased during the composting process, but declined in the final phase (**Fig. 1**). Cu-F3 fraction showed a continuous decrease throughout composting. The residual F4 fraction after demonstrating variable behavior ultimately increased across all experimental variants. Pb exhibited minimal fractional transformation during composting, with only slight conversion from residual fraction F4 to the moderately available fraction F3 (**Fig. 1**). This transformation was quantitatively insignificant.

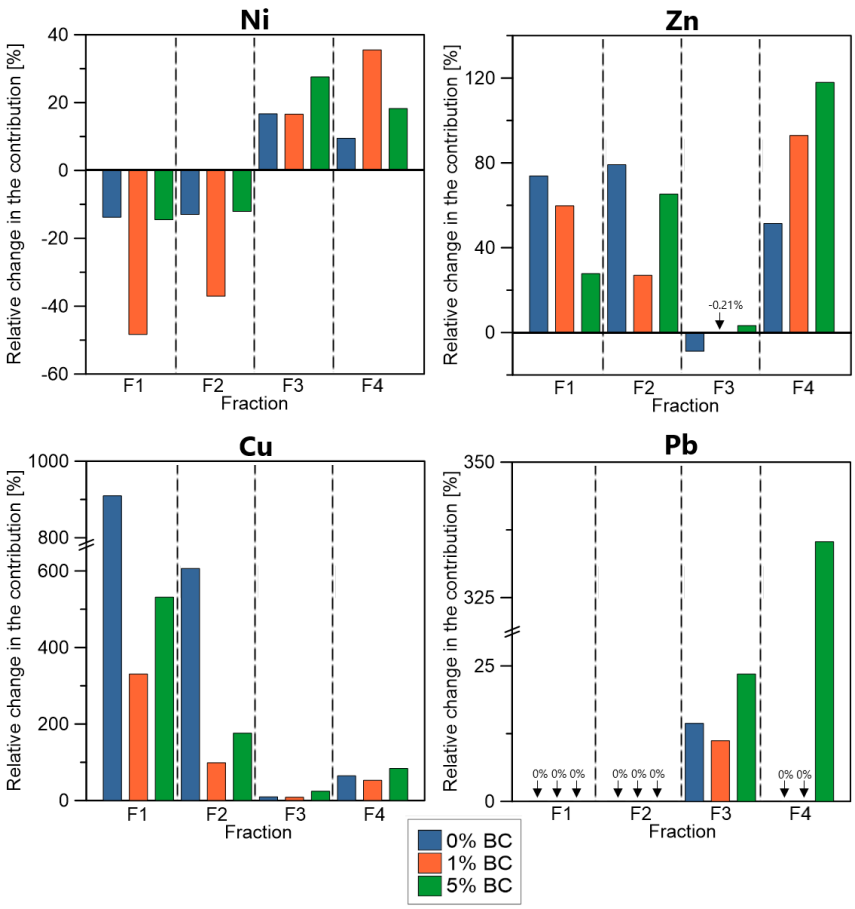


Fig. 2. Relative changes in the contribution of particular PTEs forms in composts with various biochar (BC) doses at the end of the experiment in comparison with the beginning of the treatment.

223 The relative change in distribution of the examined PTEs at the end of the experiment
224 compared to the beginning of the study is presented on **Fig. 2**. Positive values indicate an
225 increase in the contribution of a particular PTE fraction at the end of the experiment (T3)
226 compared to the beginning of composting (T0), while negative values indicate a decrease. Cu
227 and Zn exhibited the most pronounced redistribution among the studied PTEs. In the control
228 samples, the particular fractions, mostly F1, F2, and F4, showed varying changes. F1 increased
229 by 909% and 73.9%, F2 by 606% and 79.1%, and F4 by 64.6% and 51.4%, for Cu and Zn,
230 respectively (**Fig. 2**). The treatments with BC demonstrated smaller increases in the mobile
231 fractions (F1 and F2) of Cu and Zn compared to the control (**Fig. 2**). The conversion of Zn, Cu,
232 and Pb to the hard-to-access F3 and immobile F4 fractions correlated positively with BC dose
233 in the compost mixture (**Fig. 2**). BC can interact with organic substances present in compost,
234 through releasing of labile organic carbon and/or the interaction and activation of dissolved
235 organic matter [23]. This may indirectly change the availability of PTEs in the biogeochemical
236 cycle, which resulted in the transformation of PTEs into less available forms (F3 and F4) and
237 the effect deepened with the elevated BC dose. The observed increases in the F1, F2, and F4
238 fractions indicated that composting does not effectively remove Cu and Zn from the system
239 (Fig. 2). Nevertheless, among the PTEs analyzed in this study, Zn poses the lowest toxicity risk
240 [3]. Considering Ni, it was observed that the addition of BC (particularly at a lower dose)
241 contributed to a more effective reduction of the available fractions F1 and F2 contribution, as
242 well as an increase of the contribution of F3 and F4 at the end of the experiment, compared to
243 the control (**Fig. 2**). Compared to the beginning of the experiment, the control noted decrease
244 in F1 and F2 by 13.8% and 13.0%, and increase in F3 and F4 by 16.7% and 9.5%, respectively.
245 The lower addition of BC proved to be more effective for Ni, contributing to a decrease in F1
246 and F2 by 48.3% and 37.1%, and an increase in F3 and F4 by 16.6% and 35.5%. For Pb, almost
247 equal contribution of all fractions was noted at the end of the experiment as at the beginning of

248 the study, which shows that this element did not undergo visible speciation changes during the
249 process (**Fig. 2**). The only significant change was noted for the compost enriched with 5% BC,
250 which at the end of the experiment demonstrated a 335% increase in the contribution of
251 immobile F4 fraction relative to the beginning of the study. Constantly, the vast majority of Pb
252 (> 92%) was in the hard-to-access form F3 (**Fig. 2**).

253 The experimental results demonstrated that BC concentration exerted varying effects on
254 the behavior of PTEs during the SL composting process (**Fig. 2**). The effect of BC on the
255 distribution of metal fractions depended primarily on the type of PTE and its specific chemical
256 properties. The BC dose also had a variable impact, but similarly, it depended on a particular
257 PTE. For Ni, compost with 1% BC exerted a greater effect, while for Zn, Cu, and Pb, a more
258 pronounced impact was noted for a 5% BC dose. The better results achieved with a 5% BC
259 addition could be attributed to the greater number of adsorption sites, resulting in less ion
260 competition and slower saturation of the BC surface [24]. Furthermore, a higher BC content
261 facilitates humification, resulting in the formation of more stable humic substances capable of
262 permanently complexing metals [25].

263 BC addition during SL composting affected PTEs speciation, generally by slight
264 limiting their mobility and bioavailability (by reducing the F1 and F2 contribution) compared
265 to the control. The most pronounced effect was observed for Ni (37 – 48% and 12 – 14%
266 decrease of F1 and F2 for 1 and 5% BC, respectively) (**Fig. 2**). For Pb, the addition of BC
267 promoted the transfer of this element from the F3 to the F4 fraction (**Fig. 2**). This
268 immobilization of PTEs can be attributed to the combined effects of pH increase and surface
269 complexation mechanisms provided by BC [26]. Previous research have showed more evident
270 transfer of investigated PTEs from mobile to less available phases [8, 9]. This discrepancy may
271 be due to differences in BC dose and properties, composting conditions, or initial sludge
272 characteristics, highlighting the need for further investigation into the factors influencing PTEs

speciation in BC-amended SL during composting. The role of BC in PTEs passivation, removal and/or transformation may depend on many factors, including: (1) high porous structure of BC, which retain PTEs and thus preventing metals moving to leachates, and engender an environment for microorganisms, positively influencing their metabolism, (2) charge effect which is responsible for electrostatic attraction between PTEs cations and the negative charge of BC [27], (3) presence of functional groups on the surface, which easily form inert composite aggregates with PTEs and effectively immobilizes metals [28] and can fix PTEs due to complexation and co-precipitation with PTEs ions [14], and finally (4) increased microbial activity stimulating creation of metabolites that may interact with functional groups on the BC surface, which promotes the passivation of metals [13–15]. The observed effect was a cumulative result of all the properties mentioned here, each contributing to the final outcome in a complex and interdependent manner.

3.2. Mobility index

The mobility of PTEs - specifically their transfer from various environmental matrices into plants and other organisms - has traditionally been assessed using total PTE concentration. However, research has demonstrated that analyzing the relative proportions of specific chemical fractions provides significantly more accurate mobility predictions [7]. To quantify this, the mobility index (MI) was employed, which can be calculated using the following equation [29] (1):

$$MI = \frac{F1}{F1+F2+F3+F4} \cdot 100\% \quad (1)$$

where: F1, F2, F3, F4 are contents of the particular fractions of the PTE [mg/kg]. Elevated MI correlate with a heightened mobility given metal shows in the environment/matrix [7].

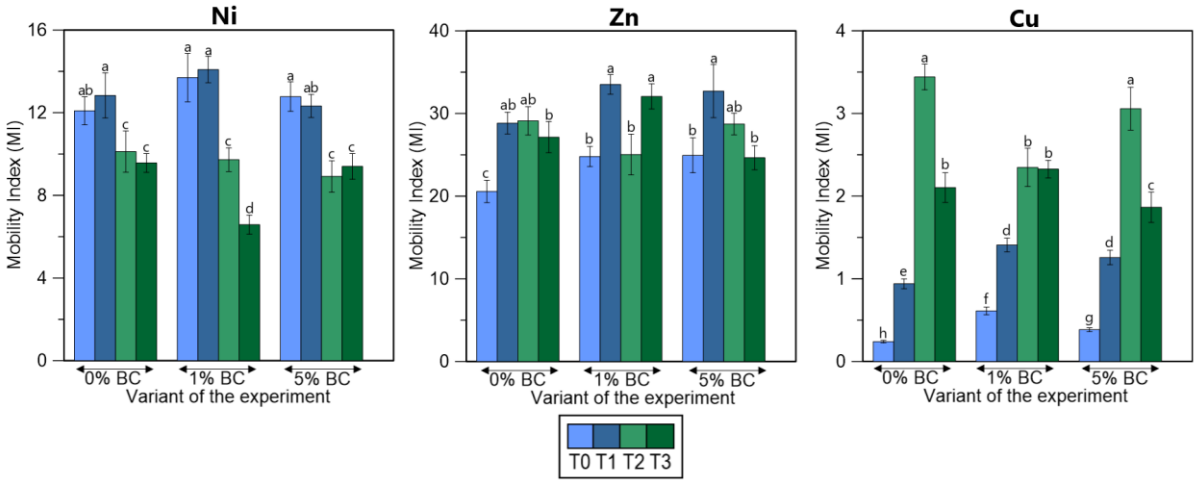


Fig. 3. Changes of the mobility index (%) values of PTEs in the different treatments during composting. Where: T0 – 0 day, T1 – 3 day, T2 – 14 day, T3 – 98 day of the composting. Error bars indicate the standard deviation (calculated from three replicates), while distinct letters above the bars denote statistically significant differences among sampling times ($p \leq 0.05$) based on Tukey's HSD test at $\alpha = 0.05$.

Fig. 3 illustrates the temporal changes of MI during the composting for all analyzed PTE, with the exception of Pb, which was undetectable in F1 fraction. Slightly higher initial values of MI were observed for BC-amended experiments for Zn and Cu, relative to control (**Fig. 3**). Looking at initial MI for Ni, there was no statistically significant change among all experimental variants. Although there are no official standards for critical MI thresholds for phytotoxicity and ecological impact in soil amendment applications, Cu exhibits 4 to 10 times lower values than Ni and Zn, indicating the lowest availability and therefore toxicity of this metal. Throughout the composting duration, element-specific MI patterns occurred. Ni demonstrated a consistent decline in mobility across all treatments, with the 1% BC treatment achieving the most significant reduction (31% lower relative to control) (**Fig. 3**). In contrast, both Zn and Cu exhibited progressive increases in MI throughout the composting period with the lowest values observed in the 5% BC treatment at the end of the composting for Cu.

These results indicate that the composting process effectively facilitated passivation of all investigated elements with efficiency varying according to the applied dose. The observed passivation can be attributed to the progressive degradation of lignocellulosic materials and subsequent formation of humic substances containing hydrophilic functional groups [13]. These groups facilitate metal complexation, thereby reducing mobility by forming stable metal-organic complexes [13].

3.3. Ecotoxicological assessment

3.3.1. *Aliivibrio fischeri* – leachates toxicity to bacteria

Leachates serves as an essential method for evaluating toxicity in aquatic ecosystems, particularly during periods of increased water presence such as precipitation and snow melt events. These conditions can facilitate the mobilization of contaminants into aquatic systems. The experiment results demonstrated that leachates from all tested variants demonstrated inhibitory effects on the luminescence of *A. fischeri* throughout each phase of the composting process (**Fig. 4**).

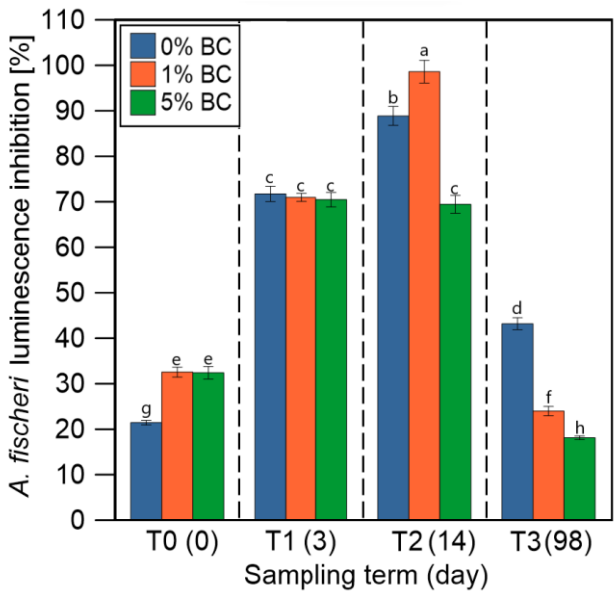


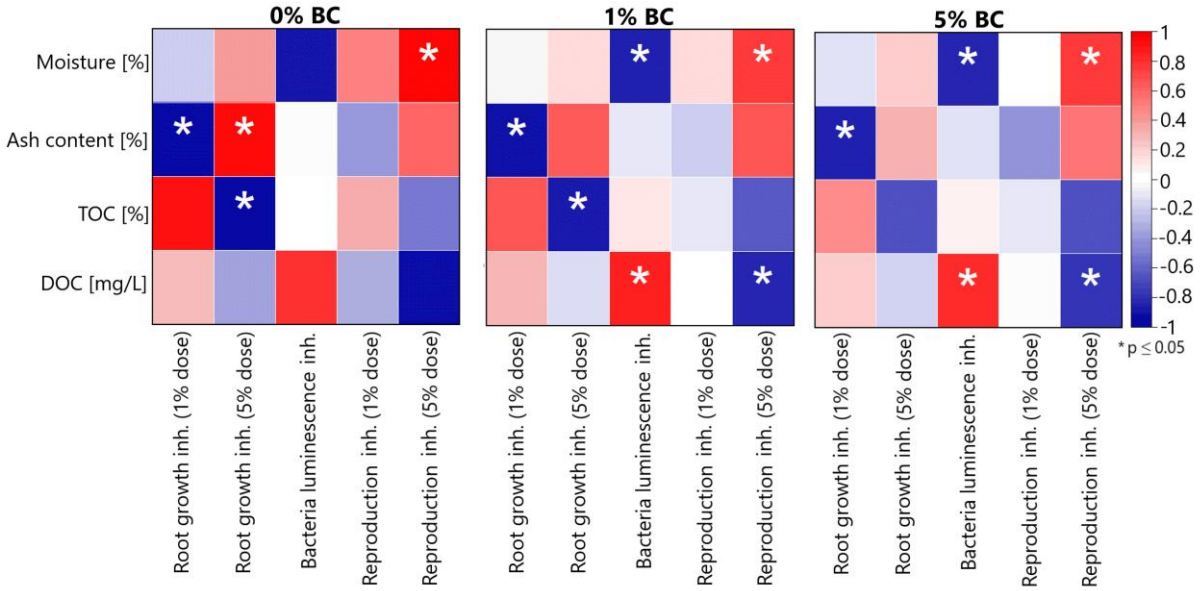
Fig. 4. Influence of leachates from materials taken at various stages of composting on inhibition of *Aliivibrio fischeri* luminescence. Error bars indicate the standard deviation

(calculated from three replicates), while distinct letters above the bars denote statistically significant differences among sampling times ($p \leq 0.05$) based on Tukey's HSD test at $\alpha = 0.05$.

A. fischeri exhibited elevated toxicity responses in the BC-enriched treatments at the beginning of the composting (**Fig. 4**). This heightened toxicity can be attributed to BC's direct inhibitory effects on bacteria. Previous research [30] has documented BC's intrinsic toxicity to *A. fischeri* because of high salinity, pH, presence of particular PTEs and low nutrient content. High salinity, pH, and PTE content can cause oxidative stress and disrupt metabolic processes, while too low nutrient content does not sufficiently support the growth of microorganisms [30]. The toxicity of the leachates substantially increased from the beginning of the study (T0) (luminescence inhibition from 21.5 to 32.6% depending on the variant) to the stage T2 (luminescence inhibition from 69.4 to 98.6% depending on the variant) (**Fig. 4**). This pronounced increase likely stems from the sequential release of various toxic substances during intensive organic matter mineralization. Additionally, during the decomposition of organic matter, a change in its structure occurs, which may lead to a decrease in the affinity to the substances and an increase in the concentration of the contaminants bioavailable fraction, as occurred for Ni and Cu in the T1 and T2 periods (**Fig. 1**). Following the maturation phase (T3), toxicity levels declined markedly, with BC-enriched variants ultimately showing lower toxicity than their initial level (**Fig. 4**). Notably, at the end of the experiment BC-amended treatments also demonstrated 44.4% (1% BC dose) and 58.0% (5% BC dose) lower toxicity than BC-free variant in the same period (T3). Increasing the BC dose in the compost significantly improved the positive effect on toxicity reduction.

During the maturation phase, organic matter undergoes intensive humification and stabilization processes, including condensation and polymerization reactions, during which organic substances become less susceptible to further decomposition [31]. In this process,

356 contaminants (both organic and inorganic) can be incorporated into transformed humic
357 structures, rich in functional groups (carboxyl, phenolic, hydroxyl) [31]. Liu et al. (2022)
358 demonstrated that mobile fractions of Zn and Cu transformed into hard-to-access forms through
359 binding with organic matter and fulvic acids. During maturation, humic substances are
360 condensed from aromatic compounds (reducing sugars and/or amino acid analogues), and their
361 degree of aromaticity usually increases during composting [31]. The formation of complexes
362 between compost stable organic compounds and contaminants (mainly organic) causes toxic
363 substances to be "encapsulated" within the organic structure and become more difficult to
364 release or use by microorganisms or plants [31, 32]. As a result of adsorption on transformed
365 organic matter, some of the hazardous substances can be permanently incorporated into the
366 compost structure, which reduces toxic activity towards plants or animals [33]. Al-Mashaqbeh
367 and McLaughlan (2014) demonstrated that the aging composts exerted a significant effect on
368 Zn adsorption. Maturation can also lead to the formation of compounds with a high affinity for
369 contaminants, which affects their immobilization [32]. Increasing the dose of BC in the compost
370 resulted in a more beneficial effect toward *A. fischeri*, due to BC's ability to accelerate the
371 maturation phase, help stabilize organic matter, increase water retention capacity and act as a
372 habitat for microorganisms, which promotes greater microbiological diversity [25].
373



374

375 **Fig. 5.** Correlation plot presenting the values of Pearson correlation coefficients between the
376 ecotoxicological tests endpoints and physico-chemical properties of composts (A – 0% BC, B
377 – 1% BC, C – 5% BC) calculated over the entire composting period, where: * indicates a
378 statistically significant correlation ($p \leq 0.05$), TOC – total organic carbon content, DOC –
379 dissolved organic carbon, inh. – inhibition.

380 Analysis of the relationship between inhibition of *A. fischeri* luminescence and the
381 physico-chemical properties of the material found limited statistically significant correlations
382 ($p \leq 0.05$) (**Fig. 5**). No correlations were found for control, while with the addition of BC to
383 composting, an inverse correlation with moisture and a positive correlation with DOC content
384 were showed ($p \leq 0.05$) (**Fig. 5**). Higher DOC levels indicate a greater amount of dissolved
385 organic compounds in the compost enriched via BC, which may include bioavailable substances
386 that could exert toxic effects on *A. fischeri*, thereby increasing reproductive inhibition. Analysis
387 of the three-way interaction plot implies that higher moisture levels combined with certain
388 elevated DOC concentrations are associated with increased toxicity towards *A. fischeri*, as
389 indicated by the red shades (for both BC doses) (**Fig. 6a and 6c**). This pattern suggests a
390 potential interaction between moisture and DOC in influencing the toxic response measured by
391 Microtox® test, where elevated levels of both may exacerbate toxicity in the compost

environment. Notably, a potential mitigating effect of the highest DOC levels on toxicity occurred (represented in green hues), possibly due to interactions that reduce the bioavailability of toxic components at higher DOC concentrations (**Fig. 6a and 6c**).

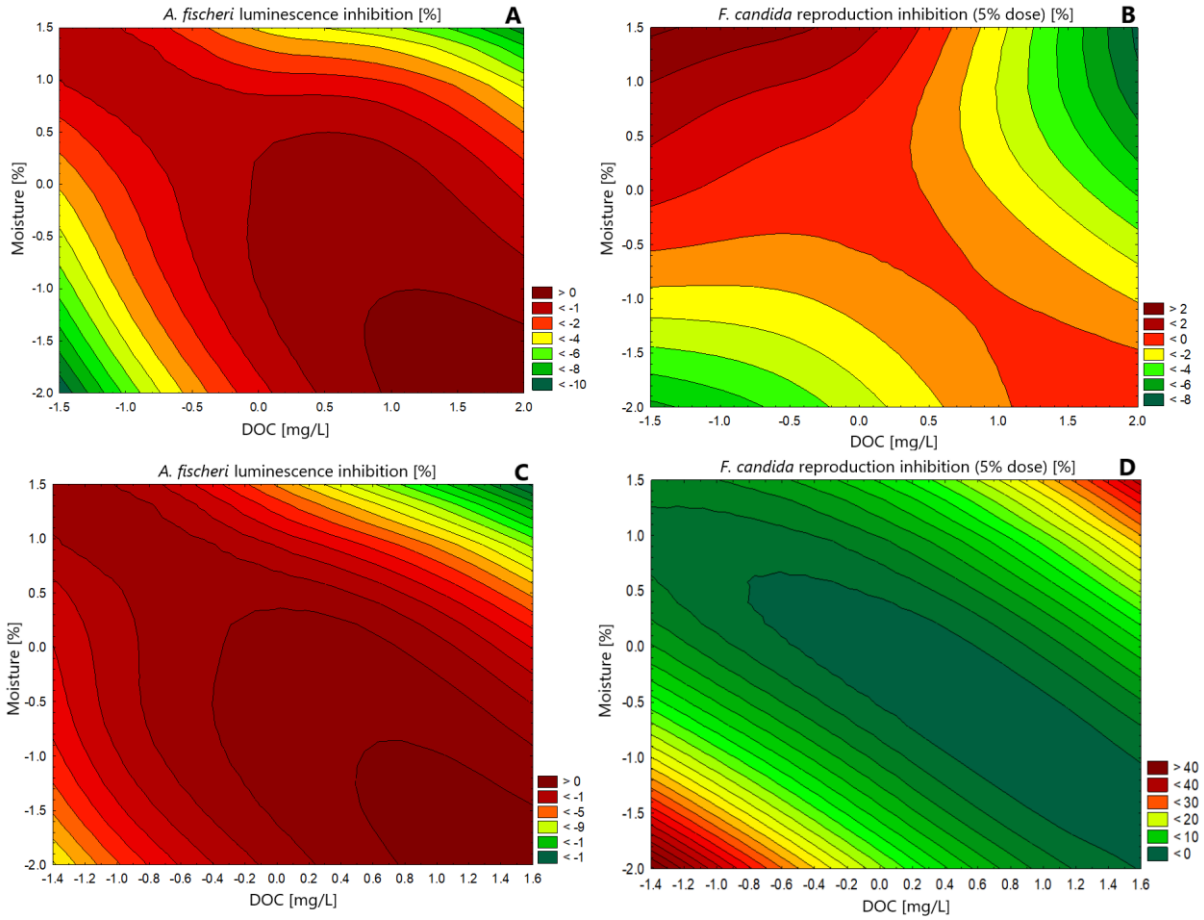


Fig. 6. The three-way interaction plot of *Aliivibrio fischeri* luminescence inhibition after 15-minutes exposure (A and C) and *Folsomia candida* reproduction inhibition (at 5% dose to the soil) (B and D), highlighting parameters impacting performance, with optimal results represented by deep green regions. Where: A and B represents compost enriched with 1% BC, C and D – with 5% BC. Meaning: DOC – dissolved organic carbon.

3.3.2. *Lepidium sativum* – leachates toxicity to plant

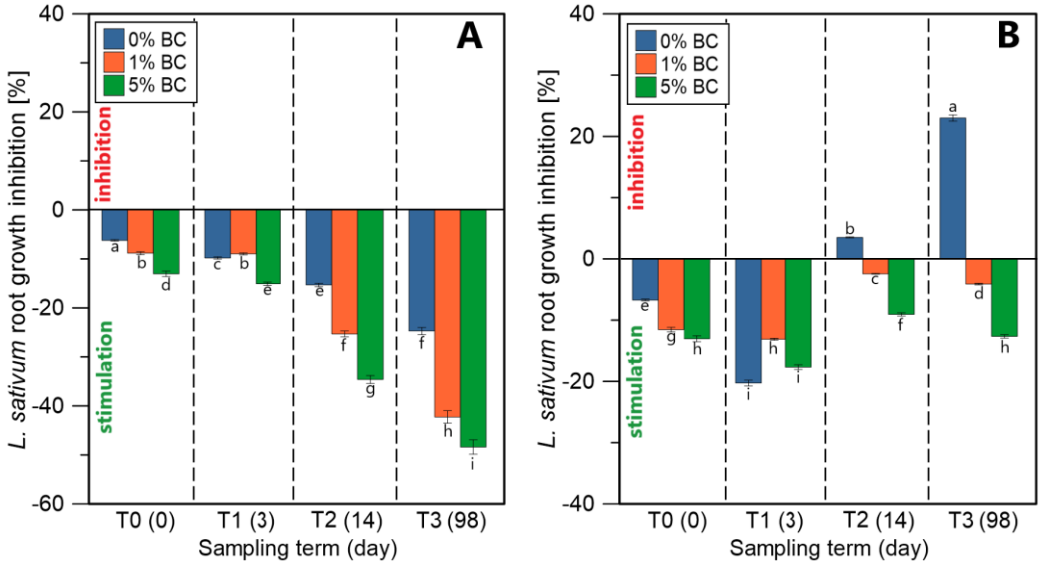


Fig. 7. Influence of the materials in different stages of composting on *Lepidium sativum* root growth inhibition (A – 1% dose to the soil, B – 5% dose to the soil). Positive and negative values present inhibition and stimulation, respectively. Error bars indicate the standard deviation (calculated from three replicates), while distinct letters above the bars denote statistically significant differences among sampling times ($p \leq 0.05$) based on Tukey's HSD test at $\alpha = 0.05$.

All experimental variants, including the control and experiments with BC, demonstrated a pronounced stimulatory effect on L. sativum root growth when a 1% dose of the composted material was applied to the soil (Fig. 7a). The positive influence intensified in proportion to composting duration. Both direct and indirect mechanisms can contribute to the enhanced growth of *L. sativum*. The direct mechanism involves the progressive elimination of root growth inhibitors through multiple pathways, including biological degradation, adsorption process, sequestration mechanisms, and the formation of bound residue [35], collectively resulting in diminished toxicity of the composted material over time. Previous research demonstrated that during SL composting, various contaminants exhibited increased affinity for the composted

matrix, correlating with decreased bioavailability [36]. This observation aligns with other research indicating that during composting, contaminants undergo transformation into biologically unavailable forms through removal or effective matrix immobilization [15]. The indirect mechanism involves the enhanced release and bioavailability of nutrients and organic matter resulting from the mineralization process [37]. These mechanistic hypotheses are substantiated by the temporal increase in the stimulative effects of the composted material (**Fig. 7a**). While in the variants with BC, stimulation of *L. sativum* root growth was observed throughout the entire composting period, the higher concentration of BC in composting mixture produced more pronounced beneficial effects (**Fig. 7a**). While BC-free compost increased *L. sativum* growth by 24.7%, the addition of BC enhanced this effect significantly (from 17.6% to 23.7%, for 1% and 5% BC, respectively) (**Fig. 7a**). These findings demonstrated that BC presence in final compost creates favorable conditions for *L. sativum* root growth. This enhancement may be attributed to the providing of essential nutrients supporting various metabolic processes and/or the sequestration growth-inhibiting substances.

The impact of compost application on *L. sativum* root growth varied significantly between 1% and 5% doses at specific stages of composting (**Fig. 7**). During the initial stages (T0 and T1), the 5% dose demonstrated comparable (T0) or even superior (T1) stimulatory effect relative to the 1% application (**Fig. 7b**). However, as composting progressed to stages T2 and T3, treatments containing BC used at a 5% dose exhibited markedly reduced stimulation compared to the lower dose, while BC-free variant showed phytotoxic effect (**Fig. 7b**). These findings indicate that excessive compost application may inhibit plant root growth, even in cases where lower doses prove beneficial. While BC continues to demonstrate protective properties by promoting root growth compared to control treatments, the results emphasize the critical importance of optimal dosage for maximizing effectiveness. At the end of the composting period (after 98 days, T3), the BC-free compost exhibited a 23% inhibition of *L.*

445 *sativum* root growth, whereas the compost with BC continued to promote root growth of *L.*
446 *sativum*, with enhancement proportional to BC concentration (**Fig. 7b**).

447 The evaluation of relationships between root growth inhibition and the physico-
448 chemical properties of the composted materials reveals irregular statistically significant
449 relationships ($p \leq 0.05$) predominantly between ash and TOC content (**Fig. 5**). Across all
450 experimental variants, an inverse correlation between *L. sativum* root growth inhibition in soil
451 amended with a 1% dose of composted materials and mineral fraction content was observed (p
452 ≤ 0.05). This implies that higher ash content in composts increases the presence of inorganic
453 components, such as minerals and metal oxides. These substances could immobilize or bind
454 pollutants, thereby reducing the bioavailability of toxic compounds such as PAHs (and other
455 toxic organic contaminants) or PTEs from compost components such as BC and/or SL. As
456 organic matter degrades during composting, the inorganic fraction becomes "concentrated",
457 which may decrease the toxicity and even stimulate the plant growth. The relationship between
458 *L. sativum* root growth inhibition and ash content were not observed in soil with 5% dose of
459 composted materials with BC. This could be related to the higher number of contaminants
460 introduced with the 5% compost dose and/or with the higher BC dose, and the inorganic fraction
461 was not sufficient to bind some of them. An inverse correlation between root growth inhibition
462 and TOC was observed for control and treatment enriched with 1% BC (for a 5% dose to the
463 soil) ($p \leq 0.05$) (**Fig. 5**). It was observed that with diminishing TOC in the material, the
464 inhibition of *L. sativum* root growth increased. TOC represents the total organic carbon content,
465 including both dissolved and solid fractions. Some studies have shown that the organic fraction
466 is responsible for contaminant adsorption [38]. The lower TOC level suggests a diminished
467 amount of stable organic matter that binds toxic compounds, possibly present in compost
468 substrates.

3.3.3. *Folsomia candida* – solid phase toxicity to invertebrates

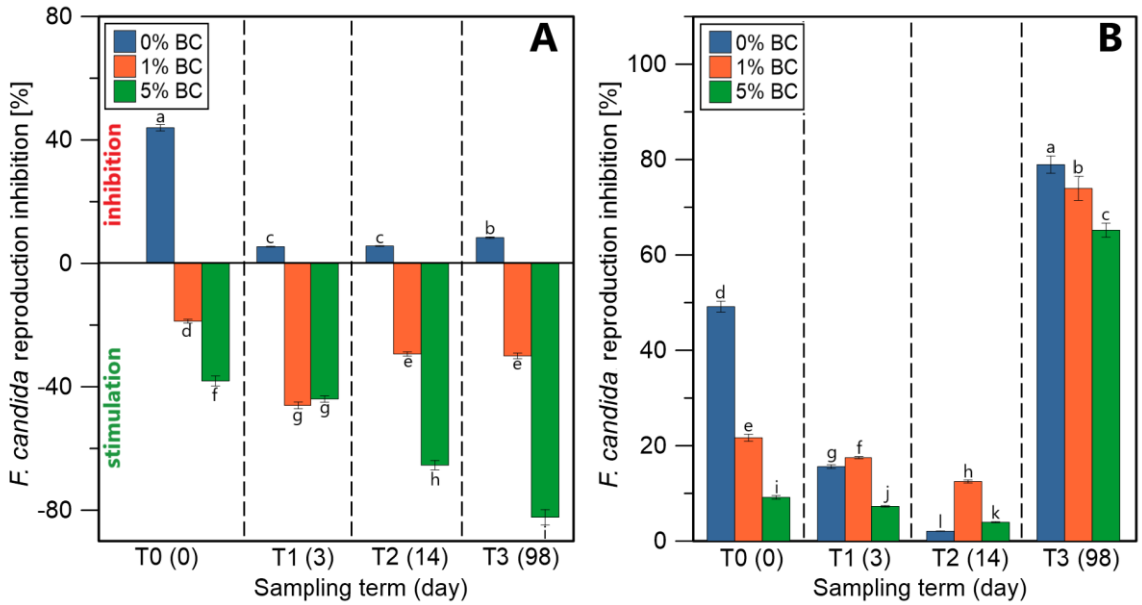


Fig. 8. Influence of the materials in different stages of composting on *Folsomia candida* reproduction inhibition (A – 1% dose to the soil, B – 5% dose to the soil). Positive and negative values present inhibition and stimulation, respectively. Error bars indicate the standard deviation (calculated from three replicates), while distinct letters above the bars denote statistically significant differences among sampling times ($p \leq 0.05$) based on Tukey's HSD test at $\alpha = 0.05$.

F. candida reproduction was controlled by both the dose of the composted material and the contribution of BC in composted material (**Fig. 8**). At a 1% concentration of composted material in soil, BC-free treatment initially (T0) inhibited the reproduction of *F. candida* by 44% (**Fig. 8a**). However, this inhibitory effect decreased significantly after three days of composting (T1) and remained at a similar level until the end of the composting (T2 – T3). Adding BC to composted material substantially altered its impact on *F. candida* reproduction, demonstrating significant stimulation of reproduction, with higher values correlating directly to increased BC concentrations in the composted material (**Fig. 8a**). Furthermore, in the treatment containing 5% BC, the stimulatory effect intensified throughout the composting

progression. Upon reaching maturity at 98 days, treatments containing 1% and 5% BC exhibited enhanced reproductive stimulation of 38.3% and 90.6%, respectively, relative to BC-free variant (**Fig. 8a**).

Increasing the dose of composted material in soil from 1% to 5% deceased the toxic effect observed in the BC-free control and mitigated the positive impact of materials with BC on *F. candida* reproduction. This highlights that an excessively high dose of the soil amendment can exert an adverse effect on *F. candida* reproduction, potentially introducing with SL an overabundance of reproduction inhibitors. However, the toxic effect was mitigated by presence of BC as a higher contribution of BC in the composted material corresponded to the least toxicity. The evaluation of correlations between inhibition of *F. candida* reproduction and the physico-chemical properties of the materials revealed only individual statistically significant relationships ($p \leq 0.05$) with moisture and DOC (**Fig. 5**). This aligns with previous observations regarding bacteria (**Fig. 5**). The statistically significant relationships were only observed for a 5% dose to the soil, irrespective of BC concentration. Specifically, a positive correlation with moisture and an inverse correlation with DOC (the latter does not occur for control) was observed (**Fig. 5**). Other studies [39] demonstrated that higher soil moisture promotes *F. candida* reproduction, but our study showed the opposite. Higher compost moisture could have contributed to physiological stress, caused anaerobic conditions (slowing down microbial degradation and leading to the accumulation of intermediate compounds such as organic acids, phenols, or ammonia, which are harmful to soil invertebrates), or limited access to suitable food sources, hence inhibition of reproduction increased over the composting period [39]. Moreover, higher moisture content during composting can increase the levels of contaminants and subsequently elevate toxicity to *F. candida* [40]. Excess moisture can enhance the mobility and bioavailability of PTEs, increasing their uptake by organisms [40]. For *F. candida*, a sensitive indicator species, such changes can result in reduced survival, reproduction, or avoidance

behavior, highlighting the importance of optimal moisture control in composting to minimize ecotoxicological risks. The decreasing DOC, responsible for providing essential bioavailable nutrients, was accountable for disturbances in the reproductive functioning of *F. candida* and led to increased inhibition of springtail reproduction. The analysis of the three-way interaction plots reveals that higher moisture levels combined with certain DOC concentrations correlate with increased toxicity of compost enriched with 1% BC, as indicated by the red areas (for a 5% dose to the soil) (**Fig. 6b**). Notably, increased DOC levels, especially at moderate to high moisture contents, appear to mitigate toxic effects of compost with 5% BC, as evidenced by the predominance of green (**Fig. 6d**). Elevated DOC concentrations may reduce the bioavailability of toxic compounds, thereby lessening their impact on *F. candida* reproduction (**Fig. 6d**).

The mortality of *F. candida* remained unaffected after addition of composted material during the mesophilic *I*, thermophilic, and mesophilic phase *II*. *F. candida* mortality increased only at the end of composting (98 days) with a 5% soil amendment dose (**Fig. S2**). These findings strongly demonstrate that a 5% soil amendment is inadvisable, as it negatively impacts *F. candida* both reproduction and mortality.

4. CONCLUSIONS

Biochar (BC) addition affected potentially toxic element (PTE) speciation and ecotoxicity in a dose- and element-specific manner. In sewage sludge and wheat straw composting, BC promoted the transformation of PTEs into less accessible forms. For Ni, 1% BC was most effective, while 5% BC enhanced Cu and Zn stabilization and supported plant and invertebrate growth. Pb remained largely immobile. Although BC consistently reduced bacterial toxicity and enhanced ecological safety, excessive soil amendment (5%) negatively affected invertebrates. The mobility index decreased for all metals, except Zn, indicating reduced PTE bioavailability over time. Toxicity variations across composting stages were linked to compost physico-chemical properties (TOC, DOC, minerals, moisture). Higher BC doses stimulated root

elongation and springtail reproduction, while bacterial toxicity declined notably during maturation. Overall BC proved effective in mitigating PTE availability and reducing compost ecotoxicity.

Acknowledgments

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Author contributions

Aleksandra Rombel: Conceptualization; Data curation; Investigation; Methodology; Visualization; Writing – original draft. Monika Raczkiewicz: Data curation; Investigation; Visualization; Writing – review and editing. Patryk Oleszczuk: Conceptualization; Formal analysis; Funding acquisition; Project administration; Resources; Supervision; Writing – review and editing.

Conflicts of interest

The authors declare that they have no known competing financial interests.

References

1. Chen X, Du Z, Liu D, et al (2022) Biochar mitigates the biotoxicity of heavy metals in livestock manure during composting. Biochar 4:1–13. https://doi.org/10.1007/S42773-022-00174-X
2. Ignatowicz K (2017) The impact of sewage sludge treatment on the content of selected heavy metals and their fractions. Environ Res 156:19–22. https://doi.org/10.1016/J.ENVRES.2017.02.035
3. Bogusz A, Oleszczuk P (2018) Sequential extraction of nickel and zinc in sewage sludge- or biochar/sewage sludge-amended soil. Sci Total Environ 636:927–935. https://doi.org/10.1016/j.scitotenv.2018.04.072
4. Zhao M, Zhong S, Zhou X, Yu Z (2024) Biochar derived from animal and plant

facilitates synergistic transformation of heavy metals and phosphorus in sewage sludge composting. Environ Pollut 357:124396. https://doi.org/10.1016/J.ENVPOL.2024.124396

5. Duan Y, Yang J, Guo Y, et al (2021) Pollution control in biochar-driven clean composting: Emphasize on heavy metal passivation and gaseous emissions mitigation. J Hazard Mater 420:126635. https://doi.org/10.1016/J.JHAZMAT.2021.126635

6. Lv B, Xing M, Yang J (2016) Speciation and transformation of heavy metals during vermicomposting of animal manure. Bioresour Technol 209:397–401. https://doi.org/10.1016/J.BIORTECH.2016.03.015

7. Bogusz A, Oleszczuk P (2020) Effect of biochar addition to sewage sludge on cadmium, copper and lead speciation in sewage sludge-amended soil. Chemosphere 239:124719. https://doi.org/10.1016/j.chemosphere.2019.124719

8. Liu W, Huo R, Xu J, et al (2017) Effects of biochar on nitrogen transformation and heavy metals in sludge composting. Bioresour Technol 235:43–49. https://doi.org/10.1016/J.BIORTECH.2017.03.052

9. Awasthi MK, Wang Q, Huang H, et al (2016) Effect of biochar amendment on greenhouse gas emission and bio-availability of heavy metals during sewage sludge co-composting. J Clean Prod 135:829–835. https://doi.org/10.1016/J.JCLEPRO.2016.07.008

10. Poornima S, Dadi M, Subash S, et al (2024) Review on advances in toxic pollutants remediation by solid waste composting and vermicomposting. Sci African 23:e02100. https://doi.org/10.1016/J.SCIAF.2024.E02100

11. Liu H, Wang L, Zhong R, et al (2022) Binding characteristics of humic substances with Cu and Zn in response to inorganic mineral additives during swine manure composting. J Environ Manage 305:114387. https://doi.org/10.1016/J.JENVMAN.2021.114387

12. Liu J, Hu Y, Gu S, et al (2024) Insight into mitigation mechanisms of N2O emission by biochar during agricultural waste composting. Bioresour Technol 406:130970. https://doi.org/10.1016/J.BIORTECH.2024.130970
13. Kong Y, Ma R, Li G, et al (2022) Impact of biochar, calcium magnesium phosphate fertilizer and spent mushroom substrate on humification and heavy metal passivation during composting. Sci Total Environ 824:153755. https://doi.org/10.1016/J.SCITOTENV.2022.153755
14. Chen Y, Xu Y, Qu F, et al (2020) Effects of different loading rates and types of biochar on passivations of Cu and Zn via swine manure composting. J Arid Land 12:1056–1070. https://doi.org/10.1007/S40333-020-0026-5
15. Chen Y, Liu Y, Li Y, et al (2017) Influence of biochar on heavy metals and microbial community during composting of river sediment with agricultural wastes. Bioresour Technol 243:347–355. https://doi.org/10.1016/J.BIORTECH.2017.06.100
16. Guo S, Wei J, Zhang Y, et al (2024) Effects and mechanisms of different types of biochar on heavy metal passivation during sludge composting. Bull Environ Contam Toxicol 113:1–8. https://doi.org/10.1007/S00128-024-03921-X
17. Rombel A, Różyło K, Oleszczuk P (2024) The high dose of biochar reduces polycyclic aromatic hydrocarbons losses during co-composting of sewage sludge and wheat straw. J Environ Manage 351:119628. https://doi.org/10.1016/J.JENVMAN.2023.119628
18. Pueyo M, Mateu J, Rigol A, et al (2008) Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. Environ Pollut 152:330–341. https://doi.org/10.1016/J.ENVPOL.2007.06.020
19. Li S, Pu L, Wang Z, et al (2025) Impact of the soil springtail Folsomia candida on the composition, function, and microbial network of root-associated microbes of host plant Sedum plumbizincicola. Eur J Soil Biol 126:103748.

https://doi.org/10.1016/J.EJSOBI.2025.103748

20. International Organization for Standardization (2016) ISO 18763 Soil quality - Determination of the toxic effects of pollutants on germination and early growth of higher plants

21. SDI (1992) SDI Microtox Manual. Microbics Corp

22. International Organization for Standarization (2023) ISO 11267 Soil quality - Inhibition of reproduction of Collembola (Folsomia candida) by soil contaminants

23. Zimmerman AR, Ouyang L (2019) Priming of pyrogenic C (biochar) mineralization by dissolved organic matter and vice versa. Soil Biol Biochem 130:105–112. https://doi.org/10.1016/J.SOILBIO.2018.12.011

24. Li Y, Wang B, Shang H, et al (2023) Influence of adsorption sites of biochar on its adsorption performance for sulfamethoxazole. Chemosphere 326:138408. https://doi.org/10.1016/J.CHEMOSPHERE.2023.138408

25. Teodoro M, Trakal L, Gallagher BN, et al (2020) Application of co-composted biochar significantly improved plant-growth relevant physical/chemical properties of a metal contaminated soil. Chemosphere 242:125255. https://doi.org/10.1016/J.CHEMOSPHERE.2019.125255

26. Alam MS, Swaren L, von Gunten K, et al (2018) Application of surface complexation modeling to trace metals uptake by biochar-amended agricultural soils. Appl Geochemistry 88:103–112. https://doi.org/10.1016/J.APGEOCHEM.2017.08.003

27. Sun X, Atiyeh HK, Li M, Chen Y (2020) Biochar facilitated bioprocessing and biorefinery for productions of biofuel and chemicals: A review. Bioresour Technol 295:122252. https://doi.org/10.1016/J.BIORTECH.2019.122252

28. Tang J, Zhu W, Kookana R, Katayama A (2013) Characteristics of biochar and its application in remediation of contaminated soil. J Biosci Bioeng 116:653–659.

https://doi.org/10.1016/J.JBIOSC.2013.05.035

29. Kabala C, Singh BR (2001) Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. J Environ Qual 30:485–492. https://doi.org/10.2134/JEQ2001.302485X

30. Kończak M, Oleszczuk P (2020) Co-pyrolysis of sewage sludge and biomass in carbon dioxide as a carrier gas affects the total and leachable metals in biochars. J Hazard Mater 400:. https://doi.org/10.1016/j.jhazmat.2020.123144

31. Wen X, Qin X, Long XE, Li Q (2024) Microbial necromass facilitated the humification process through amino sugar reactions during the co-composting of cow manure plus sawdust. Environ Sci Pollut Res Int 31:48175–48188. https://doi.org/10.1007/S11356-024-34381-9

32. Hu ZT, Huo W, Chen Y, et al (2022) Humic substances derived from biomass waste during aerobic composting and hydrothermal treatment: A review. Front Bioeng Biotechnol 10:878686. https://doi.org/10.3389/FBIOE.2022.878686

33. Liu L, Wang S, Guo X, Wang H (2019) Comparison of the effects of different maturity composts on soil nutrient, plant growth and heavy metal mobility in the contaminated soil. J Environ Manage 250:109525. https://doi.org/10.1016/J.JENVMAN.2019.109525

34. Al-Mashaqbeh OA, McLaughlan RG (2014) Effect of compost aging on zinc adsorption characteristics. J Environ Chem Eng 2:392–397. https://doi.org/10.1016/J.JECE.2014.01.011

35. Kästner M, Miltner A (2016) Application of compost for effective bioremediation of organic contaminants and pollutants in soil. Appl Microbiol Biotechnol 100:3433–3449. https://doi.org/10.1007/S00253-016-7378-Y

36. Oleszczuk P (2009) Sorption of phenanthrene by sewage sludge during composting in

662 relation to potentially bioavailable contaminant content. J Hazard Mater 161:1330–
663 1337. https://doi.org/10.1016/J.JHAZMAT.2008.04.094
664 37. Bolo P, Mucheru-Muna M, Kinyua M, et al (2024) Nitrogen and phosphorus
665 mineralization and their corresponding monetary values under long-term integrated soil
666 fertility management practices. J Sustain Agric Environ 3:e12100.
667 https://doi.org/10.1002/SAE2.12100
668 38. Lima JZ, Raimondi IM, Schalch V, Rodrigues VGS (2018) Assessment of the use of
669 organic composts derived from municipal solid waste for the adsorption of Pb, Zn and
670 Cd. J Environ Manage 226:386–399.
671 https://doi.org/10.1016/J.JENVMAN.2018.08.047
672 39. Hennig TB, Alves PRL, Toniolo T, et al (2022) Toxicity of fipronil to Folsomia
673 candida in contrasting tropical soils and soil moisture contents: effects on the
674 reproduction and growth. Ecotoxicology 31:64–74. https://doi.org/10.1007/S10646-
675 021-02490-7
676 40. Yousif Abdellah YA, Shi ZJ, Luo Y Sen, et al (2022) Effects of different additives and
677 aerobic composting factors on heavy metal bioavailability reduction and compost
678 parameters: A meta-analysis. Environ Pollut 307:119549.
679 https://doi.org/10.1016/J.ENVPOL.2022.119549
680

Supplementary information

Reducing metal mobility and associated ecological and human health risks in sewage sludge compost via biochar addition

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Number of figures: 3

Number of tables: 2

1. Materials and methods

1.1.Chemicals

Acetic acid (99.5 – 99.9%, pure p.a.), hydrogen peroxide (30% pure p.a.), hydrochloric acid (35 – 38%, pure p.a.), and nitric acid (65% pure p.a.) were purchased from POCH (Poland). Hydroxylammonium chloride (pure p.a.), ammonium acetate (pure p.a.), and sodium hydroxide (pure p.a.) were provided by CHEMPUR (Poland). Silica (SiO_2) was purchased from Macherey-Nagel GmbH & Co. KG (Germany). Sodium azide (grade ≥ 99%) and ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA) were supplied by Sigma-Aldrich (Germany). The n-heptane (grade ≥ 99%), hexane (grade ≥ 95%) solvents, and copper (Cu) were all provided by Merck (Germany). Acetone (grade ≥ 99.5%) was purchased from POCH (Poland). Isooctane (for GC analysis, grade ≥ 99.5%) was supplied by CHEMPUR (Poland). Polyoxymethylene (POM) was provided by C.S. Hyde Co. (USA). Milli Q water with electrical conductivity below 0.05 μS cm^{-1} was used to prepare all solutions.

1.2. Physico-chemical analyses

The analysis of total organic carbon (TOC) and dissolved organic carbon (DOC) was performed using a TOC-L Analyzer equipped with an SSM5000 furnace (Shimadzu, Kyoto, Japan). TOC was measured in solid samples, while DOC and pH were determined in the solutions after extraction. The extracts were prepared by shaking 1 g of the sample with 10 mL of Milli Q water at 10 rpm/min for 24 hours at room temperature (22 ± 2°C) using a laboratory shaker (Type 358A, ELPIN+, Katowice, Poland). The extracts were then filtered through a glass funnel using a qualitative paper filter (Munktell Filter AB, Germany). pH values were measured with a HQ430D universal laboratory multi-parameter meter (HACH, Loveland, Colorado, USA). The ash content was calculated based on the mass loss after 6-hour heating 1 g of the material in a furnace (Magma Therm, Istanbul, Turkey) at 760°C. The moisture content in freshly collected compost was analyzed by weighing about 10 g of a representative sample into a Petri

dish and 6-hour drying in a laboratory dryer (POL-EKO, Wodzisław Śląski, Poland) at 105°C until a constant mass was reached. The moisture content was calculated from the weight difference.

1.3. Metal speciation analysis

The sequential extraction of four metal fractions (Zn, Cu, Ni, Pb) was performed using a modified BCR procedure [1]. The extraction process consisted of four distinct steps:

Fraction 1 (F1) Extraction:

One gram of compost was precisely weighed into a 50 mL plastic falcon tube and combined with 40 mL of 0.11 mol/L acetic acid (POCH, Poland). The mixture was agitated at 170 rpm using an ELPIN+ shaker (Type 358A, Katowice, Poland) for 16 hours at 22 ± 2°C. Following agitation, the sample underwent centrifugation at 3000 g for 20 minutes in a MPW-352 centrifuge (Poland). The supernatant was preserved at 4°C, while the residue underwent washing with 20 mL of Milli Q water, followed by centrifugation and supernatant removal.

Fraction 2 (F2) Extraction:

The residue was treated with 40 mL of freshly prepared 0.5 mol/L hydroxylammonium chloride (CHEMPUR, Poland), adjusted to pH 2. After shaking and centrifugation, the supernatant was collected, and the residue underwent the same washing procedure as described for F1.

Fraction 3 (F3) Extraction:

The residue was transferred quantitatively to a 100 mL glass beaker and treated with 10 mL of 8.8 mol/L hydrogen peroxide (POCH, Poland) at pH 2-3. Digestion proceeded for 2 hours at 85°C in a laboratory dryer (POL-EKO Aparatura, Poland). Due to solution expansion during digestion, the large beaker volume was essential. After volume reduction to approximately 3 mL, a second 10 mL aliquot of hydrogen peroxide was added, followed by digestion at 100°C for 3 hours until near-complete evaporation (approximately 1 mL remaining). The residue was

then transferred to a plastic falcon tube and extracted with 50 mL of 1 mol/L ammonium acetate solution (CHEMPUR, Poland) at pH 2-3, followed by the standard washing procedure.

Fraction 4 (F4) Extraction:

The residual material underwent extraction using 12 mL of aqua regia ($HCl:HNO_3$, 3:1 v/v) in a StartD Microwave Digestion System (Milestone, Italy). Digestion parameters were set to 120°C for 1.5 hours under elevated pressure.

Sample Analysis:

All extracts from F1-F3 were filtered through 0.45 µm PTFE syringe filters (AlfaChem), while F4 extracts were filtered using paper filters (Munktell Filter AB, Germany) and glass funnels into 50 mL volumetric flasks. Metal analysis was performed using an ICP-OES iCAP 7400 Duo (Thermo Scientific). Operating conditions included argon (99.9999%, AirLiquide, Poland) at flow rates of 12 L/min for plasma generation and 0.5 L/min for nebulization. Quantification employed a six-point calibration curve (0.02 – 5 mg/L) prepared from multi-element standards (Merck, Germany, 1 g/L), diluted with HNO_3-acidified Milli Q water.

2. Results and discussion

2.1. Correlations between bioassays endpoints and physico-chemical properties

The correlation results across different composting periods (from 0 day to 98 day) revealed changes in the relationships between the physicochemical properties of composts with 1% and 5% BC addition and the endpoints of ecotoxicological tests (**Fig. S3**). At the start of the composting (T0), properties such as moisture, ash content, and TOC exhibited various correlations with ecotoxicological test endpoints, with statistically significant correlations observed between ash content and inhibition of *A. fischeri* luminescence and also between DOC and TOC and inhibition of *F. candida* reproduction for a 5% compost dose ($p \leq 0.05$).

Specifically, a negative correlation was observed between the ash content in BC-enriched composts and the inhibition of *A. fischeri* luminescence ($p \leq 0.05$) (**Fig. S3**). These strong correlations at the beginning may indicate rapid initial interactions between BC-enriched compost properties and ecotoxicological factors. A positive correlation was also observed between DOC content and the inhibition of *F. candida* reproduction, alongside a negative correlation between TOC content and the inhibition of *F. candida* reproduction at a 5% compost addition ($p \leq 0.05$). After 3 days of composting (T1), a shift in correlations was observed, with moisture and DOC showing significant correlations with ecotoxicological test results, specifically with the root growth test with 1% compost dose and inhibition of *F. candida* reproduction for a 5% compost dose ($p \leq 0.05$). Specifically, a negative correlation was observed between DOC content and growth inhibition of *L. sativum* at a 5% compost dose ($p \leq 0.05$). This change in correlations after 3 days may be due to the early dynamics of interactions between BC-modified compost properties and ecotoxicological responses. After 14 days (T2), the correlations became less distinct, with most significant correlations weakening, which may indicate the stabilization of biochemical interactions affecting ecotoxicity. This reduction in significant correlations may suggest that the BC has reached an equilibrium state within the compost environment, lessening its influence on ecotoxicological outcomes. After 98 days (T3), correlations were generally weak, with no statistically significant results (**Fig. S3**). The decrease in correlations over an extended composting period may indicate the end of the initial BC interactions affecting ecotoxicological responses, transitioning into a stable phase where BC had minimal influence on both the compost's physicochemical properties and the ecotoxicological effects. In summary, these findings indicate that the impact of BC on the ecotoxicological properties of compost is strongest at the beginning of the composting process and decreases over time, suggesting that BC primarily affects ecotoxicity in the early phase, after which its influence stabilizes.

2.2.Tables

Table S1. PTEs limits [mg/kg dry matter] in soil improvers/composts in the European countries and Canada [2].

1. Pueyo M, Mateu J, Rigol A, et al (2008) Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. Environ Pollut 152:330. https://doi.org/10.1016/J.ENVPOL.2007.06.020
2. Cofie O, Nikiema J, Impraim R, et al (2016) Co-composting of solid waste and fecal sludge for nutrient and organic matter recovery. CGIAR Res Progr Water, L Ecosyst 47. https://doi.org/10.5337/2016.204
3. Official Journal of the European Union (2022) Commission Decision (EU) 2022/1244 of 13 July 2022 establishing the EU Ecolabel criteria for growing media and soil improvers. L190/141
4. European Compost Network (2014) European Quality Assurance Scheme for Compost and Digestate
5. Canadian Council of Ministers of the Environment (2005) Guidelines for Compost Quality

PTE	**Limits for soil improvers/composts**		
	EU Ecolabel [3]	**ECN Standard** [4]	**Canadian Limits A** [5]
Ni	40	40	62
Zn	300	600	700
Cu	200	300	400
Pb	100	130	150

Table S2. Fractional (F1-F4) concentration of Ni, Zn, Cu, and Pb [mg/kg] in material during composting (the average values of three measurements are presented with standard deviation). Nd – not detectable.

Day	0			3			14			98		
Variant (% biochar)	0%	1%	5%	0%	1%	5%	0%	1%	5%	0%	1%	5%
C F1 Ni	1.92 ± 0.06	2.00 ± 0.07	1.87 ± 0.08	1.88 ± 0.09	2.23 ± 0.09	1.93 ± 0.07	1.48 ± 0.06	1.58 ± 0.07	1.60 ± 0.09	1.65 ± 0.06	1.03 ± 0.04	1.60 ± 0.07
C F2 Ni	1.16 ± 0.09	1.20 ± 0.06	1.27 ± 0.10	1.12 ± 0.07	1.36 ± 0.10	1.37 ± 0.08	0.80 ± 0.06	0.95 ± 0.05	1.00 ± 0.07	1.01 ± 0.05	0.75 ± 0.03	1.12 ± 0.09
C F3 Ni	8.64 ± 0.45	8.10 ± 0.66	7.55 ± 0.40	8.31 ± 0.52	8.98 ± 0.70	8.78 ± 0.69	9.84 ± 0.60	10.9 ± 0.6	10.9 ± 0.4	10.1 ± 0.4	9.44 ± 0.53	9.64 ± 0.47
C F4 Ni	4.15 ± 0.18	3.30 ±. 0.17	3.93 ± 0.30	3.35 ± 0.24	3.29 ± 0.17	3.56 ± 0.24	2.50 ± 0.16	2.87 ± 0.15	4.45 ± 0.20	4.54 ± 0.23	4.47 ± 0.30	4.64 ± 0.26
C F1 Zn	120.4 ± 6.3	133.2 ± 10.8	132.1 ± 6.9	166.7 ± 10.4	218.6 ± 17.2	199.1 ± 15.6	187.9 ± 11.5	184.1 ± 9.4	211.6 ± 8.7	209.4 ± 8.1	212.8 ± 12.0	168.8 ± 8.2
C F2 Zn	149.7 ± 6.6	146.6 ± 7.7	154.8 ± 11.7	161.9 ± 11.5	186.9 ± 9.8	183.7 ± 12.2	213.3 ± 13.3	208.9 ± 10.7	202.5 ± 9.0	268.1 ± 13.7	186.1 ± 12.3	255.8 ± 14.5
C F3 Zn	304.3 ± 9.8	248.9 ± 9.1	234.7 ± 9.1	231.1 ± 11.2	230.8 ± 9.5	219.1 ± 8.4	237.2 ± 9.8	317.8 ± 14.5	310.9 ± 17.6	277.4 ± 10.0	248.3 ± 10.2	242.5 ± 10.0
C F4 Zn	11.0 ± 0.8	8.50 ± 0.43	8.20 ± 0.64	18.5 ± 1.2	16.0 ± 1.2	6.73 ± 0.38	6.99 ± 0.55	24.4 ± 1.4	11.6 ± 0.8	16.6 ± 0.9	16.4 ± 0.7	17.9 ± 1.4
C F1 Cu	0.20 ± 0.01	0.48 ± 0.04	0.28 ± 0.01	0.76 ± 0.03	1.28 ± 0.08	1.08 ± 0.08	3.00 ± 0.17	2.33 ± 0.18	3.08 ± 0.17	2.02 ± 0.08	2.07 ± 0.11	1.76 ± 0.08
C F2 Cu	0.08 ± 0.01	0.16 ± 0.01	0.16 ± 0.01	0.24 ± 0.01	0.36 ± 0.03	0.32 ± 0.02	0.72 ± 0.05	0.55 ± 0.03	0.60 ± 0.03	0.56 ± 0.04	0.32 ± 0.02	0.44 ± 0.03
C F3 Cu	78.3 ± 2.5	73.3 ± 2.7	67.6 ± 2.8	74.1 ± 3.6	84.7 ± 3.5	80.2 ± 3.1	78.6 ± 3.2	92.1 ± 4.2	92.3 ± 5.2	85.7 ± 3.1	79.5 ± 3.3	84.0 ± 3.5
C F4 Cu	4.60 ± 0.15	4.55 ± 0.17	4.37 ± 0.18	5.86 ± 0.28	4.29 ± 0.18	4.57 ± 0.18	4.79 ± 0.20	4.45 ± 0.20	4.85 ± 0.27	7.57 ± 0.27	6.95 ± 0.29	8.04 ± 0.33
C F1 Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C F2 Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C F3 Pb	7.49 ± 0.24	7.15 ± 0.26	6.71 ± 0.28	7.41 ± 0.36	8.58 ± 0.35	8.23 ± 0.32	10.6 ± 0.4	10.7 ± 0.5	10.3 ± 0.6	8.57 ± 0.31	7.95 ± 0.33	8.29 ± 0.34
C F4 Pb	nd	nd	0.15 ± 0.01	nd	nd	0.65 ± 0.04	nd	0.30 ±	nd	0.26 ± 0.01	0.35 ± 0.02	0.65 ± 0.05

2.3. Figures

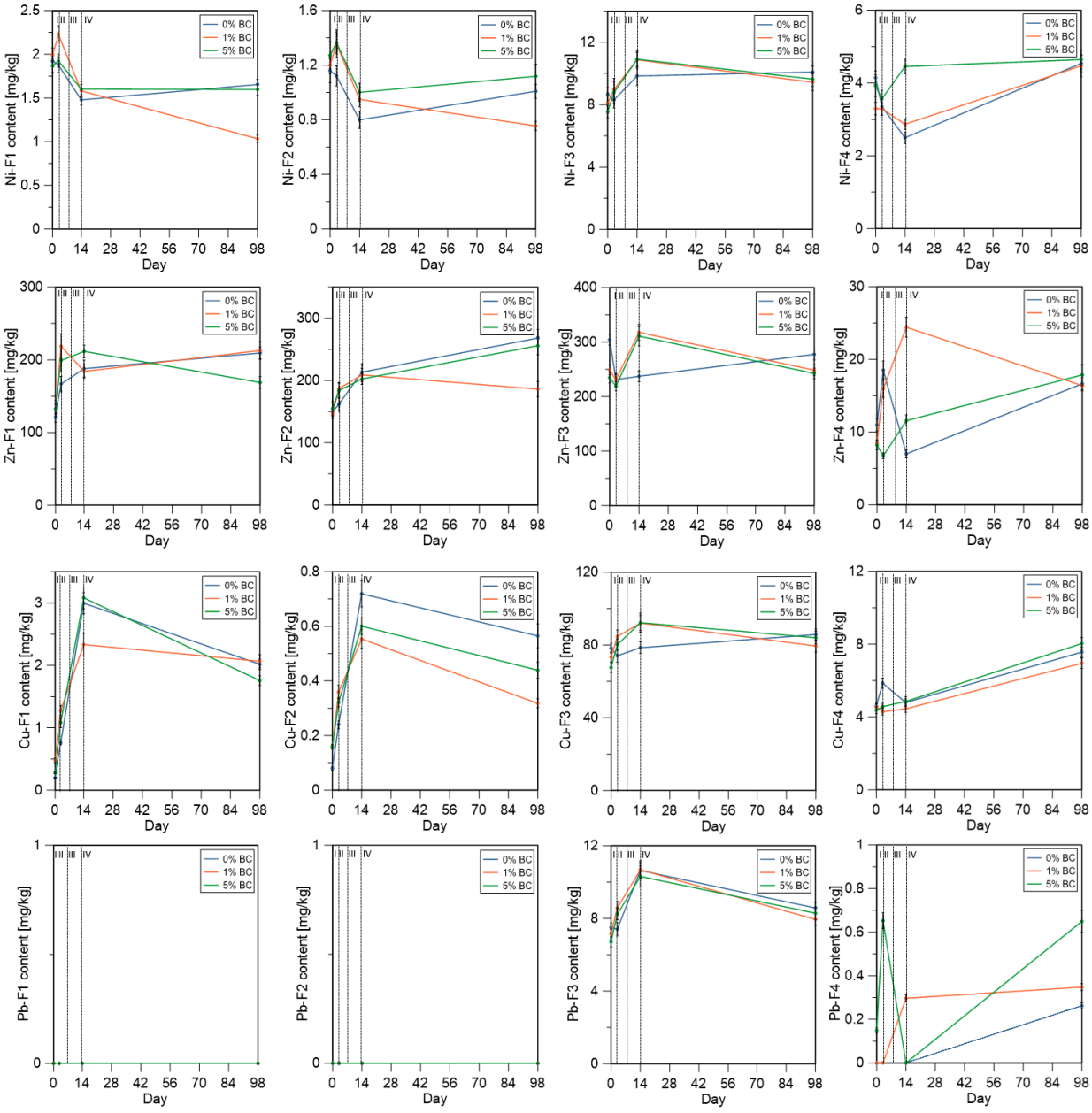
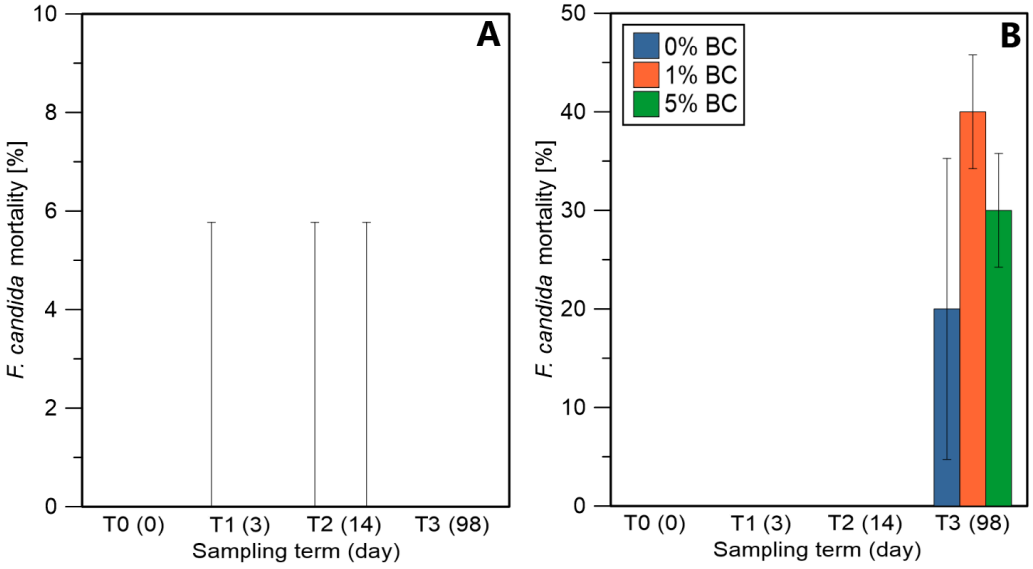
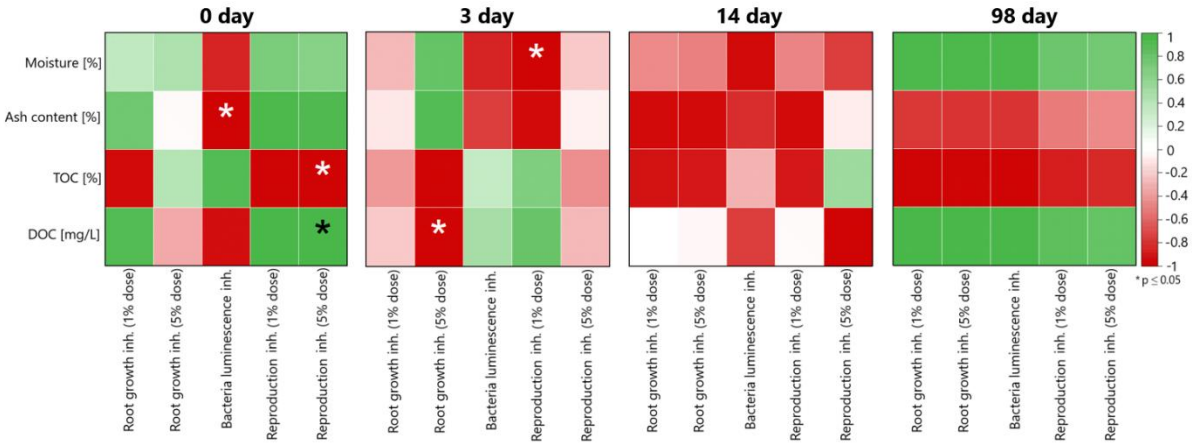


Fig. S1. Concentration of different fractions of Ni, Zn, Cu, and Pb [mg/kg] in materials with various biochar doses during composting. Error bars mean standard deviation error (in triplicate).



145

146 **Fig. S2.** Influence of the materials in different stages of composting on *Folsomia candida* mortality
147 (A – 1% dose to the soil, B – 5% dose to the soil). Error bars mean standard deviation error (in
148 triplicate).



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150 **Fig. S3.** Correlation plots presenting the values of Pearson correlation coefficients between the
151 ecotoxicological tests endpoints and physico-chemical properties of composts enriched with
152 biochar at different composting phases (days). Where * indicates a statistically significant
153 correlation ($p \leq 0.05$), TOC – total organic carbon content, DOC – dissolved organic carbon,
154 inh. – inhibition.

155 **References**

156 1. Pueyo M, Mateu J, Rigol A, et al (2008) Use of the modified BCR three-step sequential
157 extraction procedure for the study of trace element dynamics in contaminated soils. Environ
158 Pollut 152:330. https://doi.org/10.1016/J.ENVPOL.2007.06.020

159 2. Cofie O, Nikiema J, Impraim R, et al (2016) Co-composting of solid waste and fecal sludge for
160 nutrient and organic matter recovery. CGIAR Res Progr Water, L Ecosyst 47.
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162 3. Official Journal of the European Union (2022) Commission Decision (EU) 2022/1244 of 13
163 July 2022 establishing the EU Ecolabel criteria for growing media and soil improvers.
164 L190/141

165 4. European Compost Network (2014) European Quality Assurance Scheme for Compost and
166 Digestate

167 5. Canadian Council of Ministers of the Environment (2005) Guidelines for Compost Quality

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D4

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Influence of biochar characteristics on polycyclic aromatic hydrocarbons content during co-composting of sewage sludge

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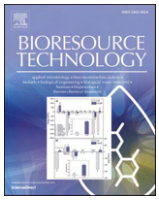

Influence of biochar characteristics on polycyclic aromatic hydrocarbons content during co-composting of sewage sludge

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HIGHLIGHTS

- Low-temperature biochars (BCs) contributed to greater losses of PAHs during composting.
- Effect of BC's feedstock on PAHs disappearance was marginal.
- BCs with a lower initial PAHs content resulted in a better reduction of C_{tot} PAHs.
- The reduction in the C_{free} PAHs was influenced by both the BC's pyrolysis temperature and feedstock.
- The bioavailability of PAHs was lower using low-temperature BCs and willow-derived BCs.

ARTICLE INFO

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Waste management
Carbon
Contaminants
Bioavailability
Degradation, sustainability

ABSTRACT

This study examined how biochar (BC) made from willow or sewage sludge at 500 °C or 700 °C affects polycyclic aromatic hydrocarbons (PAHs) during composting of sewage sludge with wheat straw. BC addition impacted both total (C_{tot}) and freely dissolved (C_{free}) PAHs, with effects dependent on pyrolysis temperature and, to a lesser extent, feedstock. Greater losses (both percentage and absolute) of C_{tot} PAHs occurred with low-temperature BC than high-temperature BC. The highest reduction was seen with sewage sludge-derived BC produced at 500 °C. For C_{free} PAHs, low-temperature BCs decreased bioavailability more than high-temperature BCs, with willow-derived BCs being more effective than sewage sludge-derived BCs. Results suggest BC's effectiveness in reducing PAHs depends mainly on feedstock for C_{tot} PAHs, but more on pyrolysis temperature for C_{free} PAHs. BC's capacity to reduce contaminants in compost could back regulations promoting its use in waste management and soil improvement.

1. Introduction

Composting is an aerobic process that transforms organic matter into a valuable agricultural product called compost (Barthod et al., 2018). Various types of biomass serve as composting materials, including green waste, food waste, municipal solid waste, or sewage sludge (SL) (Noor et al., 2024). Composting constitutes an excellent way to manage inconvenient and problematic waste (e.g. SL) through the effective degradation of the contaminants (Sharma et al., 2023). Various types of additives (organic, inorganic, and biological) that can be added during composting of organic matter have already been studied, and the pros and cons of mixed composting substrates have been previously indicated (Noor et al., 2024). Most research has centered on examining how specific composting additives affect process parameters and compost quality, particularly regarding nutrient availability or slow-release properties (Noor et al., 2024). These additives serve multiple functions, starting from deeply improving the composting process (temperature, aeration, heat transport), through promoting the activity of microorganisms, reducing gas emissions, and ending with reducing the leaking of heavy metals into the soil or increasing the bioavailability of nutrients for plants (Barthod et al., 2018).

Biochar (BC) has emerged as a widely studied composting additive in

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recent years (Du et al., 2019). As a carbon material with a highly developed specific surface area, BC excels at immobilizing contaminants (Pandey et al., 2021), while serving multiple functions during composting, e.g., it promotes the vitality of microorganisms by providing convenient conditions for their development (Song et al., 2024). Promoting the growth of microorganisms subsequently stimulates the biodegradation of pollutants (Bao et al., 2020). In addition, BC accelerates the decomposition of organic matter and the formation of humic substances (Xie et al., 2023), reduces the amount of greenhouse gases emitted during composting (Wang et al., 2023), and accelerates the maturation of compost (Bao et al., 2020). The ability to produce BC from various waste materials including SL, straw, rice husks, and wood chips (Manikandan et al., 2023), combined with its beneficial effect on compost and the composting process, makes it particularly attractive additive for both co-composting applications and mixing with finished compost (Mikajlo et al., 2024).

The use of BC as a compost additive is an effective solution that combines providing nutrients essential for plant growth and the adsorptive properties of BCs, which reduce the availability of pollutants. To date, many research have focused on mixed systems of BCs with ready-made compost (Alidou-Arzika et al., 2021; Rashid et al., 2022). However, BC added to the feedstock before composting performs much more critical functions than those provided by BC mixed with ready-made compost (Qian et al., 2023). The synergistic effect of co-composting BC with feedstock is more optimal for producing an effective soil amendment than mixing BC with ready-made compost (Mikajlo et al., 2024; Naveed et al., 2021).

Research shows extensive study of SL and BC co-composting (Du et al., 2019; Zhou et al., 2014). Most research has centered on core composting metrics: the microbial community structure, enzyme activity, compost maturity, germination index, greenhouse gases emission, nitrogen losses, formation of humic substances, and degree of degradation of organic matter. Very few works only consider the effect of BC addition during composting on contaminants content and their persistence/losses during composting (Awasthi et al., 2016; Chen et al., 2020).

Polycyclic aromatic hydrocarbons (PAHs) pose a significant ecological threat as widespread organic pollutants (Antizar-Ladislao et al., 2006). PAHs constitute a group of hydrophobic compounds with low water solubility, which are slightly degraded in the environment (Kończak et al., 2023). While PAHs can form naturally, their current environmental levels have become concerning. Usually, the research on PAHs focuses on determining the total (organic solvent extractable) content of PAHs in the tested matrices (Shi et al., 2023). To properly assess environmental safety, it is necessary to determine both total (C_{tot}) and bioavailable (C_{free}) PAHs content in the environmental samples. The content of the bioavailable PAHs only truly reflects the effect that pollution has on biota in the soil/water. Many composting studies overlook PAHs bioavailability, which directly provides information about the binding mechanism of PAHs by BCs particles incorporated during composting. While researchers commonly examine how BC dosage affects PAHs persistence in composting (Du et al., 2019), the broader picture matters too. It is well-known that pyrolysis conditions and feedstock determine the properties of BCs, thus, affecting differently the PAHs persistence during composting (Bao et al., 2020). Considering this, it is crucial to carefully select the BC's production parameters as it can directly affect the content as well as the degree of PAHs reduction. To our best knowledge, no work has been done where the effect of pyrolysis temperature and/or BC feedstock on PAHs content and bioavailability was investigated during SL composting. Understanding these production variables is essential, as they directly shape BC's key characteristics from pore structure to aromaticity and hydrophobicity. These properties, in turn, determine how effectively BC can remove or mitigate PAHs during composting.

The present work aimed to evaluate how the feedstock and pyrolysis temperature of BCs affect composting and PAHs persistence and bioavailability during the process. The effect of key stages of composting (mesophilic *I*, thermophilic, mesophilic *II*, and maturation) on PAHs was also investigated to understand the interaction between PAHs and composted matrix in various thermal composting conditions. The effect of selected physico-chemical properties of BCs and composted material on the PAHs losses was also investigated to propose the possible mechanisms responsible for PAHs bioavailability and losses during composting.

2. Materials and methods

2.1. Substrate preparation

Sewage sludge (SL) was sourced from the Municipal Sewage Treatment Plant in Poland (50°44′9.39″ N, 23°14′14.92″ E). After anaerobic digestion and mechanical dehydration, the SL contained 20 % dry mass with key properties including 80 % moisture, 34 % total organic carbon (TOC), 4.5 % total nitrogen (N), and pH 6.81. Wheat straw (WS) came from a farm in Liśnik Mały, Poland, harvested and shredded during standard yield collection. The WS showed 12 % moisture, 53 % TOC, and 0.69 % N content. BCs were produced from two sources: one-year-old willow stalks and SL and processed at temperatures of 500 °C or 700 °C in a nitrogen environment, as described by Siatecka et al. (Siatecka et al., 2021). Willow stalks and SL underwent air-drying and grinding before processing. A combination of SL, WS, and BC was utilized as the base material for the composting process. Further details on these materials can be found in the supplementary material and our earlier study (Rombel et al., 2024). In total, four distinct types of BCs were tested in this experiment. The physico-chemical characteristics of the BCs is presented in Table 1. Initially, SL and WS were combined in equal parts by weight (dry mass), followed by the addition of 1 % BC (by weight), which was then gently mixed to ensure uniformity. The choice of a 1 % BC addition was informed by our prior research (Rombel et al., 2024), which identified this amount as optimal for the composting process and for the reduction of PAHs. A control experiment was conducted with SL and WS composted without BC under the same conditions. In order to introduce beneficial microorganisms isolated from the soil, which are responsible for the proper course of composting, the bicompost microbiological preparation was used (Organika-Agrarius Sp. z o.o., Przemyśl, Poland). It contains mixture of various strains of *Bacillus* sp. bacteria in the amount of not less than $1{\cdot}10^9$ JTK in 1 g of the product. A solution was prepared by dissolving of 20 g in 10 L of deionized water (DI) water and 1 L of the solution was added per bioreactor (100 L of mixed material).

2.2. Composting experimental design and operation

The mixture of SL, WS, and BC was placed into 100-liter composting bioreactors (BKB-100, ROTAMETR, Gliwice, Poland), equipped with electronic systems for temperature and aeration control, and composted over a period of five weeks. Initial aeration in bioreactors was set at 60 L/h. After the first day of composting, the aeration was increased to 100 L/h, then on the third day to 120 L/h and on the fourth day to 140 L/h, after which the parameter was gradually reduced, until on 12th day the aeration value was reduced to 30 L/h and keep on this level to the end of composing in bioreactors. DI water was added periodically to the bioreactors to maintain the desired moisture content during composting. The OPTIMA7 Biogas Analyzer (MRU GmbH, Germany) was used to measure the levels of various gases, such as oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), nitric oxide (NO), methane (CH_4), and nitrogen (N_2), released during composting. After five weeks, the composted material was moved to barrels for a maturation period of two months. Compost samples, each around 100 g in dry mass, were collected systematically at set intervals throughout the composting process. These intervals were at the start and then at 3, 7, 14, 21, 28, 35, 70, and 98 days, labeled as T0 through T8. Specifically, T0 represents the beginning of composting, T1 marks the end of the mesophilic *I*

Table 1
Physico-chemical properties of biochars used in the experiments.

Type of biochar	pH	EC [mS/cm]	Ash [%]	TOC [%]	DOC [mg/L]	O/C *	H/C *	$\frac{O+N}{C}_*$	N/C *	S_{BET} [m^2/g]	V_p [cm^3/g]	d_{BET} [nm]
WL500	9.93	0.73	6.19	81.8	8.97	0.05	0.476	0.064	0.012	236.2	0.11	1.85
WL700	12.2	2.53	6.97	85.0	5.88	0.04	0.222	0.055	0.011	275.0	0.12	1.18
SL500	10.6	0.73	72.3	21.0	2.43	0.14	0.433	0.240	0.105	41.6	0.05	5.27
SL700	11.9	4.48	77.3	19.9	0.85	0.01	0.209	0.066	0.056	71.4	0.08	4.69

EC – electrical conductivity, ash – mineral fraction content, TOC – total organic carbon content, DOC – dissolved organic carbon, * molar ratios, S_{BET} – specific surface area based on BET model, V_p – total pore volume, d_{BET} – pore diameter based on BET model.

phase, T2 the conclusion of the thermophilic phase, T4 the end of the mesophilic *II* phase, and T6 the point when the compost is transferred to barrels for maturation. Before analysis, the samples were air-dried, ground using a laboratory knife grinder (TESTCHEM, Radlin, Poland), and stored at 4 °C in sealed plastic bags.

2.3. Physico-chemical characterization of samples

The methodologies and analyses related to sample characterization have been previously detailed (Rombel et al., 2024). In summary, TOC and dissolved organic carbon (DOC) were assessed using a TOC-L Analyzer with an SSM5000 furnace (Shimadzu, Kyoto, Japan). Measurements of DOC, electrical conductivity (EC), and pH were conducted on solutions post-extraction. A HQ430D universal laboratory multi-parameter meter (HACH, Loveland, Colorado, USA) was used for determining pH and EC values. The ash content was measured after the material was held in a furnace (Magma Therm, Istanbul, Turkey) at 760 °C for 6 h. Moisture content was determined by drying a representative sample of the material in a laboratory dryer (POL-EKO, Wodzisław Śląski, Poland) at 105 °C for 6 h until a stable mass was achieved. For more detailed information on composting parameters and changes in physico-chemical properties, please refer to the supplementary material.

2.4. Total (C_{tot}) and freely dissolved (C_{free}) PAHs concentration

The total concentration of PAHs, denoted as C_{tot}, was extracted from compost samples using an Accelerated Solvent Extraction (ASE) system, specifically the Dionex ASE 350 Accelerated Solvent Extractor (ThermoFisher Scientific based in Waltham, Massachusetts, USA) following the protocol outlined in references (Hilber et al., 2012; Kim et al., 2003). The content of freely dissolved PAHs, referred to as C_{free}, was determined using the method previously described in reference (Rombel et al., 2024). The comprehensive procedures are outlined in the reference (Rombel et al., 2024). Both qualitative and quantitative analyses of PAHs were conducted using a Trace 1300 gas chromatograph (ThermoFisher Scientific, Waltham, Massachusetts, USA). This instrument was equipped with an Rxi-5 ms column (length 30 m, id 0.25 mm, and 0.25 μm film thickness, Restek, Glastron, France).

The following equations were implemented to calculate the PAH partitioning coefficient between organic carbon and water (K_{oc}) (Arp et al., 2014):

$$Kd = \frac{\Sigma 16\ Ctot\ PAHs}{\Sigma 16\ Cfree\ PAHs} \quad (1)$$

$$Koc = \frac{K_d}{TOC} \bullet 100\% \quad (2)$$

where: Σ16 C_{tot} PAHs – Σ16 PAHs solvent extractable content (μg/kg), Σ16 C_{free} PAHs – Σ16 PAHs freely dissolved content (μg/L), and TOC – total organic carbon content (%).

3. Results and discussion

3.1. Characterization of biochars

The BCs used in the experiment differed in terms of physico-chemical properties (Table 1). WL-derived BCs were characterized by a low mineral fraction (6.2 – 7.0 %) and a high organic carbon content (82 – 85 %). The opposite trend was observed for SL-derived BCs. It was noted that the ash content ranged from 72 to 77 % and the TOC content from 20 to 21 %, depending on the pyrolysis temperature (Table 1). Additionally, WL-derived BCs demonstrated a specific surface area more than four times greater than those from SL. Higher production temperatures resulted in BCs with increased specific surface area. These high-temperature BCs also showed enhanced aromaticity (demonstrated by lower H/C molar ratios) and hydrophobicity (shown by lower O/C molar ratios) compared to their low-temperature counterparts, which is consistent with previous findings (de Oliveira Paiva et al., 2024). Furthermore, high-temperature BCs had significantly higher EC than those produced at lower temperature (Table 1).

The SL-derived BCs used in the experiment contained 36 – 85 % less Σ16 C_{tot} PAHs (503 – 594 μg/kg) than the WL-derived BCs (685 – 1098 μg/kg). These contents were lower or comparable to other BCs obtained from WL (Buss et al., 2022) and SL (Xing et al., 2021). The high-temperature BCs were characterized by lower Σ16 C_{tot} PAHs (from 18 % to 60 %) than low-temperature BCs, which is a commonly observed phenomenon (Wang et al., 2017). This is due to the higher porosity (specific surface area and total pore volume) of high-temperature BCs compared to low-temperature BCs, as also demonstrated in Table 1. During pyrolysis, PAHs tend to volatilize more readily when porosity increases (Luo et al., 2019). Across all feedstocks, 2- and 3-ring PAHs predominated in BCs accounting from 42 to 54 % and 32 to 36 %, respectively (Fig. 1). This aligns with previous research (Buss et al., 2022). When comparing feedstocks, WL-derived BCs had a higher contribution of 2-ring PAHs, but a lower contribution of 4–6-ring PAHs than those produced from SL (Fig. 1). Notably, the total PAHs content in all tested BCs fell within acceptable limits set by the Swiss Chemical Risk Reduction Act, meeting standards for both basic grade (12 mg/kg) and premium grade materials (4 mg/kg) (EBC, 2015).

In contrast to C_{tot} PAHs, Σ16 C_{free} PAHs content in the WL-derived BCs (135 – 143 ng/L) was found to be lower than that in SL-derived BCs (138 – 155 ng/L), which is a common observation for BCs obtained from the same feedstock (Xing et al., 2021). Σ16 C_{free} PAHs content in investigated BCs was also much lower than in the soil under the strong anthropogenic pressure (Arp et al., 2014). The higher content of C_{free} PAHs in SL-derived BCs is linked to the lower TOC content in these BCs, which may affect PAHs availability (Zheng et al., 2024). Because SL-derived BCs do not contain much organic carbon, they are less hydrophobic and aromatic which translates into lower affinity for the hydrophobic aromatic molecules like PAHs. This means they are not very good at binding to PAHs, leaving more of these compounds in solution (in the form of C_{free} PAHs) (Siatecka et al., 2021). Naphthalene (NAP) (2-ring PAH) was predominant in all obtained BCs (Fig. 1).

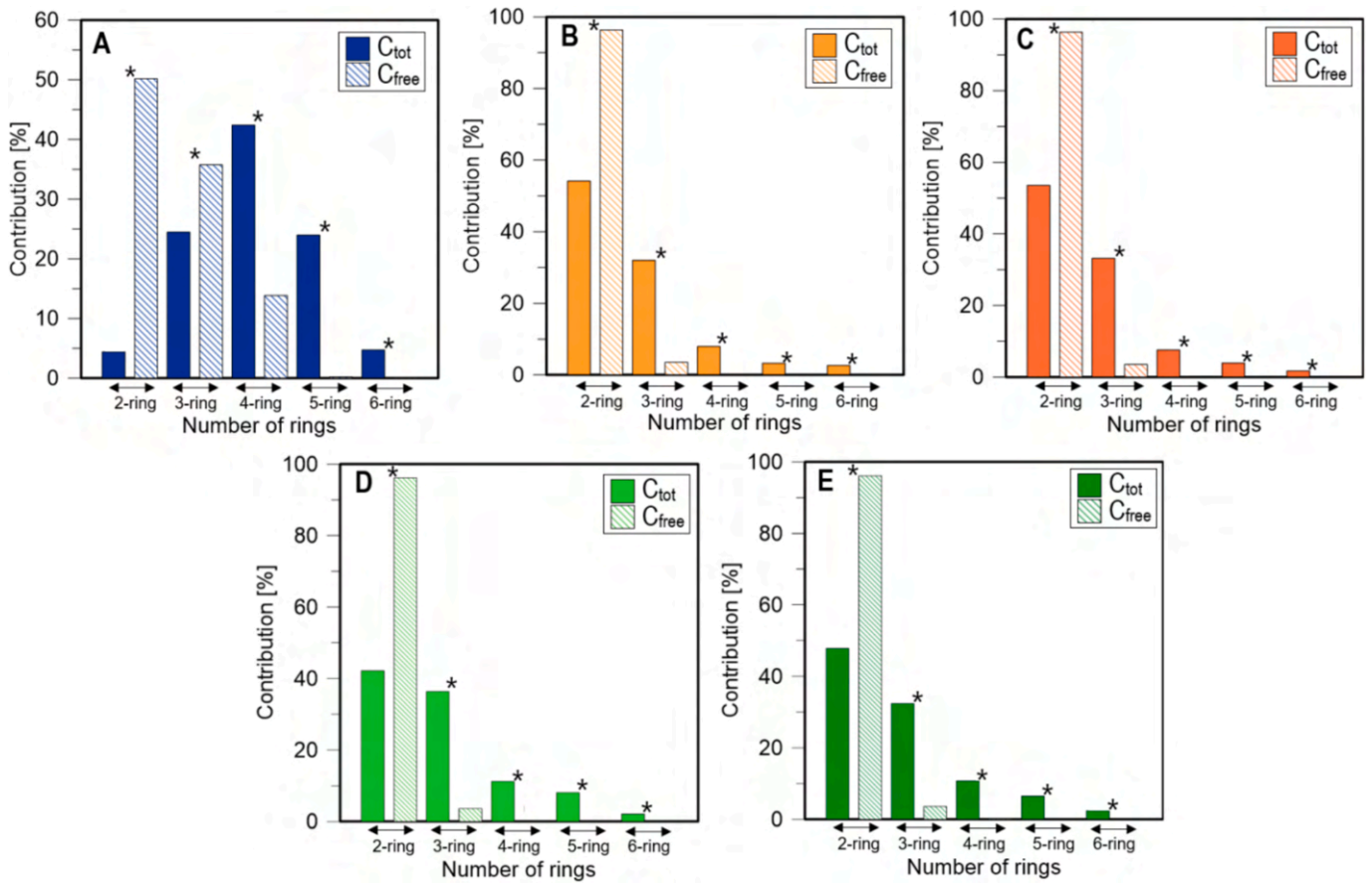

Fig. 1. Contribution of particular PAHs groups in the sewage sludge (A) and biochars: WL500 (B), WL700 (C), SL500 (D), and SL700 (E) regarding number of rings in the solvent extractable (C_{tot}) and freely dissolved (C_{free}) PAHs content where * means statistically significant change ($p \leq 0.05$).

3.2. *Composting parameters and compost samples characterization*

Temperature changes during composting followed distinct phases (see supplementary material). The mesophilic phase *I* lasted 2 – 3.5 days, with BC additions shortening this initial phase. During this time, pH decreased while EC increased by 8.7 – 21 % in BC variants. WL-BCs caused greater changes than SL-derived ones. The critical thermophilic phase, reaching above 45 °C, began earliest with WL500, WL700, and SL700 additions (day 2). WL-derived BCs maintained the longest thermophilic phase (4 days) and achieved the highest temperatures (56 °C), compared to just 3 days and 50.5 °C in the control. This phase saw slight pH increases and continued EC elevation. The mesophilic *II* phase lasted about 14 days, characterized by stabilizing pH and decreasing EC. SL-BCs showed greater ability to bind dissolved organic carbon than WL-BCs during this period. Oxygen consumption returned to normal levels, indicating the end of major aerobic processes. The final maturation phase (days 21 – 98) showed varying pH trends, with WL-BCs reaching final values of 5.08 – 5.13. TOC decreased more significantly with WL-BCs (4.5 – 7.2 % reduction) than SL-BCs (3.5 – 3.6 % reduction), while mineral content increased by 8.3 – 11 %, with higher values in SL-BC experiments.

3.3. *C_{tot} and C_{free} PAHs changes during sewage sludge composting*

Analysis of Fig. 2**A** reveals a significant 30 % reduction in the content of Σ16 C_{tot} PAHs during the first 14 days of composting, specifically in the mesophilic *I* and thermophilic phases. This finding confirms previous research by Hua et al. (2008), which identified the thermophilic phase as the period of maximum PAH reduction during SL composting. The elevated temperatures during this phase enhance both the mass transfer and solubility of organic contaminants, increasing their bioavailability to microorganisms (Hua et al., 2008). The overall decrease of Σ16 PAHs was primarily driven by a 65 % reduction in 5-ring PAHs, with 4-ring PAHs showing a more modest decrease of 9.3 % (Fig. 3**C and D**). Other PAH groups showed an increase from 9.3 to 19 %. While some fluctuations in C_{tot} PAHs were noted in the control samples during later composting stages – particularly in 2-ring PAHs – levels remained stable throughout the mesophilic *II* and maturation phases (Fig. 3**A**). According to the results of a 98-day composting, the Σ16 C_{tot} PAHs decreased by 30 % compared to the beginning of the experiment, with the first 14 days being the most crucial for their disappearance (Fig. 2**A**). The majority of the reduction in total PAHs was due to the loss of 5-ring PAHs, which decreased by 65 % compared to the initial content (Fig. 3). Additionally, there was a lesser reduction in 4- and 6-ring PAHs (12 % and 16 %, respectively).

A significant increase of Σ16 C_{free} PAHs (by 56 %) in the control was observed during the first seven days of composting (mesophilic *I* and thermophilic phases, Fig. 2**B**). This change was predominantly attributable to the increased content of 2-rings PAHs (Fig. 4). The increase could be caused by the weakening of the interactions between this group of PAHs and other PAHs and matrix, which facilitates the transfer of PAH into the aqueous phase. During the mesophilic phase *II*, C_{free} PAHs decreased in control to the level observed at the beginning of the composting and continued at this level until day 70 of the composting (Fig. 2**B**). It was caused by a decrease in the content of all PAHs (Fig. 4), and the most visible effect occurred for 2-rings PAHs (almost twofold). During the last period of maturation (70 – 98 days) an increase in Σ16 C_{free} PAHs was observed, and again was caused by an increase in 2-rings PAHs (Fig. 4). Regarding individual PAH groups and their changes during composting, a 43 % increase was observed for NAP only. In

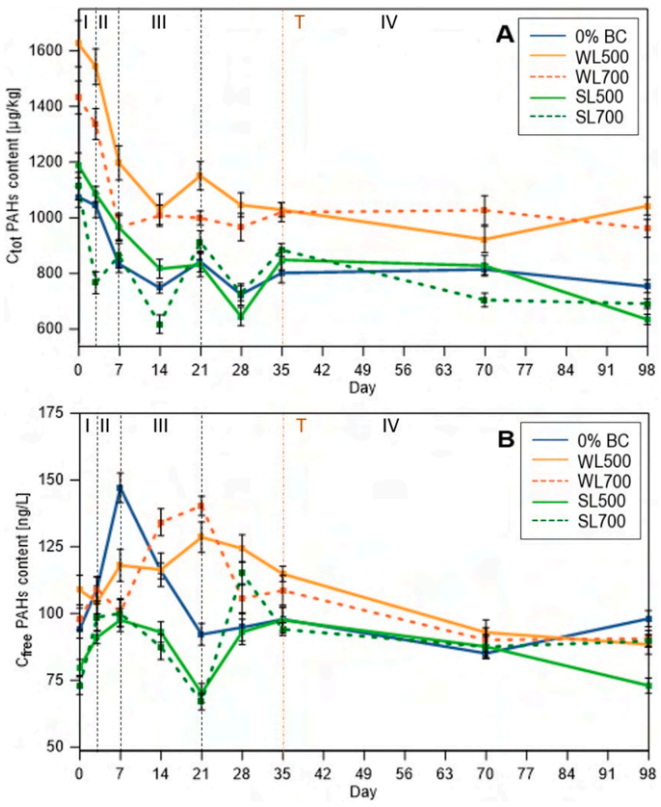

Fig. 2. Change of solvent extractable (A) and freely dissolved (B) Σ16 PAHs content during composting. Composting phases: I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation, T – transfer to a plastic barrel. Error bars means standard deviation error (in triplicate).

contrast, a 34 – 45 % decrease was observed for other groups (≥ 3-ring PAHs) compared to the beginning of the experiment (Fig. 4).

3.4. *Effect of the BC pyrolysis temperature on C_{tot} PAHs*

BCs derived from WL at a lower pyrolysis temperature showed higher initial content of C_{tot} PAHs compared to high-temperature BCs, a pattern that persisted throughout composting (Fig. 2**A**). In contrast, SL-derived BCs showed no statistically significant ($p \leq 0.05$) differences in C_{tot} PAHs based on pyrolysis temperature at composting initiation (Fig. 2**A**). During mesophilic phase *I*, only SL-BCs exhibited a significant reduction in Σ16 C_{tot} PAHs (Fig. 2**A**), primarily due to 5-ring PAHs losses ranging from 27 % (SL500) to 44 % (SL700) compared to initial levels (Fig. 3**D**). The thermophilic phase brought notable reduction in Σ16 C_{tot} PAHs for both WL-BCs (22 % for WL500 and 28 % for WL700) and SL500 (11 % decrease) compared to mesophilic *I* phase endpoints. Interestingly SL700 showed an increased Σ16 C_{tot} PAHs during this phase (Fig. 2**A**). During the thermophilic phase, a reduction of C_{tot} for selected BCs occurred. This reduction was mainly due to a decrease of BaP (70 – 74 % compared to the beginning of the experiment). Similar observations were made earlier for the control. The decrease of other individual PAHs was generally less significant, with a reduction of < 15 % (see supplementary material). The mesophilic *II* phase revealed two distinct stages in Σ16 C_{tot} PAHs changes (Fig. 2**A**). The first stage (from 7 to 14 days) showed decreases for WL500, SL500 and SL700, while the second stage (from 14 to 21 days) showed increases for WL500 and SL700, returning to early mesophilic *II* phase levels. WL700 showed no statistically significant ($p \leq 0.05$) changes in Σ16 C_{tot} PAHs content during this phase (Fig. 2**A**). During maturation, PAH levels showed minimal variations, with no clear correlation to BC pyrolysis temperature (Fig. 2**A**).

Degradation of PAH, both percentage and absolute, was significantly more effective when using BCs obtained at a lower pyrolysis temperature compared to a higher (554 – 583 µg/kg and 423 – 471 µg/kg, for low- and high-temperature BCs, respectively). This difference could be attributed to the lower specific surface area and pore volume and lower aromaticity (higher H/C molar ratio) and hydrophobicity (higher O/C molar ratio) of low-temperature BCs than high-temperature BCs

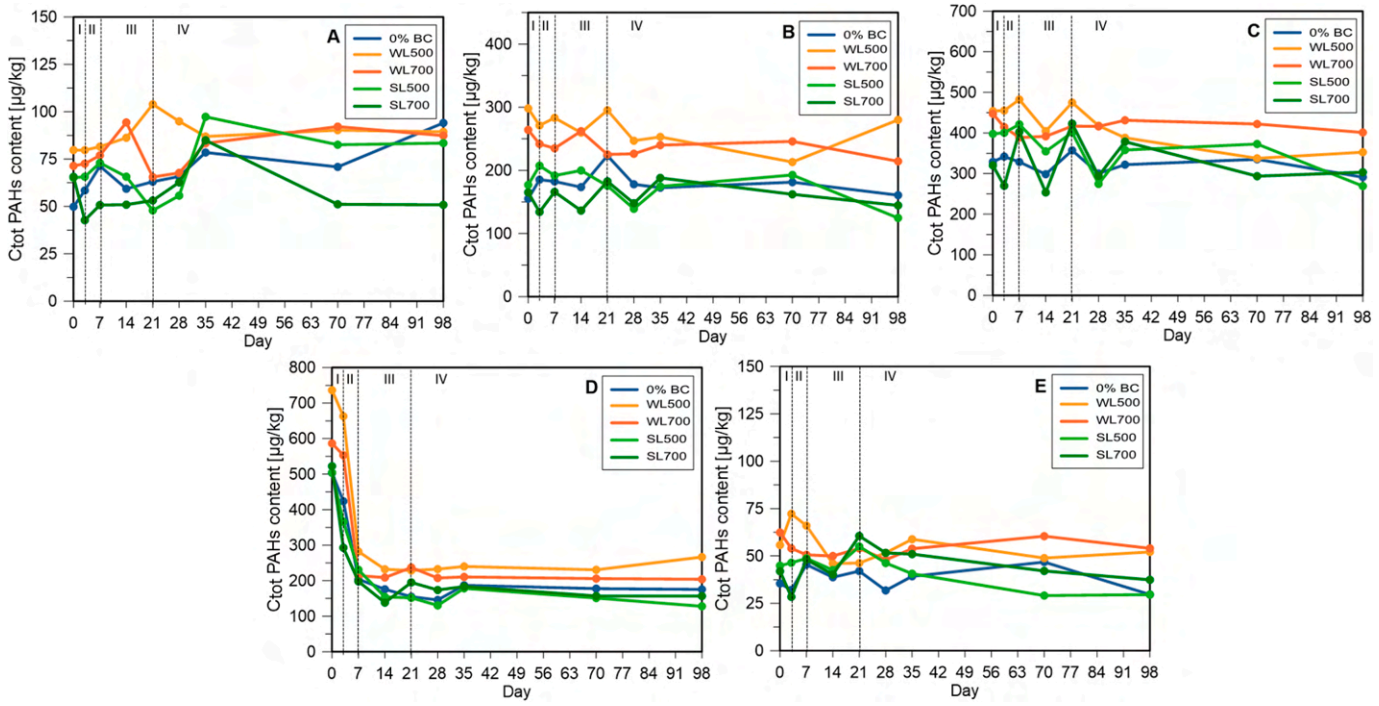

Fig. 3. Change of solvent extractable Σ16 PAHs (C_{tot}) content, depending on the number of rings, during composting (A – 2-ring, B – 3-ring, C – 4-ring, D – 5-ring, E – 6-ring PAHs). Composting phases: I – mesophilic *I*, *II* – thermophilic, III – mesophilic II, IV – maturation.

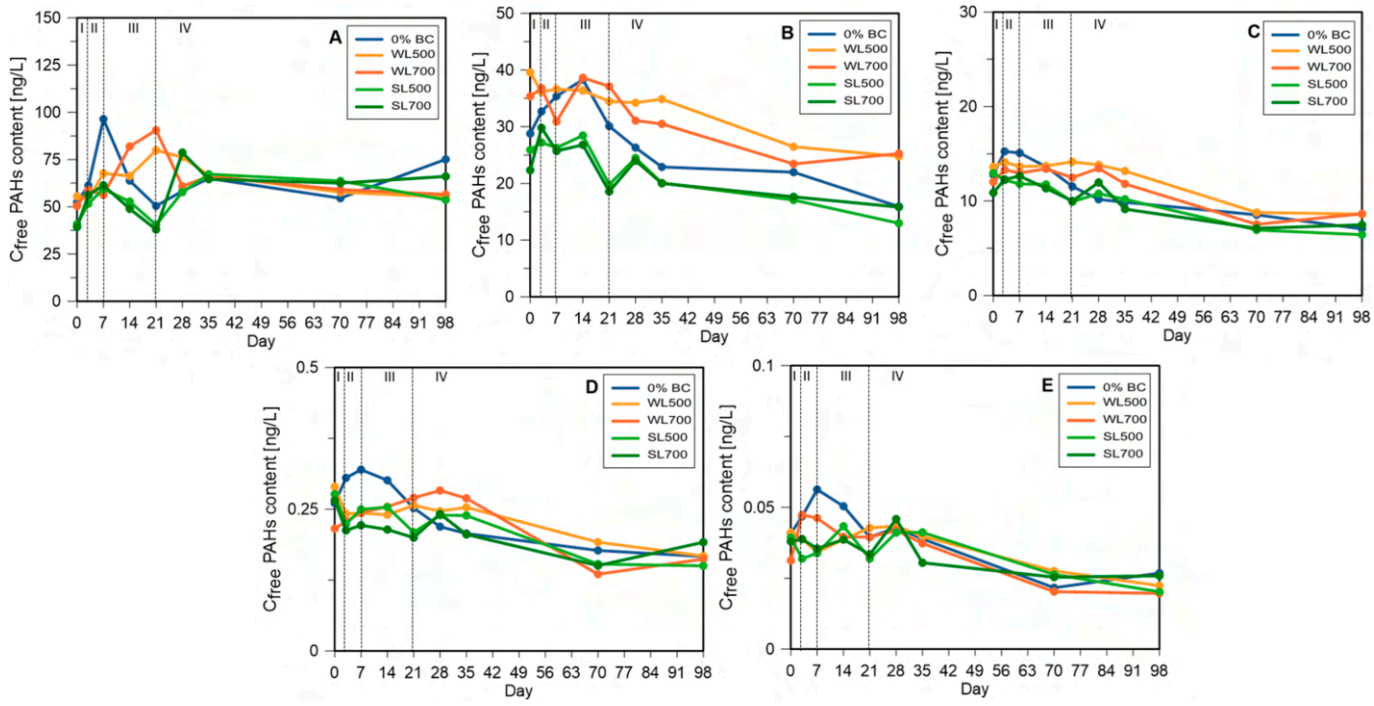

Fig. 4. Change of freely dissolved Σ16 PAHs (C_{free}) content, depending on the number of rings, during composting (A – 2-ring, B – 3-ring, C – 4-ring, D – 5-ring, E – 6-ring PAHs). Composting phases: I – mesophilic *I*, *II* – thermophilic, III – mesophilic II, IV – maturation.

(Table 1). The surface parameters of BCs are extremely important in the context of their adsorption capacity. Low values of specific surface area, pore volume, aromaticity, and hydrophobicity do not favor the occurrence of PAHs adsorption processes on the BC surface. This allows to conclude that the leading mechanism responsible for the greater reduction of C_{tot} PAHs in the variants with low-temperature BCs was microbiological degradation, and to a lesser extent adsorption on the surface of BCs. On the other hand, the higher porosity of high-temperature BCs could promote the PAHs ability to adsorb contaminants that become more difficult to extract by solvents (Kończak et al., 2023).

3.5. *Effect of the BC feedstock on C_{tot} PAHs*

The initial content of Σ16 C_{tot} PAHs was significantly higher in the treatments containing WL-derived BCs than in the control (from 25 to 34 %) and containing SL-derived BCs (from 22 to 26 %) ($p \leq 0.05$) (Fig. 2**A**). Addition of SL-derived BCs to composted material did not significantly alter the initial content of Σ16 C_{tot} PAHs compared to the control ($p \leq 0.05$) (Fig. 2**A**). The composting process revealed an interesting pattern, where treatments with SL-derived BCs showed significantly lower final Σ16 C_{tot} PAHs concentration (reduced by 8.4 – 18 %) compared to the control ($p \leq 0.05$) (Fig. 2**A**). This finding points to SL-derived BCs' potential role in accelerating PAHs degradation. In fact, these treatments demonstrated the highest PAHs rates across all experimental conditions (Fig. 2**A**). SL-derived BCs performed marginally better at PAHs reduction (in %) than WL-derived BCs, likely due to their larger pore diameters (5.27 and 4.69 nm vs. 1.85 and 1.18 nm) (Table 1). These larger pores create optimal conditions for microbiological growth (Gul et al., 2015). The BC pores serve as a microhabitats, enhancing material density, air circulation, and/or nutrient retention within the matrix (Gul et al., 2015). These conditions support more efficient PAHs degradation by fostering the growth of microorganisms responsible for the decomposition of these compounds. Additionally, the larger pores may improve the transfer of PAHs from BCs to the compost solution, making them more accessible for (bio)degradation. Another key factor was the higher polarity of SL-BCs indicated by their increased molar ratio (O + N)/C compared to WL-BCs (Table 1). This higher polarity weakens the bonds between PAHs and the more polar surface of SL-derived BCs (Guo et al., 2010). As a result, fewer PAHs remain reversibly adsorbed to the BC surface, allowing microorganisms greater access for decomposition.

The results demonstrated that the absolute degradation of Σ16 C_{tot} PAHs during composting was highly consistent across the variants with BCs, regardless of the BC feedstock. The reduction ranged from 422.5 to 554.0 μg/kg for SL-BCs and 470.6 to 583.4 μg/kg for WL-BCs, indicating that the absolute amount of degraded PAHs was nearly identical between the two BC feedstocks.

It should be emphasized, however, that the use of WL-derived BCs led to a higher final (after 98 days) Σ16 C_{tot} PAHs content compared to the BC-free variant (by 39 and 28 %, for WL500 and WL700, respectively). This highlights that, apart from the excellent PAHs reduction achieved by the use of WL-BCs, they ultimately contributed to a higher concentration of PAHs in the BC-enriched compost compared to the control. This could be linked to the higher content of Σ16 C_{tot} PAHs in WL-BCs compared to SL-BCs. Nevertheless, it emphasizes the need of conducting extensive studies to prove the importance of precise and accurate selection of BCs production conditions in order to achieve the stated environmental objective.

The dendrogram derived from cluster analysis of values determined for each compost mixture effectively visualizes the (dis)similarities between the samples based on their fingerprinting data (Fig. 5**A-B**). The compositional analysis of individual PAHs makes it possible to predict their behavioral patterns during the composting process. When different variants exhibit similar trends (maintaining comparable compositions), this indicates that the PAH transformation mechanisms are analogous (identical factors govern PAH behavior). Conversely, when the composition undergoes differential changes across variants, this suggests that distinct factors may influence the transformation pathways of these compounds. While the initial and final stages of the experiment provide limited insights into the feedstock's and pyrolysis temperature's influence and individual C_{tot} PAH content, some trends emerge. The closest similarity was observed between the control and the experiment containing SL700 (Fig. 5**A**). Notably, the (dis)similarities at the final

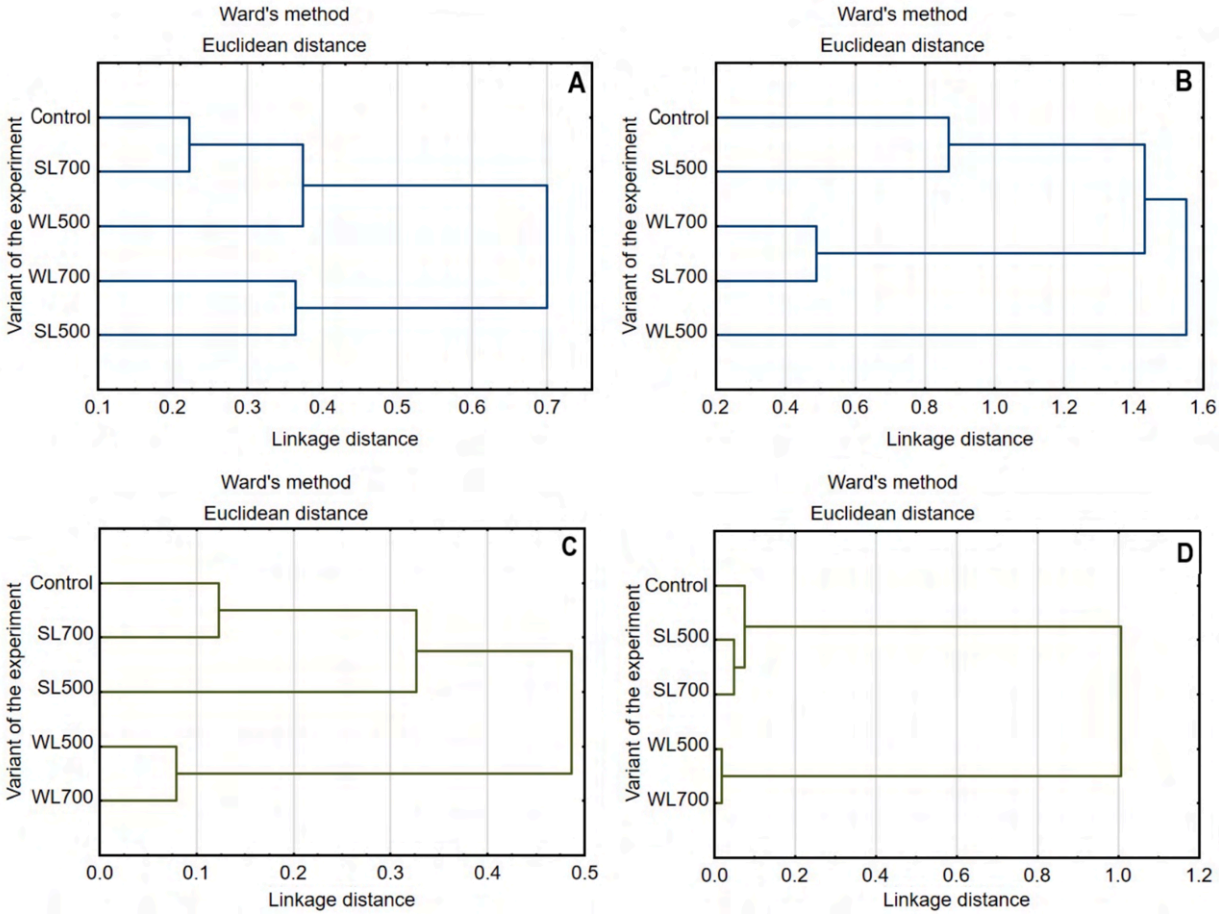

Fig. 5. Dendrogram of the solvent extractable (C_{tot}) individual PAHs content at the beginning (A) and at the end (B) of the experiment and of the freely dissolved (C_{free}) individual PAHs content in the material at the beginning (C) and at the end (D) of the experiment.

composting stage were distinct from those at the beginning of composting. The addition of BCs obtained at a higher pyrolysis temperature showed the most similarity, regardless of the feedstock (Fig. 5**B**). This finding strongly supports our previous suggestion that the pyrolysis temperature of BC has a greater impact on the change in individual C_{tot} PAHs content during composting than the BC's feedstock. The experiment with SL500 demonstrated the closest similarity to the control, contributing to the highest absolute and percentage disappearance of Σ16 C_{tot} PAHs at the end of the experiment.

We have therefore shown that the effect of BC's feedstock on PAHs disappearance was marginal and better disappearance of PAHs observed for SL-BCs than WL-BCs was determined by the initial content of PAHs in the BCs. A more important parameter which affect PAHs disappearance was temperature of pyrolysis. Although the addition of BC can lead to an increase in the initial PAH content in the compost material, the degree of reduction in the content of the tested compounds during composting was higher when BC was added. Looking at the changes in Σ16 C_{tot} PAHs content compared to the beginning of the experiment, slightly greater PAHs losses were observed in the experiment with SL-derived BCs (38 – 47 %) than with WL-BCs (33 – 36 %). The lowest degree of degradation/removal of PAHs was achieved in the variant without BC (30 % compared to the beginning of the study). Significantly ($p \leq 0.05$) higher losses of Σ16 C_{tot} PAHs were noted for treatments with BCs produced at lower temperature than at higher temperature.

Several studies have investigated the level of C_{tot} PAHs during composting of SL alone or with additives other than BCs (Cai et al., 2007; Guo et al., 2020; Hua et al., 2008; Poluszyńska et al., 2017). The degree of PAH reduction achieved in the present experiment was generally lower compared to other studies (62 – 94 % compared to 33 – 47 % in this study). Hua et al. (2008), for example, achieved a 79 % reduction of C_{tot} PAHs after composting SL and sawdust with rapeseed pomace for 30 days (initial concentration of PAHs was 75 mg/kg). Poluszyńska et al. (2017) showed an 85 % reduction of Σ16 PAH with an initial PAH content in the range of 10 – 25 mg/kg (representation of the concentrations range from 6 measurements of SL samples taken monthly). Guo et al. (2020) observed a 62 to 75 % PAH removal efficiency during composting SL with green forest waste (initial PAH content was 5.6 – 9.8 mg/kg). Cai et al. (2007) achieved a reduction of PAHs from 64 to 94 % after composting SL and rice straw (the initial concentration was 29 mg/kg). It should be emphasized that a similar reduction level was achieved in almost all the studies mentioned, regardless of the initial PAH content in the material. We hypothesize that discrepancies observed between the current results and previous findings can be attributed to the initial concentration of C_{tot} PAHs. In the present study, C_{tot} PAHs levels were significantly lower (ranging from 1.1 to 1.6 mg/kg) compared to those reported in the literature (ranging from 5.6 to 75 mg/kg in others). This matters because PAH degradation rates in soil and sediments are closely tied to their concentration (Sayara et al., 2010). Sayara et al. (2010) found that lower PAHs concentrations led to slower degradation rates. It is suggested that when low concentration of PAHs is present in the matrix (soil/sediment), the degradation process struggles to begin at all (Sayara et al., 2010). Microorganisms are more likely to start degradation using easily available compounds in larger quantities than those that are scarce and less available. Over time, the activity of microorganisms is limited and low concentrations of PAHs remain undegraded. Moreover, Jørgensen et al. (2000) demonstrated that the degradation of PAHs takes place according to first-order kinetics, which proves that the degradation rate is directly proportional to

the concentration of the degraded compound. It should be mentioned that the effect of a high concentration of PAHs will not always lead to a proportionally high degradation rate due to the fact that reaching a certain level of the contaminant concentration will lead to retardation/inhibition of the microbial activity (Sayara et al., 2010).

3.6. Effect of the BC pyrolysis temperature on C_{free} PAHs

For BCs produced at a lower pyrolysis temperature, an elevated initial concentration (10 % increase, irrespective of feedstock) of Σ16 C_{free} PAHs was noted in comparison to high-temperature BCs (Fig. 2**B**). The primary disparities in PAH content and behavior between low- and high-temperature WL-BCs experiments were demonstrated during the mesophilic *I*, thermophilic, and mesophilic *II* phases (Fig. 2**B**). However, for WL500 and WL700, an increasing trend in PAHs content was noted during these phases (Fig. 2**B**). Over the initial 21 days, C_{free} PAHs concentration increased by 18 % and 43 % relative to the beginning of composting for WL500 and WL700, respectively. This suggests that intensive processes transpiring during mesophilic *I*, thermophilic, and mesophilic *II* phases significantly impact PAH-compost matrix interactions, primarily diminishing their binding affinity. Regarding SL-BCs, their influence on C_{free} PAHs fluctuations was largely analogous (no statistically significant differences, $p \leq 0.05$) throughout the composting, irrespective of BC pyrolysis temperature (Fig. 2**B**).

A notable observation was that the lower pyrolysis temperature of added BC had a more favorable impact on C_{free} PAHs reduction than higher temperature (Fig. 2**B and** Fig. 4), irrespective of feedstock. Lower BCs' pyrolysis temperature facilitated greater losses of 5–6-ring PAHs relative to the control (Fig. 4). This underscores the importance of BC's role in mitigating the bioavailability of the higher molecular weight PAHs.

All BCs treatments resulted in lower Σ16 C_{free} PAH concentrations compared to the control, with reductions ranging from 7.8 % to 26 % (Fig. 2**B**). SL500 showed significantly better performance in reducing Σ16 C_{free} PAHs than in SL700. WL-derived BCs showed similar effectiveness regardless of the pyrolysis temperature (Fig. 2**B**). Notably, BCs obtained at lower pyrolysis temperature, irrespective of feedstock, facilitated greater percentage and absolute reductions in C_{free} PAHs.

The results showed that for reducing the bioavailability of PAHs, as in the case of the C_{tot} PAHs, the pyrolysis temperature of the added BCs plays a crucial role in reducing PAH bioavailability, although this effect is controlled by the BC feedstock. It can be concluded that lower pyrolysis temperature BCs enhance the affinity of PAHs for the composting matrix, thereby diminishing PAHs bioavailability.

3.7. Effect of the BC feedstock on C_{free} PAHs

The initial Σ16 C_{free} PAHs content in experiments containing SL-derived BCs was lower than for WL-derived BCs (by 36 %, irrespective of the pyrolysis temperature) (Fig. 2**B**), although there were SL-BCs that had higher C_{free} content than WL-BCs (Subsection 3.1). This could be attributed to enhanced PAH sorption by SL-BCs and consequent difficulties in their extraction relative to WL-BCs. Due to the lower initial content of Σ16 C_{free} PAHs in the experiments with SL-derived BCs compared to WL-derived BCs and control treatments (Fig. 2**B**), it was inferred that PAHs exhibit greater affinity for BCs derived from SL than for raw SL used in composting.

When comparing control samples with WL-derived BC experiments, we found no statistically significant differences ($p \leq 0.05$) in C_{free} PAHs content (Fig. 2**B**). During the initial composting period (0 – 35 day), which include the mesophilic *I*, thermophilic and mesophilic *II* phases, there were notable treatment-specific variations in C_{free} PAHs levels (Fig. 2**B**). Treatments containing SL-BCs showed remarkably similar patterns in C_{free} PAHs changes throughout composting, with differences emerging only in the final maturation period (day 70 – 98). The maturation phase revealed three distinct stages based on the changes in Σ16 C_{free} PAHs. The initial maturation period (21 – 35 days) was characterized by C_{free} PAHs reduction for WL-BCs treatments (11 % and 23 % for WL500 and WL700, respectively) and C_{free} PAHs increase for SL-BCs experiments (39 % and 41 % for SL500 and SL700, respectively). From 35 to 70 days, a slight C_{free} content decrease was observed across all treatments. This trend persisted until the end of the experimental period for all BC variants, except SL500, which facilitated an 18 % C_{free} PAHs decrease (70 – 98 day). Ultimately, the addition of SL500 resulted in the lowest absolute final Σ16 C_{free} PAHs content among all experimental variants (21 – 24 % lower compared to the remaining variants with BCs and 34 % lower than in control) (Fig. 2**B**).

Better results (both percentage reduction and absolute change) were recorded for WL-derived BCs compared to SL-BCs. Only for WL500, the content of C_{free} PAHs was statistically significantly ($p \leq 0.05$) lower (19 %) than at the beginning of the experiment (Fig. 2**B and 4**).

Based on the dendrogram (Fig. 5**C-D**), we found that from the beginning of the experiment, there was a similarity between the WL-derived BCs, regardless of the pyrolysis temperature (Fig. 5**C**). SL-BCs also showed similarity, but to a lesser extent than WL-BCs. The closest similarity to the control was observed in the experiment with SL700 (Fig. 5**C**), similar to the cluster analysis for C_{tot} (Fig. 5**A**). In contrast to the observations for C_{tot} PAHs (Fig. 5**A-B**), many similarities were observed for C_{free} with the dendrogram obtained at the final stage of the experiment (Fig. 5**D**). The highest similarity was found between WL-BCs and a slightly lower similarity was observed for SL-BCs. The control showed a high similarity with SL-BCs. The treatments with WL-BCs were significantly different from the other treatments, which may indicate a different mechanism of their action related to the reduction of PAHs bioavailability.

Comparing the changes in C_{tot} and C_{free} reveals whether these concentrations changed together or resulted from separate interactions between PAHs and the matrix (see supplementary material). In early composting stages, C_{tot} and C_{free} profiles showed notable differences across all variants, with WL500 displaying the closest relationship between the two measurements (see supplementary material). During the final maturation phase, C_{tot} and C_{free} demonstrated stronger correlation, particularly in the variant with SL500 (see supplementary material).

3.8. Log K_{oc} coefficient values

The K_{oc} coefficient quantifies the sorption capacity of a PAH to a matrix such as BC, SL or compost, providing insight into the PAH's environmental mobility. Elevated log K_{oc} values correlate with a heightened affinity of the compound to the matrix and diminished mobility (Fouad et al., 2024). A subset of PAHs, including NAP, PHE, FLA, and BaP, representing various ring number, were selected to exemplify the log K_{oc} dynamics through the composting trajectory (Fig. 6). The variable log K_{oc} values throughout the experiment reflect the shifting sorptive interactions of the PAHs with the compost matrix.

Predominantly, the SL700 variant exhibited the lowest log K_{oc} values during composting, particularly for NAP and BaP (Fig. 6) suggesting reduced sorptive interactions with PAHs, which could enhance mobility and PAH degradation potential. About 23 % increase in the content of C_{free} PAHs was noted for this treatment compared to the start of the study, providing support for the hypothesis. Moreover, this was the only experimental variant showing an increase in C_{free} PAHs after composting.

Concerning BaP, a marked decrease in log K_{oc} values was observed across all treatments during composting (Fig. 6**D**), with the most pronounced reduction associated with the SL700 addition. Comparatively, SL-derived BCs presented lower log K_{oc} values for BaP than those derived from WL, suggesting that composting with SL-BCs facilitates greater mobility and weaker matrix binding of 5-ring PAHs than WL-BCs.

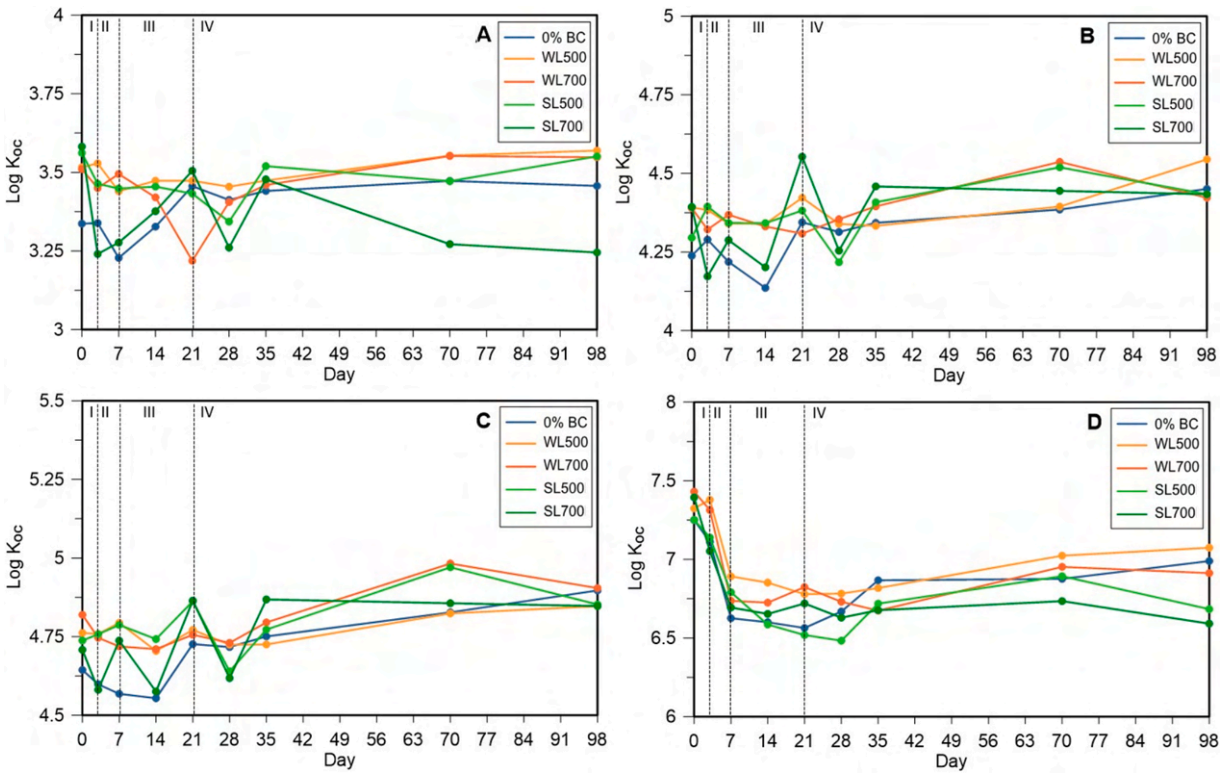

Fig. 6. Log organic carbon – water partitioning coefficients (K_{oc}) values for four chosen PAHs: A – naphthalene (NAP), B – phenanthrene (PHE), C – fluoranthene (FLA), D – benzo(a)pyrene (BaP) during composting. Composting phases: I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation.

3.9. Relationship between PAHs levels and physico-chemical characteristics of compost

The relationship between PAH losses during composting and the material physico-chemical properties was examined through correlation analysis of both C_{tot} or C_{free} PAHs content. The analysis revealed statistically significant relationships between C_{tot} PAHs and TOC, DOC, EC, mineral content (ash), and material moisture ($p < 0.1$, see supplementary material). Experiments with BC showed more frequent correlations between individual and Σ16 C_{tot} PAHs compared to the control, highlighting BC's key role in PAHs loss mechanisms. BCs can release organic substances after adding to the composting feedstock, which may cause a positive effect on the growth of microorganisms implicated in PAH degradation, but also the extraordinary adsorptive characteristics of BCs may facilitate pollutant permanent immobilization (Gorovtsov et al., 2020). The correlations between material properties were observed more frequently for WL-BCs than SL-BCs (see supplementary material), which could suggest a more substantial influence of WL-BCs in PAH reduction than SL-BCs. Additionally, these correlations appeared more often for variants with BCs obtained at a lower temperature, possibly due to their diminished aromaticity and hydrophobicity relative to high-temperature pyrolysis BCs. This findings aligns with Zhang et al. (2018) observation of an inverse relationship between bacterial population and organic carbon content in BC-amended soil. Their research suggests that low-temperature BCs create more favorable conditions for PAH-degrading microorganisms than high-temperature BCs, which exhibit greater aromaticity. These results emphasize that both pyrolysis temperature and feedstock source are crucial factors in determining how BCs influence PAH bioavailability and degradation during composting.

The relationship between C_{tot} and ash varied depending on the individual PAH. Typically, 2–3-ring PAHs showed a positive relationship with ash content, whereas 4–5-ring PAHs exhibited a negative relationship ($p < 0.1$, see supplementary material). This distinction may be attributed to the pronounced hydrophobicity of high molecular weight compounds (Kończak et al., 2023), which predisposes them to a stronger association with the mineral fraction of the compost, leading to their persistent adsorption and sequestration with less accessible sites of the matrix (Lamichhane et al., 2016). The mineral fraction can trap PAHs within pores (Lu et al., 2012), complicating or precluding their extraction. Additionally, ash can also form mineral-organic complexes that encapsulate PAHs (Han et al., 2020), which is especially observed for SL. Consequently, an increase in ash content within the compost correlates with C_{tot} PAH reduction for both individual heavy PAHs and Σ16 C_{tot} PAHs. The tendency for a negative association with ash was more frequently observed in experiments involving BCs produced at 500 °C, which possess a higher mineral content relative to BCs obtained at 700 °C (Table 1). High ash content most often leads to clogging of pores in BCs, which makes it difficult or even impossible for adsorption/binding processes to occur on their surface (Kończak et al., 2023).

The high affinity of PAHs for organic matter, results in strong adsorption and sequestration within matrices with elevated TOC content, thereby reducing PAH bioavailability and susceptibility to biodegradation (Kończak et al., 2023). In this study, positive correlations between C_{tot} and TOC ($p < 0.1$) were observed mainly for the experiment containing WL-BCs (see supplementary material), indicating that irreversible adsorption played a more significant role in the observed PAH reductions than biodegradation processes.

The relationship between material moisture and PAH adsorption plays a crucial role in various matrices (Antizar-Ladislao et al., 2006). This study revealed consistent negative correlations between C_{tot} and material moisture across all BC-amendment variants, with WL-500 showing the strongest correlations. One notable exception was SL700, which rarely exhibited these correlations (see supplementary material). The relationships were more pronounced for BCs obtained at a lower than higher pyrolysis temperature. Previous research has suggested that material moisture can enhance PAH adsorption (Antizar-Ladislao et al., 2006). The strong correlation with moisture can be explained by favorable conditions for development of microorganisms and thus

indirectly contribute to the effective biodegradation of PAHs. This finding particularly applies to low-temperature BCs, where microbial degradation appears to be the primary mechanism for PAHs reduction. Supporting evidence comes from earlier studies (Antizar-Ladislao et al., 2006) showing significant moisture effects on the Σ16 C_{tot} PAHs losses during composting. More recently, Suszek-Łopatka et al. (2019) explored how soil moisture affects PHE toxicity toward soil microorganisms. Their work revealed that higher soil moisture levels increased PHE toxicity, though this effect varied depending on the soil type.

Correlations between C_{free} and compost properties emerged more frequently than those with the C_{tot}, with statistically significant relationships observed between C_{free} and moisture, pH, EC, ash content, TOC, and DOC ($p < 0.1$, see supplementary material). Usually, statistically significant relationships were more frequent for variants with BCs than for control. The frequency of these significant correlations was higher for BCs obtained at 500 °C compared to 700 °C.

pH plays a vital role in microbial activity, which indirectly influences biological PAH degradation. For WL-BCs, we found positive correlations between pH ($p < 0.1$) and PAH levels (see supplementary material), indicating that biological breakdown might be the primary mechanism reducing C_{free} PAHs content in these variants. pH regulates numerous microbial metabolic processes, and higher pH levels tend to increase PAH extractability (Yu et al., 2018). Other studies has found similar positive correlations between the pH of the matrix (usually soil) and PAHs content (Kończak et al., 2023). In contrast, negative correlations between individual PAHs (≥ 3-ring) and EC ($p < 0.1$) emerged for all BC variants except SL700 (see supplementary material). It was likely due to the reduced solubility of PAHs under increasingly saline conditions, leading to greater losses. Kończak et al. (2023) reported comparable findings while studying PAH persistence and bioavailability in SL-BC-amended soils. The negative correlation between C_{free} and ash ($p < 0.1$) appeared more frequently for WL-BCs than for SL-BCs (see supplementary material). This pattern might result from the PAH binding to minerals in the compost material, either through pore-filling or by adsorption onto the BC/SL surface.

4. Conclusions

Adding BC to SL/WS composting affects PAH concentrations in complex ways. While BC initially increased PAH levels, it ultimately led to greater PAH reduction compared to control. The pyrolysis temperature proved crucial: lower-temperature BCs resulted in better PAH removal and decreased PAH bioavailability during composting. The feedstock used to make BC also mattered, though less than temperature. Wood-like-derived BC showed better results in reducing PAH bioavailability than those made from SL-like materials. These different source materials worked through distinct mechanisms – SL-derived BC mainly trapped PAHs through adsorption, while wood-derived BC appeared to help break them down biologically.

CRediT authorship contribution statement

Aleksandra Rombel: Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Krzysztof Różyło:** Resources, Methodology, Investigation. **Yong Sik Ok:** Writing – review & editing, Validation. **Patryk Oleszczuk:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Formal analysis, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2025.132220.

Data availability

Data will be made available on request.

References

Alidou-Arzika, I., Lebrun, M., Miard, F., Nandillon, R., Baycu, G., Bourgerie, S., Morabito, D., 2021. Assessment of compost and three biochars associated with Ailanthus altissima (Miller) Swingle for lead and arsenic stabilization in a post-mining Technosol. Pedosphere 31, 944–953. https://doi.org/10.1016/S1002-0160(21)60025-5.

Antizar-Ladislao, B., Lopez-Real, J., Beck, A.J., 2006. Degradation of polycyclic aromatic hydrocarbons (PAHs) in an aged coal tar contaminated soil under in-vessel composting conditions. Environ. Pollut. 141, 459–468. https://doi.org/10.1016/J.ENVPOL.2005.08.066.

Arp, H.P.H., Lundstedt, S., Josefsson, S., Cornelissen, G., Enell, A., Allard, A.S., Kleja, D. B., 2014. Native oxy-PAHs, N-PACs, and PAHs in historically contaminated soils from Sweden, Belgium, and France: Their soil-porewater partitioning behavior, bioaccumulation in Enchytraeus crypticus, and bioavailability. Environ. Sci. Technol. 48, 11187–11195. https://doi.org/10.1021/es5034469.

Awasthi, M.K., Wang, Q., Huang, H., Li, R., Shen, F., Lahori, A.H., Wang, P., Guo, D., Guo, Z., Jiang, S., Zhang, Z., 2016. Effect of biochar amendment on greenhouse gas emission and bio-availability of heavy metals during sewage sludge co-composting. J. Clean. Prod. 135, 829–835. https://doi.org/10.1016/J.JCLEPRO.2016.07.008.

Bao, H., Wang, J., Zhang, H., Li, J., Li, H., Wu, F., 2020. Effects of biochar and organic substrates on biodegradation of polycyclic aromatic hydrocarbons and microbial community structure in PAHs-contaminated soils. J. Hazard. Mater. 385, 121595. https://doi.org/10.1016/J.JHAZMAT.2019.121595.

Barthod, J., Rumpel, C., Dignac, M.F., 2018. Composting with additives to improve organic amendments. A Review. Agron. Sustain. Dev. 38, 1–23. https://doi.org/10.1007/S13593-018-0491-9.

Buss, W., Hilber, I., Graham, M.C., Mašek, O., 2022. Composition of PAHs in biochar and implications for biochar production. ACS Sustain. Chem. Eng. 10, 6755–6765. https://doi.org/10.1021/acssuschemeng.2c00952.

Cai, Q.Y., Mo, C.H., Wu, Q.T., Zeng, Q.Y., Katsoyiannis, A., Férard, J.F., 2007. Bioremediation of polycyclic aromatic hydrocarbons (PAHs)-contaminated sewage sludge by different composting processes. J. Hazard. Mater. 142, 535–542. https://doi.org/10.1016/J.JHAZMAT.2006.08.062.

Chen, H., Awasthi, S.K., Liu, T., Duan, Y., Zhang, Z., Awasthi, M.K., 2020. Compost biochar application to contaminated soil reduces the (im)mobilization and phytoavailability of lead and copper. J. Chem. Technol. Biotechnol. 95, 408–417. https://doi.org/10.1002/JCTB.5986.

de Oliveira Paiva, I., de Morais, E.G., Jindo, K., Silva, C.A., 2024. Biochar N content, pools and aromaticity as affected by feedstock and pyrolysis temperature. Waste and Biomass Valorization 15, 3599–3619. https://doi.org/10.1007/S12649-023-02415-X.

Du, J., Zhang, Y., Hu, B., Qv, M., Ma, C., Wei, M., Zhang, H., 2019. Insight into the potentiality of big biochar particle as an amendment in aerobic composting of sewage sludge. Bioresour. Technol. 288, 121469. https://doi.org/10.1016/J.BIORTECH.2019.121469.

Ebc, 2015. European Biochar Certificate - Guidelines for a sustainable production of biochar. European Biochar Foundation (EBC). https://doi.org/10.13140/RG.2.1.4658.7043.

Fouad, M.R., El-Aswad, A.F., Badawy, M.E.I., Aly, M.I., 2024. Impact of organic amendments addition to sandy clay loam soil and sandy loam soil on leaching process of chlorantraniliprole insecticide and bispyribac-sodium herbicide. Curr. Chem. Lett. 13, 277–286. https://doi.org/10.5267/J.CCL.2023.12.004.

Gorovtsov, A.V., Minkina, T.M., Mandzhieva, S.S., Perelomov, L.V., Soja, G., Zamulina, I. V., Rajput, V.D., Sushkova, S.N., Mohan, D., Yao, J., 2020. The mechanisms of biochar interactions with microorganisms in soil. Environ. Geochem. Health 42, 2495–2518. https://doi.org/10.1007/s10653-019-00412-5.

Gul, S., Whalen, J.K., Thomas, B.W., Sachdeva, V., Deng, H., 2015. Physico-chemical properties and microbial responses in biochar-amended soils: Mechanisms and future directions. Agric. Ecosyst. Environ. 206, 46–59. https://doi.org/10.1016/J.AGEE.2015.03.015.

Guo, X., Luo, L., Ma, Y., Zhang, S., 2010. Sorption of polycyclic aromatic hydrocarbons on particulate organic matters. J. Hazard. Mater. 173, 130–136. https://doi.org/10.1016/J.JHAZMAT.2009.08.065.

Guo, Y., Rene, E.R., Wang, J., Ma, W., 2020. Biodegradation of polyaromatic hydrocarbons and the influence of environmental factors during the co-composting

of sewage sludge and green forest waste. Bioresour. Technol. 297, 122434. https://doi.org/10.1016/J.BIORTECH.2019.122434.
Han, D., Jiang, L., Zhong, M., Zhang, R., Fu, Q., Zhang, D., Xia, T., 2020. Desorption and bioaccessibility of high-molecular-weight PAHs in aged field soil and humin-like fraction from a coke plant. Environ. Earth Sci. 79, 1–11. https://doi.org/10.1007/s12665-020-08989-2.
Hilber, I., Blum, F., Leifeld, J., Schmidt, H.P., Bucheli, T.D., 2012. Quantitative determination of PAHs in biochar: A prerequisite to ensure its quality and safe application. J. Agric. Food Chem. 60, 3042–3050. https://doi.org/10.1021/JF205278V.
Hua, L., Wu, W., Liu, Y., Chen, Y., McBride, M.B., 2008. Effect of composting on polycyclic aromatic hydrocarbons removal in sewage sludge. Water. Air. Soil Pollut. 193, 259–267. https://doi.org/10.1007/S11270-008-9687-Y.
Jørgensen, K.S., Puustinen, J., Suortti, A.M., 2000. Bioremediation of petroleum hydrocarbon-contaminated soil by composting in biopiles. Environ. Pollut. 107, 245–254. https://doi.org/10.1016/S0269-7491(99)00144-X.
Kim, J.H., Moon, J.K., Li, Q.X., Cho, J.Y., 2003. One-step pressurized liquid extraction method for the analysis of polycyclic aromatic hydrocarbons. Anal. Chim. Acta 498, 55–60. https://doi.org/10.1016/J.ACA.2003.08.049.
Kończak, M., Godlewska, P., Wiśniewska, M., Oleszczuk, P., 2023. Chemical properties of soil determine the persistence and bioavailability of polycyclic aromatic hydrocarbons in sewage sludge- or sewage sludge/biomass-derived biochar-amended soils. Environ. Pollut. 319, 120909. https://doi.org/10.1016/J.ENVPOL.2022.120909.
Lamichhane, S., Bal Krishna, K.C., Sarukkalige, R., 2016. Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: A review. Chemosphere 148, 336–353. https://doi.org/10.1016/J.CHEMOSPHERE.2016.01.036.
Lu, Z., Zeng, F., Xue, N., Li, F., 2012. Occurrence and distribution of polycyclic aromatic hydrocarbons in organo-mineral particles of alluvial sandy soil profiles at a petroleum-contaminated site. Sci. Total Environ. 433, 50–57. https://doi.org/10.1016/J.SCITOTENV.2012.06.036.
Luo, X., Cai, Y., Liu, L., Zeng, J., 2019. Cr(VI) adsorption performance and mechanism of an effective activated carbon prepared from bagasse with a one-step pyrolysis and ZnCl2 activation method. Cellulose 26, 4921–4934. https://doi.org/10.1007/S10570-019-02418-9.
Manikandan, S., Vickram, S., Subbaiya, R., Karmegam, N., Woong Chang, S., Ravindran, B., Kumar Awasthi, M., 2023. Comprehensive review on recent production trends and applications of biochar for greener environment. Bioresour. Technol. 388, 129725. https://doi.org/10.1016/J.BIORTECH.2023.129725.
Mikajlo, I., Lerch, T.Z., Louvel, B., Hynšt, J., Záhora, J., Pourrut, B., 2024. Composted biochar versus compost with biochar: effects on soil properties and plant growth. Biochar 6, 1–17. https://doi.org/10.1007/S42773-024-00379-2.
Naveed, M., Tanvir, B., Xiukang, W., Brtnicky, M., Ditta, A., Kucerik, J., Subhani, Z., Nazir, M.Z., Radziemska, M., Saeed, Q., Mustafa, A., 2021. Co-composted biochar enhances growth, physiological, and phytostabilization efficiency of Brassica napus and reduces associated health risks under chromium stress. Front. Plant Sci. 12, 2568. https://doi.org/10.3389/fpls.2021.775785.
Noor, R.S., Shah, A.N., Tahir, M.B., Umair, M., Nawaz, M., Ali, A., Ercisli, S., Abdelsalam, N.R., Ali, H.M., Yang, S.H., Ullah, S., Assiri, M.A., 2024. Recent trends and advances in additive-mediated composting technology for agricultural waste resources: A comprehensive review. ACS Omega 9, 8632–8653. https://doi.org/10.1021/ACSOMEGA.3C06516.
Pandey, D., Singh, S., Dutta, K., Daverey, A., Arunachalam, K., 2021. Biochar-based nanocomposites: A sustainable solution for water and wastewater treatment. Nanotechnol. Life Sci. 619–639. https://doi.org/10.1007/978-3-030-61985-5_22.
Poluszyńska, J., Jarosz-Krzemińska, E., Helios-Rybicka, E., 2017. Studying the effects of two various methods of composting on the degradation levels of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. Water. Air. Soil Pollut. 228, 1–10. https://doi.org/10.1007/S11270-017-3481-7.
Qian, S., Zhou, X., Fu, Y., Song, B., Yan, H., Chen, Z., Sun, Q., Ye, H., Qin, L., Lai, C., 2023. Biochar-compost as a new option for soil improvement: Application in various problem soils. Sci. Total Environ. 870, 162024. https://doi.org/10.1016/J.SCITOTENV.2023.162024.
Rashid, M.S., Liu, G., Yousaf, B., Song, Y., Ahmed, R., Rehman, A., Arif, M., Irshad, S., Cheema, A.I., 2022. Efficacy of rice husk biochar and compost amendments on the translocation, bioavailability, and heavy metals speciation in contaminated soil: Role of free radical production in maize (Zea mays L.). J. Clean. Prod. 330, 129805. https://doi.org/10.1016/J.JCLEPRO.2021.129805.
Rombel, A., Różyło, K., Oleszczuk, P., 2024. The high dose of biochar reduces polycyclic aromatic hydrocarbons losses during co-composting of sewage sludge and wheat straw. J. Environ. Manage. 351, 119628. https://doi.org/10.1016/J.JENVMAN.2023.119628.
Sayara, T., Sarrà, M., Sánchez, A., 2010. Effects of compost stability and contaminant concentration on the bioremediation of PAHs-contaminated soil through composting. J. Hazard. Mater. 179, 999–1006. https://doi.org/10.1016/J.JHAZMAT.2010.03.104.
Sharma, A., Soni, R., Soni, S.K., 2023. From waste to wealth: exploring modern composting innovations and compost valorization. J. Mater. Cycles Waste Manag. 2023, 1–29. https://doi.org/10.1007/S10163-023-01839-W.
Shi, R., Sun, Y., Zheng, X., Shen, L., 2023. Speciation and influencing factors of polycyclic aromatic hydrocarbons in soils of southwest China. J. Soils Sediments. https://doi.org/10.1007/S11368-023-03555-2.
Siatecka, A., Różyło, K., Ok, Y.S., Oleszczuk, P., 2021. Biochars ages differently depending on the feedstock used for their production: Willow- versus sewage sludge-derived biochars. Sci. Total Environ. 789, 147458. https://doi.org/10.1016/J.SCITOTENV.2021.147458.
Song, H., Chen, S.F., Si, G., Bhatt, K., Chen, S.H., Chen, W.J., 2024. Removal of environmental pollutants using biochar: current status and emerging opportunities. Environ. Geochemistry Heal. 2024 4610 46, 1–21. https://doi.org/10.1007/S10653-024-02142-9.
Suszek-Łopatka, B., Maliszewska-Kordybach, B., Klimkowicz-Pawlas, A., Smreczak, B., 2019. The drought and high wet soil condition impact on PAH (phenanthrene) toxicity towards nitrifying bacteria. J. Hazard. Mater. 368, 274–280. https://doi.org/10.1016/J.JHAZMAT.2019.01.055.
Wang, C., Wang, Y., Herath, H.M.S.K., 2017. Polycyclic aromatic hydrocarbons (PAHs) in biochar – Their formation, occurrence and analysis: A review. Org. Geochem. 114, 1–11. https://doi.org/10.1016/J.ORGGEOCHEM.2017.09.001.
Wang, Z., Xu, Y., Yang, T., Liu, Y., Zheng, T., Zheng, C., 2023. Effects of biochar carried microbial agent on compost quality, greenhouse gas emission and bacterial community during sheep manure composting. Biochar 5, 1–17. https://doi.org/10.1007/s42773-022-00202-w.
Xie, J., Xia, H., Guan, M., Huang, K., Chen, J., 2023. Accelerating the humification mechanism of dissolved organic matter using biochar during vermicomposting of dewatered sludge. Waste Manag. 159, 102–113. https://doi.org/10.1016/J.WASMAN.2023.01.022.
Xing, J., Xu, G., Li, G., 2021. Comparison of pyrolysis process, various fractions and potential soil applications between sewage sludge-based biochars and lignocellulose-based biochars. Ecotoxicol. Environ. Saf. 208, 111756. https://doi.org/10.1016/J.ECOENV.2020.111756.
Yu, L., Duan, L., Naidu, R., Semple, K.T., 2018. Abiotic factors controlling bioavailability and bioaccessibility of polycyclic aromatic hydrocarbons in soil: Putting together a bigger picture. Sci. Total Environ. 613–614, 1140–1153. https://doi.org/10.1016/J.SCITOTENV.2017.09.025.
Zhang, G., Guo, X., Zhu, Y., Liu, X., Han, Z., Sun, K., Ji, L., He, Q., Han, L., 2018. The effects of different biochars on microbial quantity, microbial community shift, enzyme activity, and biodegradation of polycyclic aromatic hydrocarbons in soil. Geoderma 328, 100–108. https://doi.org/10.1016/J.GEODERMA.2018.05.009.
Zheng, Y., Xu, X., Han, B., Wang, G., Zheng, L., 2024. Correlation between polycyclic aromatic hydrocarbons and total organic carbon in surface sediments of the Bohai Sea and the North Yellow Sea. Environ. Sci. Pollut. Res. Int. 31, 2883–2890. https://doi.org/10.1007/S11356-023-31254-5.
Zhou, Y., Gao, B., Zimmerman, A.R., Chen, H., Zhang, M., Cao, X., 2014. Biochar-supported zerovalent iron for removal of various contaminants from aqueous solutions. Bioresour. Technol. 152, 538–542. https://doi.org/10.1016/j.biortech.2013.11.021.

Supplementary material

Influence of Biochar Characteristics on Polycyclic Aromatic Hydrocarbons Content during Co-Composting of Sewage Sludge

Number of pages: 9 (including this page)

Number of figures: 1

Number of tables: 4

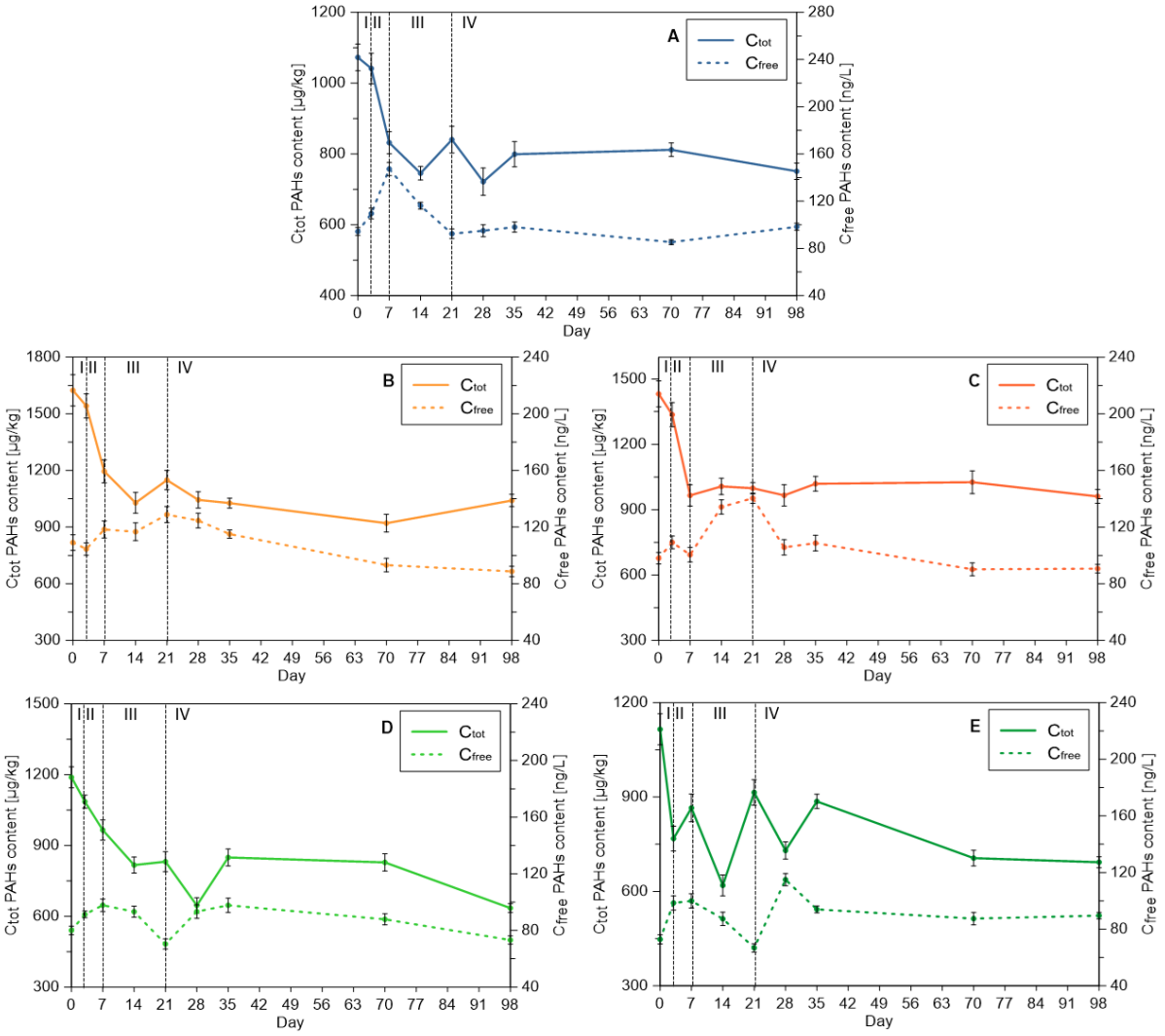

Fig. S1. The profile of solvent extractable Σ16 PAHs (C_{tot}) and freely dissolved Σ16 PAHs (C_{free}) content changes during composting: A – without BC, B – with WL500, C – with WL700, D – with SL500, E – with SL700. Composting phases: I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation. Error bars means standard deviation error (in triplicate).

Table S1. Temperature of the compost pile and various gases concentration in the exhaust gas mixture during composting. Composting phases: I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation. Nd – not detected.

Day	Composting phase	Average temperature [°C]	O_2 [%]	CO_2 [%]	CO [ppm]	NO [ppm]	CH_4 [ppm]	N_2 [%]
0% BC								
0	I	21.9	14.6	5.80	2	7	nd	79.6
3	II	43.0	13.9	7.32	3	1	160	78.8
7	III	39.9	15.3	6.25	7	1	nd	78.2
14	III	25.9	19.1	1.80	nd	nd	310	79.1
21	IV	25.2	19.3	1.10	nd	nd	nd	79.6
28	IV	25.2	19.4	1.09	nd	nd	20	79.5
35	IV	24.0	19.2	1.15	nd	nd	200	79.6
WL500								
0	I	29.5	14.0	6.30	11	4	290	79.5
3	II	56.5	4.40	16.7	19	3	160	78.8
7	III	42.9	17.3	3.44	1	nd	250	79.2
14	III	25.5	19.6	1.06	nd	1	210	79.3
21	IV	23.1	19.7	0.87	nd	2	110	79.4
28	IV	22.3	20.2	0.59	nd	5	nd	79.6
35	IV	21.8	20.0	0.70	nd	9	150	79.2
WL700								
0	I	28.4	11.4	8.83	14	8	920	79.6
3	II	55.9	2.29	19.1	13	14	nd	78.6
7	III	40.0	15.9	4.73	1	nd	20	79.3
14	III	24.9	20.0	0.57	nd	3	30	79.4
21	IV	23.0	19.0	1.51	nd	4	150	79.1
28	IV	22.1	20.1	0.56	nd	5	nd	79.3
35	IV	21.8	19.9	0.66	nd	12	50	79.4
SL500								
0	I	22.4	15.0	5.34	2	4	nd	79.7
3	II	46.2	12.4	8.76	8	2	290	78.8
7	III	39.1	15.3	5.50	5	1	nd	79.2
14	III	26.5	19.1	1.70	nd	nd	340	79.2
21	IV	25.7	19.2	1.36	nd	nd	10	79.5
28	IV	25.9	19.4	1.20	nd	nd	210	79.6
35	IV	24.5	19.2	1.24	nd	nd	190	79.5
SL700								
0	I	22.0	14.8	5.67	2	6	nd	79.5
3	II	50.9	12.0	9.08	11	2	280	78.9
7	III	36.9	16.1	4.70	5	1	10	79.2
14	III	26.0	18.9	1.90	nd	nd	440	79.2
21	IV	25.6	18.8	1.87	nd	nd	100	79.4
28	IV	25.8	19.2	1.57	nd	nd	400	79.2
35	IV	24.5	19.4	1.16	nd	nd	230	79.4

Table S2. Physico-chemical properties of compost depending on the composting phase (I – mesophilic *I*, II – thermophilic, III – mesophilic *II*, IV – maturation).

Day	Composting phase	Moisture [%]	pH	Electrical conductivity [mS/cm]	Ash content [%]	Total organic carbon content [%]	Dissolved organic carbon [mg/L]
0% BC							
0	I	71.6	6.06	3.84	18.5	43.7	835.9
3	II	67.2	5.33	3.92	20.0	41.2	1450
7	III	82.6	5.71	4.28	22.8	39.9	1962
14	III	70.8	5.80	3.70	23.2	39.7	1300
21	IV	67.5	5.78	3.59	24.0	40.0	1155
28	IV	75.2	6.05	3.82	23.2	39.5	935.5
35	IV	77.4	6.18	3.73	25.7	37.2	745.6
70	IV	76.9	5.60	4.90	27.4	38.3	443.6
98	IV	71.7	5.57	5.33	27.2	36.6	401.7
WL500							
0	I	60.5	6.38	3.90	17.4	43.7	893.1
3	II	64.9	5.77	4.37	18.7	42.5	1958
7	III	64.7	5.77	4.77	21.8	41.4	2541
14	III	71.4	5.90	5.25	25.4	38.1	2203
21	IV	73.2	6.15	4.86	24.9	39.9	1771
28	IV	72.7	6.57	5.13	23.0	40.2	1727
35	IV	73.7	6.17	4.80	24.7	39.8	1363
70	IV	79.2	5.32	5.88	25.0	38.8	699.4
98	IV	62.7	5.08	6.61	26.6	36.5	602.0
WL700							
0	I	59.0	6.42	3.38	17.7	42.2	1092
3	II	62.5	5.75	4.09	20.6	42.6	2227
7	III	71.4	5.92	4.40	21.6	38.9	2269
14	III	76.6	5.77	4.22	22.7	41.1	2035
21	IV	76.4	6.04	4.50	24.1	41.0	1999
28	IV	72.7	6.20	4.79	23.7	41.6	1761
35	IV	68.0	6.09	4.90	25.0	39.0	1198
70	IV	76.9	5.56	5.95	25.6	39.4	618.5
98	IV	67.2	5.13	6.20	26.0	37.7	556.1
SL500							
0	I	65.2	6.06	3.32	19.7	40.0	704.8
3	II	67.3	5.57	3.61	20.4	40.1	1339
7	III	70.0	5.67	4.12	22.6	38.1	1662
14	III	72.7	5.69	3.69	23.9	39.2	1264
21	IV	71.8	6.21	3.58	23.3	34.5	1070
28	IV	70.4	6.29	3.75	24.9	36.9	977.3
35	IV	74.8	6.15	3.81	27.3	37.2	636.1
70	IV	77.8	5.69	4.86	27.9	36.5	480.7

98	IV	75.5	5.45	5.40	29.2	34.7	365.5
SL700							
0	I	70.3	6.01	3.81	19.2	38.9	965.1
3	II	70.5	5.80	4.17	20.9	39.0	1580
7	III	68.8	5.83	4.63	24.6	38.1	1723
14	III	74.1	5.82	3.77	25.7	37.7	1105
21	IV	71.4	5.80	3.53	25.1	36.8	998.5
28	IV	71.4	5.89	3.46	25.9	37.2	874.8
35	IV	75.1	6.02	3.63	27.4	37.2	772.3
70	IV	75.6	5.98	4.36	28.8	37.2	434.3
98	IV	76.8	5.64	5.09	29.8	35.3	371.7

Table S3. Pearson correlation coefficients for the relation between C_{tot} [µg/kg] of individual PAHs and Σ16 C_{tot} PAHs and physico-chemical characteristics of material during composting.

Variant	0% BC					WL500					WL700					SL500					SL700				
PAH \ Property	Moisture	EC	Ash	TOC	DOC	Moisture	EC	Ash	TOC	DOC	Moisture	EC	Ash	TOC	DOC	Moisture	EC	Ash	TOC	DOC	Moisture	EC	Ash	TOC	DOC
NAP	0.342	0.707	0.818	-0.904	-0.410	0.587	0.366	0.617	-0.465	-0.258	0.312	0.511	0.398	-0.539	-0.442	0.556	0.535	0.604	-0.053	-0.478	0.177	-0.467	0.076	-0.064	-0.299
ACY	0.391	0.797	0.653	-0.730	-0.257	-0.282	-0.136	-0.011	0.066	-0.294	-0.039	-0.261	-0.035	0.208	-0.200	0.232	0.484	0.291	0.031	-0.359	0.660	0.379	0.656	-0.623	-0.848
ACE	0.167	-0.134	0.554	-0.581	0.240	-0.448	0.472	0.331	-0.457	-0.326	0.122	-0.134	0.061	-0.033	-0.196	0.166	-0.192	-0.062	0.540	0.175	0.221	-0.374	0.236	-0.309	-0.635
FLO	-0.373	-0.620	-0.340	0.353	0.669	-0.696	-0.586	-0.583	0.575	0.579	-0.127	-0.726	-0.400	0.496	0.281	-0.466	-0.593	-0.697	0.818	0.651	0.082	-0.277	0.536	-0.417	0.052
PHE	-0.217	-0.238	0.207	-0.090	0.201	-0.701	-0.513	-0.410	0.430	0.508	-0.175	-0.651	-0.459	0.561	0.193	-0.226	-0.499	-0.537	0.575	0.569	-0.060	-0.350	-0.019	-0.014	-0.103
ANT	-0.437	-0.684	-0.539	0.533	0.620	-0.908	-0.063	-0.296	0.154	-0.031	-0.549	-0.085	0.049	0.085	-0.605	-0.127	-0.101	-0.411	0.439	0.347	-0.498	-0.321	-0.302	0.124	0.279
FLA	-0.333	-0.065	-0.236	0.290	0.129	-0.424	-0.803	-0.635	0.750	0.819	-0.713	-0.668	-0.506	0.706	-0.033	-0.510	-0.544	-0.751	0.519	0.575	-0.360	-0.295	-0.050	-0.076	0.257
PYR	-0.207	-0.482	-0.247	0.289	0.330	-0.365	-0.823	-0.596	0.720	0.824	-0.425	-0.178	0.111	0.291	-0.544	-0.552	-0.468	-0.772	0.514	0.473	-0.241	-0.232	0.088	-0.181	0.141
BaA	0.245	-0.094	-0.070	0.354	0.198	-0.173	0.093	0.088	-0.052	0.271	0.166	0.493	0.615	-0.374	-0.631	0.257	-0.068	0.065	-0.052	0.322	-0.271	-0.235	0.147	-0.272	0.116
CHR	0.144	-0.091	-0.113	0.344	0.108	-0.417	-0.805	-0.759	0.812	0.782	-0.112	0.300	0.320	-0.130	-0.519	0.091	-0.171	-0.143	0.093	0.302	-0.286	-0.262	0.055	-0.183	0.126
BbF	0.397	0.050	0.196	0.052	0.020	-0.723	0.030	-0.182	0.030	-0.001	-0.066	0.408	0.276	-0.202	-0.539	-0.060	-0.440	-0.308	-0.025	0.589	-0.181	-0.233	0.193	-0.299	0.042
BkF	0.389	0.008	0.034	0.215	0.069	-0.747	0.072	-0.183	0.049	0.120	0.264	0.438	0.531	-0.434	-0.587	-0.641	-0.425	-0.704	0.207	0.823	-0.317	-0.180	0.044	-0.173	0.065
BaP	-0.355	-0.184	-0.803	0.761	0.112	-0.646	-0.667	-0.908	0.778	0.192	-0.817	-0.667	-0.811	0.700	0.137	-0.753	-0.288	-0.710	0.720	0.027	-0.459	-0.105	-0.847	0.678	0.212
IcdP	0.524	-0.236	0.213	-0.091	0.462	-0.459	-0.484	-0.611	0.558	0.448	-0.383	-0.089	0.160	-0.050	-0.538	-0.312	-0.599	-0.531	0.190	0.791	0.220	-0.571	0.367	-0.405	-0.376
DahA	-0.139	-0.502	-0.127	0.122	0.469	0.822	0.317	0.398	-0.248	-0.267	0.842	-0.059	0.222	-0.032	0.456	-0.013	-0.162	-0.011	-0.065	0.616	-0.420	-0.574	-0.318	0.209	0.085
BghiP	0.059	0.397	0.155	0.085	-0.401	-0.508	-0.411	-0.623	0.598	-0.248	-0.132	0.101	-0.261	0.184	-0.271	-0.682	-0.649	-0.540	0.132	0.275	-0.634	-0.371	-0.112	-0.026	0.368

Σ16 C_{tot} PAHs	-0.356	-0.239	-0.769	0.783	0.201	-0.722	-0.758	-0.927	0.841	0.383	-0.793	-0.640	-0.732	0.674	0.025	-0.710	-0.449	-0.811	0.749	0.331	-0.521	-0.344	-0.627	0.421	0.201

Where: moisture [%], EC – electrical conductivity [mS/cm], ash – mineral content [%]; TOC – total organic carbon content [%], DOC – dissolved organic carbon [mg/L]; NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene); indicates statistically significant correlation ($p < 0.1$).

Table S4. Pearson correlation coefficients for the relation between C_{free} [ng/L] of individual PAHs and Σ16 C_{free} PAHs and physico-chemical characteristics of material during composting.

Variant	0% BC						WL500						WL700						SL500						SL700					
PAH \ Property	Moisture	pH	EC	Ash	TOC	DOC	Moisture	pH	EC	Ash	TOC	DOC	Moisture	pH	EC	Ash	TOC	DOC	Moisture	pH	EC	Ash	TOC	DOC	Moisture	pH	EC	Ash	TOC	DOC
NAP	0.625	-0.195	0.344	0.136	-0.286	0.498	0.463	0.564	-0.097	0.336	-0.095	0.383	0.648	0.047	-0.082	0.210	0.112	0.400	0.604	-0.248	0.320	0.615	-0.081	-0.134	0.286	0.242	0.221	0.550	-0.350	-0.223
ACY	0.260	-0.438	0.064	-0.474	0.377	0.743	-0.779	0.272	-0.717	-0.932	0.835	0.355	-0.615	0.481	-0.539	-0.212	0.415	-0.224	-0.556	-0.406	-0.218	-0.544	0.661	0.639	-0.438	-0.366	0.256	-0.567	0.541	0.524
ACE	-0.046	-0.124	-0.572	-0.431	0.340	0.836	-0.103	0.697	-0.482	-0.206	0.239	0.261	0.165	0.242	-0.479	-0.184	0.492	0.410	-0.233	-0.176	-0.491	-0.307	0.681	0.590	-0.258	0.244	-0.478	-0.264	0.466	0.475
FLO	-0.206	-0.107	-0.645	-0.816	0.762	0.834	-0.353	0.682	-0.947	-0.811	0.843	0.720	-0.148	0.565	-0.892	-0.674	0.765	0.770	-0.808	-0.020	-0.710	-0.887	0.899	0.734	-0.757	-0.144	-0.350	-0.811	0.824	0.894
PHE	-0.059	0.034	-0.669	-0.479	0.487	0.805	-0.164	0.745	-0.822	-0.494	0.648	0.905	-0.133	0.487	-0.836	-0.653	0.708	0.831	-0.762	0.263	-0.853	-0.842	0.723	0.770	-0.556	0.084	-0.251	-0.520	0.724	0.783
ANT	-0.022	-0.089	-0.574	-0.707	0.755	0.663	-0.358	0.376	-0.856	-0.817	0.847	0.784	-0.087	0.463	-0.808	-0.686	0.698	0.906	-0.849	-0.016	-0.634	-0.915	0.870	0.715	-0.842	-0.205	-0.370	-0.759	0.709	0.919
FLA	-0.100	-0.179	-0.584	-0.792	0.706	0.897	-0.196	0.796	-0.849	-0.539	0.663	0.871	-0.128	0.631	-0.817	-0.598	0.635	0.880	-0.874	0.277	-0.833	-0.899	0.808	0.691	-0.860	-0.104	-0.497	-0.703	0.689	0.900
PYR	-0.075	-0.161	-0.592	-0.765	0.681	0.911	-0.095	0.825	-0.811	-0.469	0.611	0.858	-0.111	0.629	-0.786	-0.565	0.607	0.873	-0.834	0.323	-0.874	-0.868	0.774	0.697	-0.846	-0.029	-0.521	-0.664	0.677	0.866
BaA	-0.063	-0.211	-0.530	-0.786	0.688	0.881	-0.155	0.643	-0.800	-0.510	0.630	0.905	-0.005	0.605	-0.754	-0.547	0.615	0.918	-0.900	0.279	-0.770	-0.921	0.779	0.677	-0.786	-0.154	-0.400	-0.670	0.662	0.962
CHR	-0.051	-0.194	-0.521	-0.796	0.695	0.874	-0.132	0.797	-0.844	-0.526	0.654	0.855	-0.036	0.632	-0.747	-0.499	0.542	0.886	-0.873	0.300	-0.754	-0.874	0.809	0.592	-0.799	-0.151	-0.485	-0.660	0.586	0.776
BbF	-0.093	-0.180	-0.561	-0.710	0.619	0.934	0.080	0.740	-0.722	-0.316	0.495	0.881	0.002	0.661	-0.713	-0.423	0.547	0.852	-0.745	0.466	-0.882	-0.746	0.618	0.620	-0.706	-0.084	-0.565	-0.434	0.402	0.765
BkF	-0.043	-0.174	-0.556	-0.711	0.627	0.942	0.118	0.774	-0.685	-0.282	0.481	0.801	0.221	0.540	-0.543	-0.248	0.371	0.836	-0.744	0.405	-0.846	-0.754	0.618	0.693	-0.712	0.065	-0.692	-0.507	0.479	0.618
BaP	-0.081	-0.172	-0.560	-0.796	0.710	0.915	-0.406	0.825	-0.939	-0.769	0.848	0.664	-0.028	0.556	-0.647	-0.422	0.375	0.836	-0.699	0.476	-0.731	-0.613	0.619	0.381	-0.143	-0.411	0.079	0.008	-0.119	0.261
IcdP	-0.029	-0.190	-0.354	-0.602	0.501	0.881	0.068	0.953	-0.814	-0.509	0.665	0.570	0.239	0.695	-0.543	-0.106	0.413	0.668	-0.286	0.141	-0.570	-0.377	0.468	0.412	-0.554	-0.002	-0.547	-0.604	0.558	0.409
DahA	-0.202	0.291	0.140	0.573	-0.548	-0.664	-0.239	-0.129	0.004	-0.231	0.135	-0.579	0.061	0.547	-0.045	0.478	-0.003	-0.151	-0.509	0.276	-0.447	-0.512	0.763	0.262	-0.093	-0.153	0.015	-0.472	0.245	-0.212
BghiP	0.192	0.381	-0.785	-0.531	0.326	0.741	0.098	0.895	-0.755	-0.366	0.523	0.677	-0.187	0.305	-0.617	-0.799	0.460	0.905	-0.343	0.645	-0.664	-0.284	0.391	0.188	-0.768	-0.010	-0.697	-0.526	0.468	0.711
Σ16 C_{free} PAHs	0.429	-0.203	-0.077	-0.258	0.117	0.852	0.190	0.810	-0.544	-0.096	0.321	0.718	0.426	0.270	-0.418	-0.101	0.383	0.631	0.028	-0.115	-0.306	-0.067	0.538	0.437	-0.068	0.214	0.022	0.199	0.028	0.195

Where: moisture [%], EC – electrical conductivity [mS/cm], ash – mineral content [%]; TOC – total organic carbon content [%], DOC – dissolved organic carbon [mg/L]; NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene);  indicates statistically significant correlation ($p < 0.1$).

D5

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Stage-dependent effects of willow- and sewage sludge-derived biochar on compost ecotoxicity across multiple trophic levels

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ABSTRACT

This study evaluated how biochar (BC) derived from willow (WL) and sewage sludge (SL), produced at two pyrolysis temperatures (500 °C and 700 °C), influences the ecotoxicity of SL–wheat straw compost at key stages of composting (initial, early thermophilic, mesophilic II, and maturation). Composting was carried out in bioreactors with controlled aeration, and ecotoxicity was assessed using *Aliivibrio fischeri* (bacteria), *Lepidium sativum* (plants), and *Folsomia candida* (invertebrates). The SL-derived BC produced at 700 °C (SL700) was a superior composting additive, as it was the only treatment inducing an 18 % bacteria luminescence stimulation, whereas all other variants, including the control, resulted in luminescence inhibition ranging from 7 % to 35 % (considering the end of the experiment). SL700 additionally resulted in a 52 % greater root growth stimulation relative to the control, while WL-BCs variants caused root growth inhibition ranging from 9 % to 12 % at the end of the experiment. These effects are attributable to the highest electrical conductivity and elevated mineral and nutrient (Na and Mg) contents observed for SL700 among the tested BCs. In contrast, WL-derived BCs exhibited superior performance in springtail reproduction assay, resulting in 11 – 26-fold lower reproductive inhibition relative to the corresponding SL-BCs and 9 – 20-fold lower inhibition than control (at the end of maturation). This phenomenon was likely due to WL-BCs' higher dissolved organic carbon content. As experimental outcomes demonstrate organism-dependent effects and identify distinct BCs as beneficial, broad generalization of BC production parameters is inappropriate; rather, these parameters should be deliberately selected and optimized according to the intended application.

1. Introduction

Global waste generation is increasing rapidly, with sewage sludge (SL) representing a particularly challenging stream due to its high content of organic matter and nutrients, but also potentially harmful organic, inorganic, and biological contaminants [1], which pose a challenge to waste application in soil fertilization. Although numerous effective approaches have already been proposed for managing biowastes including SL [2], millions of tons of SL are still either landfilled or directly applied to soil [3], posing risks to ecosystems and human health [4]. One of the frequently used solutions to mitigate risk associated with SL is composting, offering a sustainable and straightforward approach to waste management [5]. During the thermophilic phase many pathogens and hazardous organic compounds are eliminated [6]. However, not all contaminants are removed during composting; some remain in the final compost, presenting environmental risks when applied to soil [7]; moreover new metabolites may form, with largely unknown ecotoxicological effects [8,9]. Examples of contaminants that may be found in compost, depending on its feedstock, are: microplastics, heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls, pharmaceuticals, parasite eggs, pathogenic bacteria [10,11]. To improve the composting, various additives have been used, including minerals (zeolite, diatomite), ashes, sawdust, microbial inoculum, shells, charcoal, lime, or clay [5]. While these materials primarily aim to improve composting efficiency and final compost quality [12], they also bind potentially hazardous substances, limiting their environmental spreading [5]. This increased immobilization reduces contaminant uptake by plants and other soil organisms, making the otherwise controversial SL-derived compost suitable for specific applications, such as growing energy crops or recultivation degraded areas [13].

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Among numerous composting additives, biochar (BC) has attracted much interest in recent years [14]. When introduced during composting process, BC yields multiple advantages including acceleration of the process, extension of the thermophilic phase, mitigation of greenhouse gas emissions and reduction of contaminants content and bioavailability (through multiple mechanisms) [15–17]. However, there is still a huge research gap on the effect of BC during composting on the toxicity of composted material and final compost regards to temperature and feedstock used for BC production. These factors largely determine the properties of BC, which can have varying effects on the composting process.

Recent research on BC and biowaste co-composting has primarily examined the composting process dynamics, contaminant profiles, and optimal application rates [15]. A key aspect of the complex characterization of toxic substances within the compost is a reliable assessment of compost ecotoxicity. This assessment is particularly crucial for SL-derived composts, which contain multiple contaminants that may interact and create potentially toxic metabolites. Toxicity assessment throughout the composting stages serves two essential functions: (1) it reveals the impact of various compounds on the composting process and (2) serves as a maturity indicator [18]. Immature compost can induce several detrimental effects, including oxidative stress, nitrogen and oxygen competition with crops, and introduction of harmful compounds such as ammonia and organic acids [19]. The overall ecotoxicity profile stems from multiple factors, notably elevated salinity levels, various contaminants, ammonia concentration, and organic acids content [20].

An important issue is the assessment of the ecotoxicity of organic fertilizers across multiple trophic levels. Carraturo et al. [21] investigated the ecotoxicity of seven organic fertilizers, including SL digestate, using, among others, *Lepidium sativum* (plants) and *Aliivibrio fischeri* (bacteria) as test organisms. The results were highly promising and demonstrated positive effects on soil properties, including improved organic matter and nutrient content. Puddephatt et al. [22] evaluated the chronic, sub-lethal, and lethal effects of biosolids applied to agricultural land at rates of 8 and 22 tons ha^{-1}, using *Folsomia candida* (springtails) and *Lumbricus terrestris* (earthworms) as test organisms. Their findings indicated that biosolids had no adverse effects at environmentally relevant concentrations. The study by Roques et al. [23] compared the potential toxicity of SL, cow manure, and cow slurry using three groups of organisms: earthworms (*Eisenia fetida*), plants (among others *Medicago sativa)*, and soil microorganisms. Interestingly, although chemical analyses indicated that SL was the most toxic material, the application of cow manure resulted in the most pronounced toxic effects on the tested organisms. This study clearly highlight the importance of conducting ecotoxicological bioassays employing organisms from different trophic levels, as they may lead to conclusions that differ from those derived solely from chemical analyses [23].

Current literature reveals a significant gap in comprehensive ecotoxicity studies of waste-derived compost [24,25]. Most research relies on plant growth and liquid-phase germination assays [26], leaving solid-phase assessments and invertebrate behavioral studies of BC-enriched waste-derived composts notably limited [27,28]. Moreover, there are no studies that concern co-composting systems. Notably, most studies focus solely on the final product, overlooking the intermediate stages of composting [25]. Monitoring these phases is crucial to understanding the toxicological mechanisms and factors influencing biota throughout the entire composting.

The scope of research concerning the range of organisms tested remains also limited. Notably, only a handful of studies take a broad approach to compost toxicity, employing multiple bioassays and examining effects not just on plants, but also across different trophic levels including bacteria and invertebrates [29]. Most research on contamination levels, microbial populations, or impacts on the composting process focusses on the addition of BC produced from various feedstocks [24] and the dose of BC used for co-composting [30]. However, no current studies have comprehensively evaluated how BC's production conditions, such as feedstock type and pyrolysis temperature, affect ecotoxicity when added to co-composting with SL, especially across different trophic levels. This lack of multi-trophic assessment leaves a critical gap in understanding how BC influences compost safety and maturity.

The aim of this study was therefore to investigate how BC feedstock (willow vs. sewage sludge) and pyrolysis temperature (500 °C vs. 700 °C) affect the ecotoxicity of SL–wheat straw compost at different composting stages (initial, early thermophilic, mesophilic II, and maturation). By integrating bioassays with bacteria (*Aliivibrio fischeri),* plants (*Lepidium sativum*), and invertebrates (*Folsomia candida*), as well as linking toxicity outcomes to physico-chemical parameters and contaminant content, this study provides a comprehensive, multi-trophic assessment. Our findings offer new insights into optimizing BC use for reducing compost toxicity and advancing sustainable waste management practices.

2. Materials and methods

2.1. Composting experimental set up

A mixture of sewage sludge (SL), wheat straw (WS), and biochar (BC) was used as the feedstock for composting. The source, physico-chemical properties, and further details about each feedstock are provided in our previous study [16]. Four BCs were obtained by slow pyrolysis from willow (WL) stalks or SL at either 500 °C or 700 °C under the nitrogen atmosphere (for detailed information see SI). The physico-chemical characteristics of the BCs are presented in Table S1 (SI) and the pseudo-total concentration of potentially toxic elements (PTEs) are demonstrated in Fig. S1 and Table S2 (SI).

Before composting, SL and WS were combined in a 1:1 mass ratio (dry weight), and BC was added to this mixture at the dose of 1 % (w/w). The mixture was placed in 100-liter bioreactors (BKB-100, ROTAMETR, Gliwice, Poland) equipped with an electronically controlled temperature and aeration systems. Our previous research [17] has demonstrated that 1 % of BC addition is optimal for this process. A BC-free variant, containing only a mixture of SL and WS, was used as the control. Each experimental variant was enriched with beneficial soil microorganisms by adding bicompost microbiological agent (Organika-Agrarius Sp. z o. o., Przemyśl, Poland). To measure the levels of various gases (oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), nitric oxide (NO), methane (CH_4), nitrogen (N_2)), released during composting, the OPTIMA7 Biogas Analyzer (MRU GmbH, Germany) was employed. Detailed changes in composting parameters (temperature, aeration, exhaust gases, physico-chemical characteristics) are reported in SI (Table S3 and Fig. S2). After five weeks of composting in the bioreactor, the immature compost was transferred to barrels for two-month maturation period. Samples (approximately 100 g of dry mass) were collected at various stages of the composting – at the beginning and after 3, 14, and 98 days (named T0 – T3, where: T0 – beginning of the composting, T1 – early thermophilic phase, T2 – during mesophilic II phase, T3 – maturation ending). The samples were air-dried, ground, and stored at 4 °C in a plastic zip-bag before the analysis.

2.2. Ecotoxicological tests

To comprehensively assess the ecotoxicity of the composted material, organisms representing three trophic levels were used. The toxicity of material to bacteria was evaluated using the Microtox® Toxicity Test [31] with *A. fischeri* as test organisms. Leachates for this analysis were prepared following the EC protocol [32] by adding Milli Q water to the samples in a single-stage batch-test with a solid-to-liquid ratio of 100 g/L. The slurry was mixed for 24 h at a room temperature (22 ± 2 °C) using horizontal shaker (ELPIN+, Type 358 A, Katowice, Poland). After mixing, samples were filtered through a qualitative paper filter with a pore size of 0.45 μm (Munktell Filter AB, Germany). The pH of

leachates was then adjusted using 0.01 mol/L HCl (POCH, Poland) and/or NaOH (Chempur, Poland) solutions. Toxicity measurements were performed using a Microtox® M500 analyzer (JJS Technical Services, Schaumburg, Illinois, USA).

Solid phase tests were performed using plant (*L. sativum*) and invertebrate (*F. candida*) according to the ISO guideline 18763 [33] and the ISO guideline 11267 [34], respectively. Two doses of compost addition to the reference soil (OECD) were tested: 1 % and 5 %. The Phytotoxkit® test assessed the growth of young roots after a 3-day exposure to the contaminated matrix. The test setup involved mixing OECD standard soil with the composted material, maintaining 100 % of the soil's water holding capacity. As a control, a compost-free OECD soil was implemented. Ten seeds were evenly spaced (1 cm apart) on filter paper placed over the soil mixture in test plates. These plates were then incubated in an upright position at 25 ± 1°C for three days using a POL-EKO incubator (Wodzisław Śląski, Poland). A photograph of the test plates was taken after the exposure time, and the measurements were determined using The Image Tool 3.0 (UTHSCSA, San Antonio, USA). For the bioassay with *F. candida*, OECD standard soil was blended with the composted material and placed in Petri dishes. Milli-Q water was added to reach 50 % of the soil's water-holding capacity, and the mixture was thoroughly homogenized. Subsequently, ten adult *F. candida* individuals were introduced into each dish, and the total weight was recorded. The dishes were supplied with yeast once a week and regularly moistened with Milli-Q water to maintain the initial recorded weight. After 28 days of incubation under controlled conditions (20 °C, 16 h light/8 h dark), the number of adult and juvenile individuals in each dish was determined. Manual counts were performed using ImageJ 1.54 software (ImageJ 1.54, Java, USA).

2.3. Data analysis

The Statistica 13.3 software was employed to analyze the data. Mean values were calculated from three replicates. Differences between bioassays endpoints and the various BC-enriched treatments were assessed with one-way ANOVA, followed by HSD Tukey's test for a significance level of 0.05. Pearson's correlations analysis was applied to investigate relationships between physico-chemical characteristics of composts, contaminants (PAHs, PTEs) content and ecotoxicological tests outcomes in Statistica 13.3. Results were considered statistically significant at $p \leq 0.1$.

3. Results and discussion

3.1. Dynamics of composting parameters

During the composting, clear temporal changes in temperature, gas composition (Table S3), and physico-chemical properties (Fig. S2) of the compost were observed in all experimental variants, reflecting the typical progression of composting phases. A rapid temperature increase was observed within the first three days of composting, making the transition from the mesophilic I to the thermophilic phase (Table S3 and Fig. S2 G). Analogous rapid temperature increases after initial days of composting were previously observed by Abban-Baidoo et al. [20] and Ravindran et al. [35]. The highest temperatures were recorded in BC-enriched treatments, particularly with WL-BCs, reaching up to 55.9 – 56.5 ℃, compared to 43.0 ℃ in the BC-free variant (Fig. S2 G). This represents an increase of 30 – 35 % relative to the control. Other authors reported thermophilic temperatures ranging from 60 to 68°C during the composting of biowaste with BC, whereas the temperature of the BC-free variant did not exceed 50 – 60°C (a 13 – 22 % increase compared to composting without BC) [20,35]. Such significant discrepancies in the temperature of the compost material between the variants with and without BC could potentially result from BC's ability to stimulate microbial activity through greater primary fermentation intensity in BC-enriched composts [36,37]. Composition in the exhaust gas mixture reflected changes in microbial metabolism (Table S3). During the mesophilic I phase, oxygen concentration decreased markedly, especially in WL-BCs (down to 2.3 % – 4.4 %), accompanied by a sharp increase in carbon dioxide concentration (up to 16.7 % – 19.1 %). This represents a widely observed trend in composting [38]. The initial increase in CO_2 emission is a natural indicator of the organic matter degradation intensity [38]. Decomposition was most pronounced during the early stages of composting, as evidenced by elevated carbon dioxide emission (Table S3). Subsequently, a gradual decline in CO_2 release was observed as the rate of degradation decreases and the materials transition into the maturation phase, which is consistent with the findings of Feng et al. [39].

Physico-chemical parameters also differed between treatments. SL-BCs resulted in high moisture retention throughout composting (up to 78 %), while WL-BCs showed a more pronounced increase in electrical conductivity (EC) (Fig. S2). The higher EC of composts enriched with WL-BCs could be due to the greater release of mineral ions (P, K, Mg, Ca) during the process, which may result in elevated toxicity toward living organisms [40]. Total organic carbon (TOC) content decreased by approximately 15 – 20 %, with a slightly slower carbon loss observed in high-temperature BC-enriched composts (particularly WL700), which suggested enhanced carbon stabilization [41] (Fig. S2). Dissolved organic carbon (DOC) decreased more rapidly in WL-BCs composts, with the strongest decline observed for WL700, indicating faster compost maturation compared to SL-BCs treatments (Fig. S2). This resulted from the rapid utilization of readily bioavailable, soluble carbon compounds by microorganisms, which indicates greater microbial activity during composting with WL-BCs [42]. Wu et al. [43] indicate that decreasing DOC levels positively affect seed germination rate. Additionally, low DOC levels are one of the indicators of compost maturity [42]. pH dropped during the mesophilic I phase (to 5.3 – 5.8), which could be related to the elevated activity of microorganisms and the decomposition of organic matter associated with the production of organic and inorganic acids, which agrees with Mohammed et al. [38]. Subsequently, the pH recorded a slight increase followed by a gradual decrease toward the range of 5.1 – 5.6 during maturation (Fig. S2). Final pH values were slightly lower in BC variants than in the control (except SL700), primarily for WL-BCs enriched variants. The findings are in contradiction with other studies proving the addition of BC increased the final pH of the compost due to the alkaline nature of BC [20,38]. The authors reported pH of BC-enriched compost ranges from 7.5 to 9.6, gradually increasing during composting [20,38]. Such significant discrepancies in comparison to our findings could be due to higher BC doses employed in these experiments (5 % and 10 %).

Overall, the results demonstrate that BC addition enhanced thermophilic activity, improved process stability, and influenced organic matter transformation. Wood-derived BCs exerted a stronger influence on composting intensity and stabilization than SL-BCs, while higher-temperature BCs affected dynamics mainly by enhancing carbon stabilization and accelerating compost maturation rather than increasing peak temperatures in the thermophilic phase.

3.2. Ecotoxicity of biochars used during composting

All BCs used in the composting experiment either stimulated or had no impact on *A. fischeri* luminescence (Fig. S3 A). These findings surpass previously published data, where wood- and SL-derived BCs exhibit neutral or even inhibitory effects on *A. fischeri* luminescence [44,45]. The positive effect was observed for BC produced at 700 °C, while BCs obtained at 500 °C do not affect *A. fischeri* (Fig. S3 A). WL-derived BCs obtained at 700 °C demonstrated a greater stimulation of *A. fischeri* luminescence than corresponding SL-derived BCs. No differences were observed between WL- and SL-derived BC produced at 500 °C.

Regardless of the applied dose, SL-derived BCs did not affect (500 °C) or also stimulated (700 °C) growth of *L. sativum*, whereas BC derived from WL inhibited *L. sativum* root elongation up to 18.9 % (Fig. S3 B).

The range of stimulation or inhibition depended on the BC dose, with higher doses generally reducing the positive effects or increasing the toxicity of BC toward *L. sativum*.

All investigated BCs exhibited toxicity to *F. candida,* reducing their reproduction rates from 36 % to 91 %, with variations depending on the feedstock and pyrolysis temperature (Fig. S3 C). The feedstock type was found to have a greater impact on *F. candida* toxicity than the BC pyrolysis temperature, analogously to its effect on *L. sativum* root elongation. WL-derived BCs demonstrated lower *F. candida* reproduction inhibition compared to SL-derived BCs at both applied doses.

The toxicity observed in BCs is mainly linked to their physicochemical properties influenced by feedstock and pyrolysis temperature (Table S1). High-temperature BCs showed lower toxicity, likely due to higher ash content, which binds toxic substances like PTEs and reduces their bioavailability [46]. Additionally, BCs produced at higher temperatures had lower DOC, limiting soluble toxic compounds from leaching into the aqueous phase and harming bacteria [47]. In contrast, low-temperature BCs had higher DOC, increasing toxicity risks [48]. Due to the complex and heterogeneous nature of DOC [49,50], its biological effects may differ accross trophic levels. In the present study, DOC acted primarily as a modulating factor influencing carbon availability and metal complexation rather than as an independent toxicity driver. DOC is the basic substrate for heterotrophic bacteria and is responsible for their well-being [51], while high DOC concentrations can delay maturation and reduce the number of offspring [52] and cause oxidative stress and disturb the photosynthesis in plants [53]. DOC chelates PTE ions, which changes their bioavailability – on the one hand, it can protect against toxicity by transforming metals into unavailable or hard-to-access forms, and on the other hand, it can lead to the immobilization of essential nutrients [54].

Variations in the composition and properties of feedstocks also played a significant role. WL-derived BCs was characterized by higher TOC, which stabilizes organic matter and binds contaminants, reducing toxicity [55,56]. Elevated EC values in high-temperature BCs correlated with increased reproduction inhibition in *F. candida*, indicating salinity effects on soil organisms' toxicity. Overall, the balance between organic and inorganic fractions, DOC content, and EC levels explains the varying toxicity seen across BC types and doses.

3.3. Ecotoxicity changes during BC-free composting

Leachates from composted SL-straw mixtures (the BC-free experimental variant) demonstrated an adverse effect on *A. fischeri* luminescence throughout nearly the entire composting period, excluding the initial time point (T0), where toxicity remained below the permissible toxic threshold (< 20 %) [57] (Fig. 1A). Toxicity toward bacteria increased sharply until day 14 of composting, then decreased by more than half during the maturation phase, though it remained still elevated compared to initial values observed at the beginning of the composting (Fig. 1A). The increase in toxicity during the first days of composting results from the gradual release of toxic substances or their metabolites formed during complex processes occurring in the thermophilic phase [8]. The toxic factors persisted or new ones appeared over the maturation phase, as toxicity continued until the end of this period. To evaluate the potential effect of common contaminants occurring in SL, such as PAHs, correlations between toxicity parameters and the concentrations of total (C_{tot}) and freely (C_{free}) extractable PAHs were analyzed. A positive correlation ($p \leq 0.1$) was observed between luminescence inhibition and both the C_{free} ≥ 3-ring PAHs and the C_{tot} 3-ring PAHs (Fig. S4 A), indicating that these types of contaminants may contribute to the toxicity of BC-free compost. Total and bioavailable concentrations of 16 PAHs determined in composts at different stages of composting are presented in Table S4 and Table S5.

The effect of BC-free composted material on L. *sativum* root elongation was also evaluated, with results shown in Fig. 2. When applied at a 1 % dose of compost to soil, the composted material consistently stimulated root growth, with increases ranging from 24.5 % to 49.8 % throughout the composting process (Fig. 2). Notably, the stimulation peaked during the mesophilic I and thermophilic phases, then declined to the initial value by the end of the maturation phase. An inverse correlation ($p \leq 0.1$) was found between root growth inhibition and DOC, C_{tot} 3-ring PAHs and Σ16 C_{free} PAHs (Fig. S4 A). In contrast, the BC-free composted material applied to soil at a higher dose (5 %) initially exhibited neutral and non-toxic effects on root growth (< 20 % inhibition) during mesophilic I, thermophilic, and mesophilic II phases (T0 – T2) (Fig. 2). Throughout the composting process, a gradual increase in root growth inhibition was observed, reaching its peak at the final stage (T3). This inhibition slightly exceeded the toxicity threshold, likely due to depletion of growth-promoting compounds or a decline in microbial diversity [58]. Root growth inhibition correlated positively with naphthalene (C_{tot} and C_{free}) and ash content, and negatively with TOC ($p \leq 0.1$) (Fig. S4 A).

The composted material in the BC-free variant was also tested at two doses (1 and 5 %) for its effects on *F. candida* mortality and

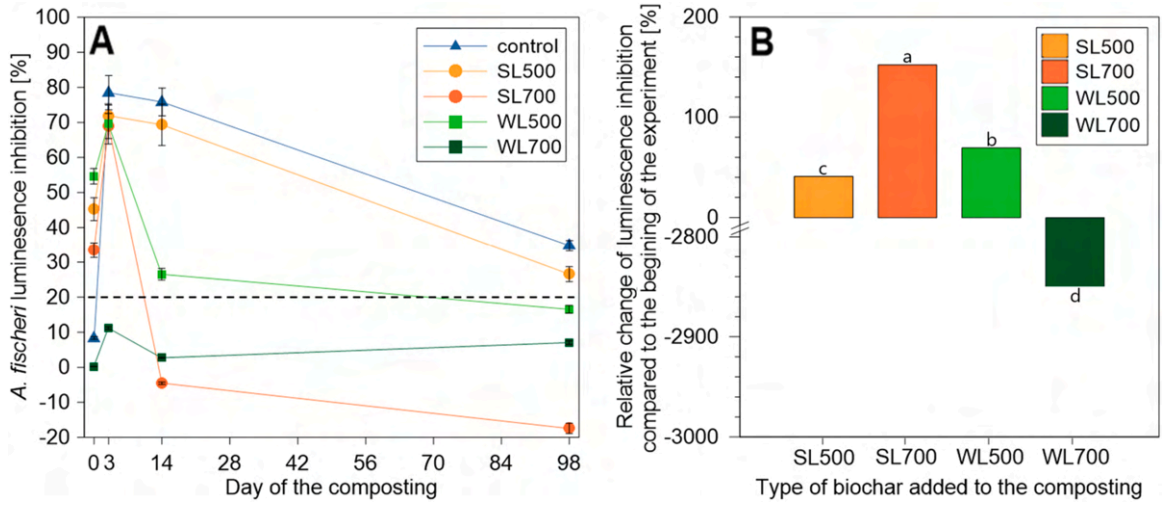

Fig. 1. *Aliivibrio fischeri* luminescence inhibition (positive values) or stimulation (negative values) (%) in the material during composting after 15 min of exposure (A) and relative change of bacteria luminescence inhibition in the material after composting (98 day, T3) in comparison to the beginning of the experiment (0 day, T0) (B). The 20 % level marked with a dashed line represents the maximum level for non-toxic material. Error bars mean standard deviation error (in triplicate) and different letters on bars indicate a significant difference between treatments ($p \leq 0.05$) according to the HSD Tukey test for $\alpha = 0.05$.

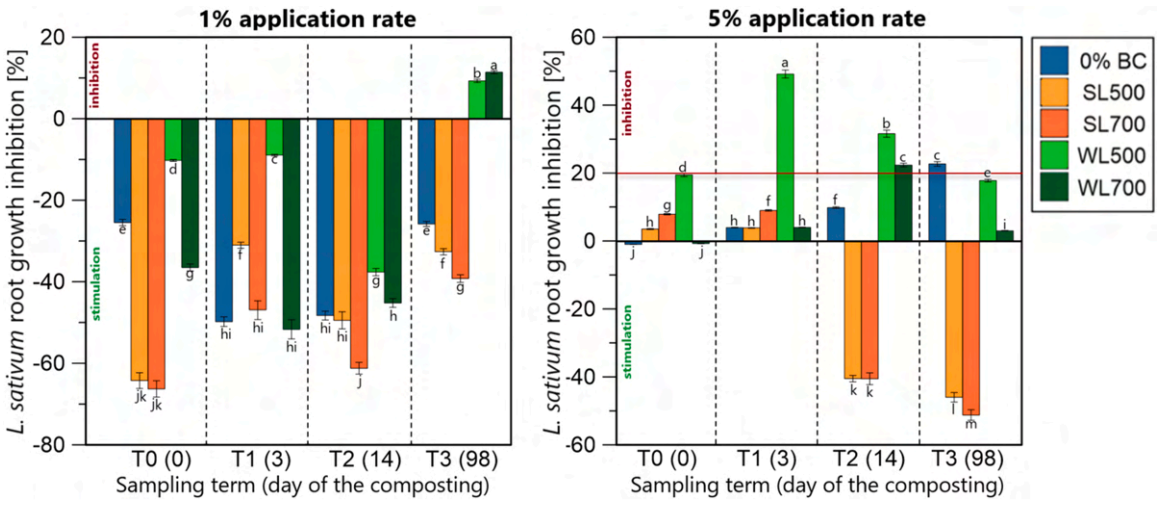

Fig. 2. *Lepidium sativum* root growth inhibition or stimulation in the experiment with different application rates of composted material in the different composting phases. The 20 % level marked with a red line represents the maximum level for non-toxic material. Error bars mean standard deviation error (in triplicate) and different letters on bars indicate a significant difference between sampling terms ($p \leq 0.05$) according to the HSD Tukey test for $\alpha = 0.05$.

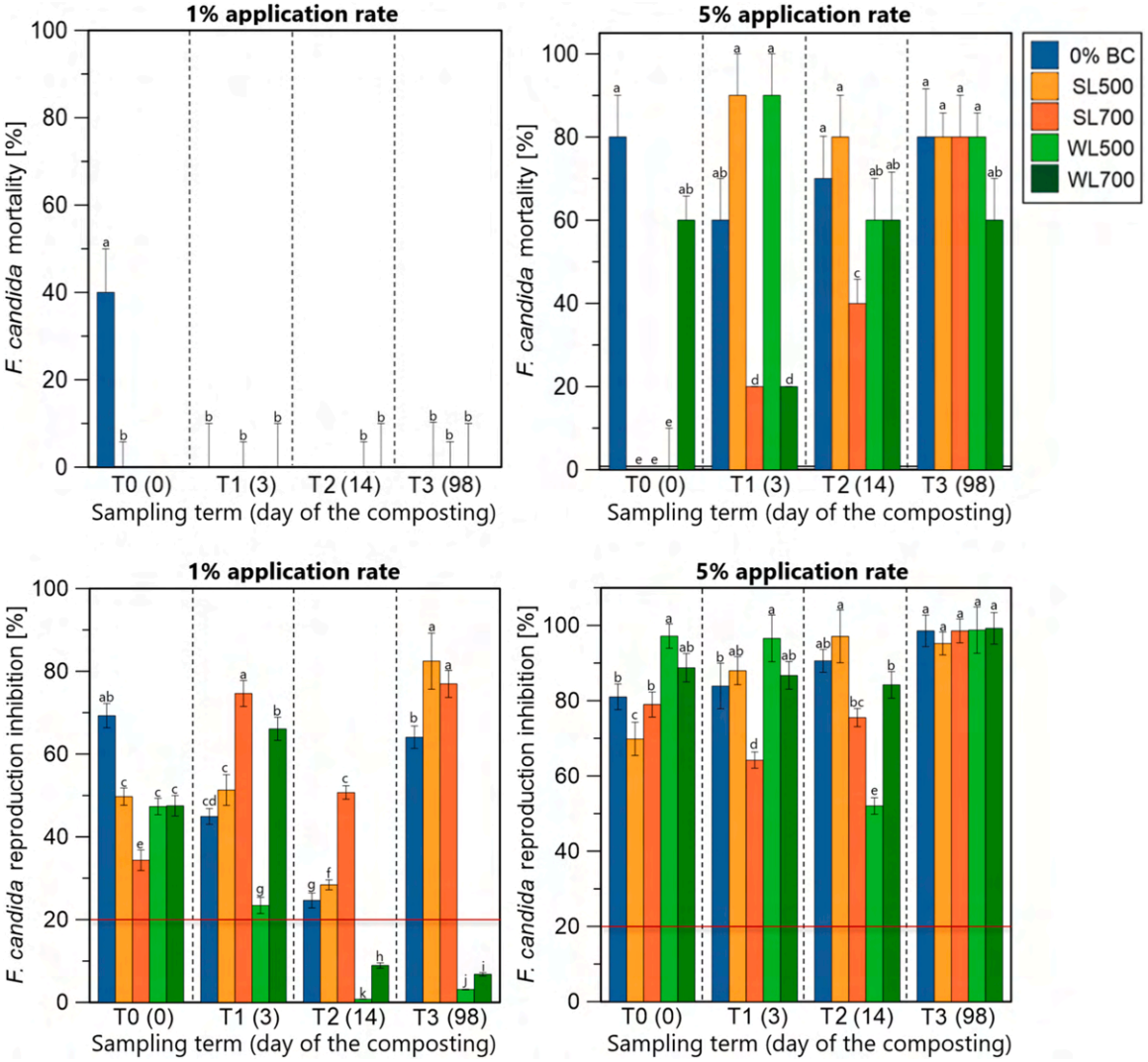

Fig. 3. *Folsomia candida* mortality (%) and reproduction inhibition (%) in the experiments with different doses of composted material in the particular composting phases. The 20 % level marked with a red line represents the maximum level for non-toxic material. Error bars mean standard deviation error (in triplicate) and different letters on bars indicate a significant difference between sampling terms ($p \leq 0.05$) according to the HSD Tukey test for $\alpha = 0.05$.

reproduction. The 1 % dose showed no effect on *F. candida* mortality, while a 5 % dose contributed to 60 – 80 % mortality (Fig. 3). At the 1 % dose, reproduction was consistently inhibited throughout the entire composting process. The strongest inhibition occurred at the beginning, gradually decreasing during stages T1 and T2, then increasing again after the maturation phase (Fig. 3). At the 5 % application rate, reproduction inhibition exceeded 80 % and increased significantly during composting, demonstrating a highly toxic effect on the tested invertebrates (Fig. 3). For a lower dose, an inverse correlation was noted between reproduction inhibition and Σ16 C_{free} PAHs, whereas a 5 % dose demonstrated positive correlations with ash content, C_{tot} and C_{free} naphthalene content and an inverse correlation with TOC content ($p \leq 0.1$) (Fig. S4 A).

3.4. Biochar feedstock and temperature effects on compost ecotoxicity

3.4.1. Impact on bacteria

The effect of BC addition during composting on bacterial luminescence varied significantly depending on the composting phase (Fig. 1A). Initially (T0), the addition of SL500, SL700, and WL500 caused a significant decrease of luminescence compared to the control. On the other hand, WL700, similar to the control, showed no toxicity at T0. During the mesophilic phase I, the WL700 addition significantly reduced the material toxicity compared to the control, to a level considered neutral (< 20 % of inhibition). Subsequent composting phases (thermophilic, mesophilic II, maturation) contributed to emphasizing the role of SL700, WL500, and WL700 in composting, which was demonstrated by a very pronounced decrease in toxicity for these BC-enriched variants (Fig. 1A). WL700, as a composting additive allowing to achieve inhibition below 20 % throughout the composting, could support the development of beneficial microorganisms that produced substances stimulating *A. fischeri* (e.g. quorum sensing signals) to the greatest extent [59]. In contrast, the SL500 treatment consistently showed levels of luminescence inhibition similar to the control, indicating no improvement (Fig. 1A). The lack of stimulation in the SL500 treatment, unlike its high-temperature counterpart (SL700), highlights a critical nutrient threshold. While SL500 exhibited low toxicity (low salinity/PTEs), it failed to provide the essential inorganic micronutrients released by the ash-rich SL700, nor did it supply sufficient DOC (as seen in WL-BCs) (Table S1). Consequently, SL500 likely created a nutrient-limited environment that neither inhibited nor stimulated bacterial metabolism, resulting in a neutral response comparable to the control. Nevertheless, all BC-enriched experimental variants, after composting (T3), exerted a positive effect on the *A. fischeri* luminescence compared to the control (Fig. 4), with SL700 standing out as it contributed almost 20 % of the luminescence stimulation (Fig. 1A).

BC pyrolysis temperature exerted a more substantial effect on *A. fischeri* luminescence compared to the feedstock type. Irrespective of composting phase and BC's feedstock, substrates co-composted with high-temperature BCs demonstrated less toxic effect toward *A. fischeri* than with low-temperature counterparts (Fig. 1A). The larger surface area of high-temperature BCs than their low-temperature counterparts, especially for SL-BCs (Table S1), resulted in more effective binding of organic contaminants [60], potentially toxic to *A. fischeri*. Furthermore, BCs obtained at 700 °C were characterized by higher hydrophobicity (based on the H/C molar ratio) than their low-temperature counterparts, which also increases tendency to bind hydrophobic contaminants (Table S1) [61]. Another possible explanation is that the high-temperature BCs acted as a buffer or adsorbent for reactive oxygen species generated in the SL, which reduced oxidative stress and allowed *A. fischeri* cells to function better [62]. The higher specific surface area of the high-temperature BCs favored the adsorption of reactive oxygen species.

Considering mature compost (T3), high-temperature BCs showed from 9.6 % to 44.1 % less inhibitory effect on *A. fischeri* luminescence than low-temperature counterparts (Fig. 1A). This could be due to

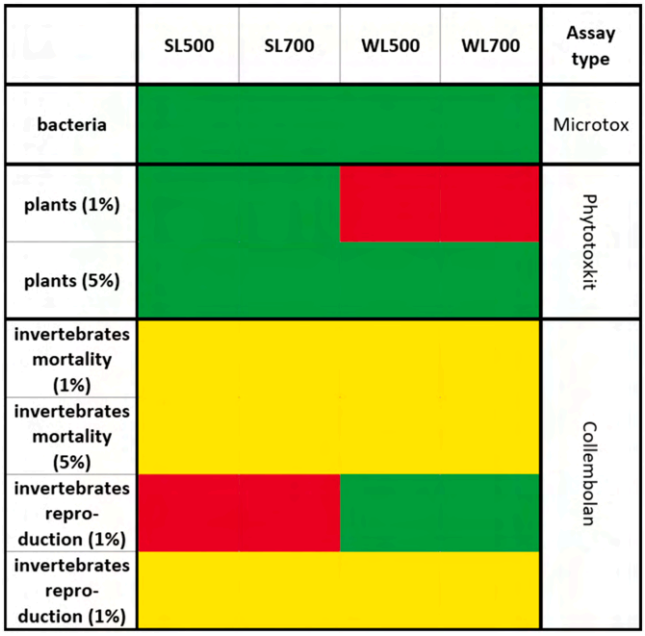

Fig. 4. Effect of BC addition compared to composting without BC (control) on toxicity to organisms at different trophic levels at the end of the experiment (after 98 days, T3). Different colors (red – negative effect, yellow – no effect, green – positive effect) indicate a significant difference between treatment and control ($p \leq 0.05$) according to the HSD Tukey test for $\alpha = 0.05$.

elevated content of inorganic fraction, as well as lower DOC content in BCs produced at 700 ℃ compared to 500 ℃ (Table S1). The compost with SL700, which performed the best effect on bacteria, demonstrated the lowest EC and the highest ash content among the experimental variants (Fig. S2). The superior performance of SL700 is mechanistically linked to its high mineral fraction (ash), which acted dually by reducing the bioavailability of toxic ions through precipitation or adsorption, and simultaneously releasing essential inorganic micronutrients (Mg, Na) that directly stimulated bacterial metabolism [63]. This indicates that for bacteria, the nutrient-supplying capacity of the mineral fraction in SL700 outweighed any potential toxicity [64], a mechanism supported by the negative correlation between ash and toxicity observed specifically for this variant (Fig. S4).

3.4.2. Impact on plants

The impact of BC addition to the composted material on toxicity toward *L. sativum*, compared to the BC-free experiment, varied mainly depending on the BC type (when a 1 % application rate was added) (Fig. 2). At the beginning of the experiment (T0), treatments with most BCs (except WL500) showed higher stimulation of *L. sativum* root growth compared to the control. However, at the next two composting stages (T1, T2), BC-enriched variants showed undistinguishable or worse effect than the control (except for SL700 at T2, which showed 12.9 % higher root growth stimulation than the BC-free variant). After the maturation phase (T3), BC-enriched variants showed differential, highly feedstock-dependent effects. SL-BCs showed greater root growth stimulation, whereas WL-BCs contributed to inhibition, in comparison with the control (Fig. 4).

For *L. sativum* root elongation both the BC feedstock and pyrolysis temperature seem to exert a visible effect (Fig. 2), which was supported by the dendrogram analysis (Fig. 5B). Considering a 1 % dose, over the entire composting period, the variants with SL-derived BCs contributed to a greater stimulation of root growth than WL-BCs enriched treatments (irrespective of pyrolysis temperature) (Fig. 2). The most pronounced effect was noted at the end of the experiment (T3), when SL-BCs demonstrated from 32.7 % to 39.2 % stimulation of *L. sativum* root

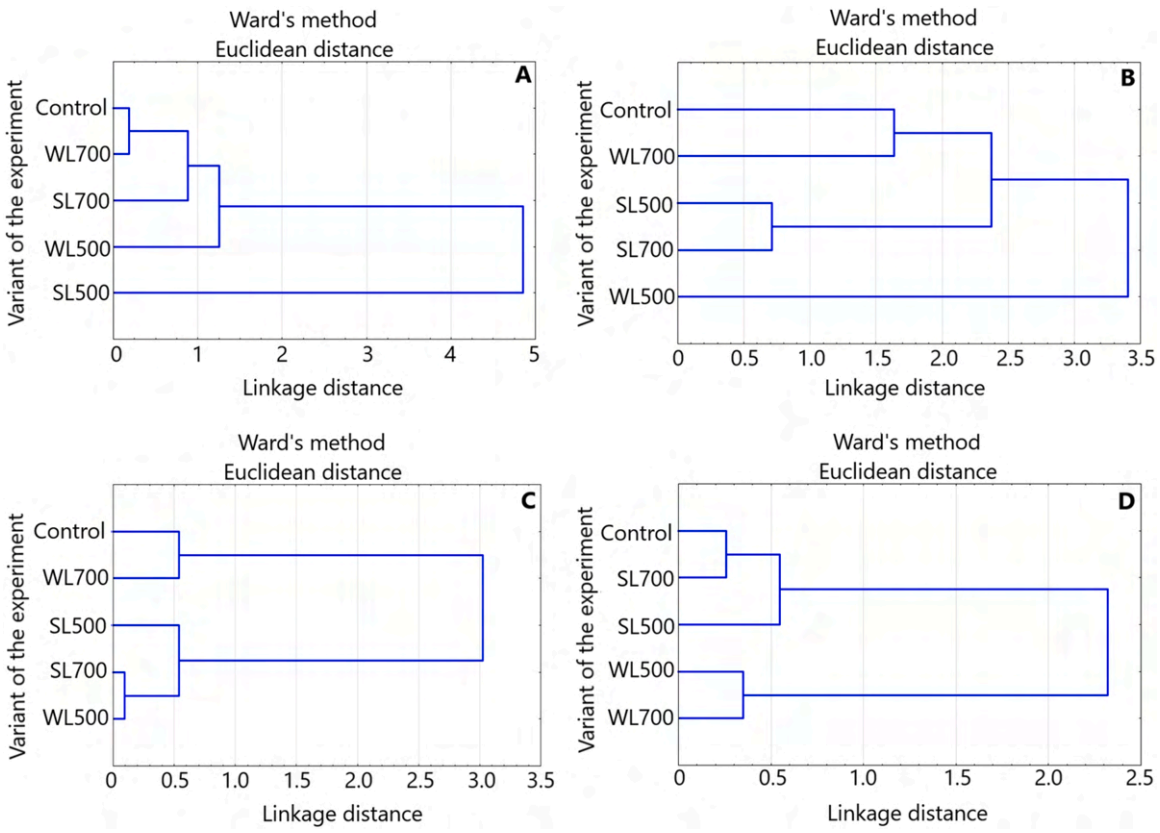

Fig. 5. Dendrograms of the endpoints results from Phytotoxkit® test at the beginning (A) and at the end (B) of the experiment and from Collembolan test at the beginning (C) and at the end (D) of the experiment.

growth, while for WL-BCs from 9.3 % to 11.4 % inhibition of root elongation was observed (Fig. 2). This could be linked (as was mentioned before) to lower DOC and EC value for the composts with SL-BCs compared to WL-BCs at time point T3 (Fig. S2). The occurrence of positive correlations between root elongation and DOC and EC at T3 ($p \leq 0.1$) strongly supports this assumption (Fig. S5 D). The inhibitory effect of WL-BCs on root elongation is attributed to their high release of DOC. Unlike the beneficial mineral-rich SL-BCs, the DOC fraction in WL-BCs likely contained phytotoxic low-molecular-weight organic acids and phenolic compounds which, entering the plant roots, induced oxidative stress and disrupted metabolic processes [53,65]. This distinct pathway explains why WL-BCs inhibited plants despite being beneficial for other trophic levels. Moreover, the experimental variants with WL-BCs were characterized by a higher Σ16 C_{tot} PAHs than SL-BCs, which suggests that elevated concentrations of PAHs can be an inhibitory factor for root elongation [66] (confirmed by a positive statistically significant correlation at T3, $p \leq 0.1$) (Fig. S5 D). Notably, correlations with EC, DOC, and Σ16 C_{tot} PAHs emerged only after the mesophilic II phase, which implies that toxic substances only at the latter stages of composting exhibit phytotoxic effects toward *L. sativum* (Fig. S5 D). The stimulation of root elongation induced by composts with SL-BCs could also result from the lower water-extractable Zn, Ni, and Pb content in these treatments compared to composts enriched with WL-BCs (Table S6). In relation to the pyrolysis temperature influence, irrespective of feedstock, high-temperature BCs generally promoted root growth more effectively than low-temperature counterparts – except for SL-BCs at T0 and WL-BCs at T3 (from 6.6 % to as much as 42.7 % greater root growth promotion) (Fig. 2), as was also observed for bacteria (Fig. 1A). The relationship between pyrolysis temperature and root elongation could result from lower Σ16 C_{tot} PAHs in BCs produced at 700 °C than at 500 °C. A lower number of potential growth inhibitors allowed for proper root elongation [67]. It could also be related to Cd-induced toxicity. For low-temperature BCs, a positive correlation was observed between *L. sativum* root elongation (for a 1 % dose) and water-extractable Cd content ($p \leq 0.1$) (Table S7). This indicates that bioavailable Cd negatively affects root growth [68], and this effect is pronounced for composts with BC obtained at 500 °

The superiority of SL-BCs over WL-BCs in stimulating root elongation could also lie in biological mechanisms. BCs with high porosity and large specific surface area (like WL-BCs) may act as a reservoir for undesirable microorganisms, for example, those that strongly immobilize nitrogen or produce phytotoxic metabolites [69], which translated into lower stimulation or even inhibition of *L. sativum* root growth using WL-BC-amended compost. Additionally, SL-BCs, as materials rich in the inorganic fraction (ash), provide essential nutrients for the metabolism and thus better stimulate the growth of mineralizing or rhizosphere microorganisms [70]. Additionally, mineral fraction, rich in compounds containing Ca, Mg, K, P, can improve plant health and increase yield [71].

For a 5 % dose, the effect of BC addition on *L. sativum* root growth inhibition depended mainly on the phase of the composting (Fig. 2). Generally, in T0 and T1, the addition of BC had either a negative impact or did not differ significantly compared to the control ($p \leq 0.05$) (Fig. 2). However, in the subsequent time points (T2, T3), it was observed that the composted material with SL-derived BC not only had a less negative effect in comparison with BC-free variant, but actually stimulated (from 40.5 % to 51.2 %) the root growth of *L. sativum* (Fig. 2). On the other hand, treatments with WL-derived BCs at T2 contributed to higher root elongation inhibition (Fig. 2), while at T3 it showed lower inhibition compared to the control (Fig. 4). Notably at the end of the experiment (T3), WL-BCs demonstrated a neutral effect (inhibition < 20 %), while SL-BCs caused as much as 46.0 – 51.2 % growth stimulation, which turned out to be a better result than for using a 1 % dose of soil amendment (Fig. 2). This could be linked to the higher

content of nutrients necessary for proper plant growth (Na, K, Mg) in SL-BCs relative to WL-BCs (Fig. S1, Table S2).

Considering the impact of the pyrolysis temperature, WL700 demonstrated lower *L. sativum* root growth inhibition in relation to the low-temperature counterpart. Additionally, over almost the entire composting period, WL700 demonstrated a non-phytotoxic effect (inhibition < 20 %) (Fig. 2). This could be linked to the lower content of Σ16 C_{free} PAHs for the variant with WL700 than with WL500 (throughout almost the entire composting, except for T0). It was supported by the occurrence of statistically significant positive correlation between root growth inhibition (with a 5 % dose of WL700-enriched compost) and Σ16 C_{free} PAHs ($p \leq 0.1$) (Fig. S4 E). The effect of temperature among SL-BCs in the 5 % dose experiment was much less pronounced and the changes demonstrated no systematic pattern (Fig. 2).

Dendrograms from cluster analysis (Fig. 5) illustrate similarities and differences between experimental variants and their respective BCs. Similar endpoint trends suggest analogous effects on composting, while significant differences indicate distinct factors influencing compost ecotoxicity. For test with *L. sativum*, the similarities/differences varied between the beginning and the end of composting, which may indicate that intense and complex processes occur during the composting, significantly affecting the phytotoxicity of the material (Figs. 5A and 5B). At the beginning of the experiment, close similarity between high-temperature BCs was noted, irrespective of the feedstock (Fig. 5A). In contrast, at the end of the experiment, the closest similarity was observed for variants enriched with SL-BCs, irrespectively of the pyrolysis temperature (Fig. 5B). These findings strongly support our previous assumption that both BC feedstock and pyrolysis temperature exerts a substantial impact on *L. sativum* root elongation. Additionally, the close similarity of variants with SL-BCs (irrespective of the pyrolysis temperature) and the high linkage distance of WL-BCs supports thesis that pyrolysis temperature exerted distinct effect on phytotoxicity, depending on the BC feedstock (Fig. 5B).

Analyzing the endpoint results of the root elongation test, it can be stated with certainty that the 1 % application rate is more beneficial compared to the higher. The only observed difference in favor of the higher dose was a 12.0 – 13.3 % higher root growth stimulation for the compost with SL-BCs in T3 (Fig. 2). These findings emphasize the necessity of ecotoxicological characterization prior to soil application, as inappropriate doses may compromise soil health and ecosystem safety. The influence of composts enriched with BC is highly dependent on feedstock type and production conditions; therefore, although higher doses may sometimes be advantageous, their suitability should always be verified in advance. Such evaluations are essential for safe, effective, and sustainable compost management.

3.4.3. Impact on invertebrates

When using a 1 % application rate of composted material to soil, the effect of BC as a co-composting additive on *F. candida* mortality and reproduction varied significantly depending on the time point of toxicity assessment and BC feedstock (Fig. 3). Looking at changes in mortality, the addition of BC to the composting material exerted a positive effect, reducing mortality at T0, compared to the control. In the subsequent composting phases (T1, T2, T3), no mortality of *F. candida* was observed both in control and BC-enriched variants (Figs. 3 and 4). Notably, BC-enriched variants showed less reproductive inhibition at the beginning of the experiment, irrespective of BC's production conditions, compared to the control (Fig. 3). At the subsequent phases (T1 – T3), increased reproductive inhibition was observed mostly for variants with SL-derived BC and significantly lower for WL-derived BCs, compared to the control ($p \leq 0.05$) (Figs. 3 and 4). Considering a 5 % dose of composted material applied to soil, more variable influences were observed for *F. candida* mortality than with a lower dose (Fig. 3). At T0, all variants with BCs reduced mortality relative to control. No mortality was observed for most BC (except of WL700). At T1, low-temperature BCs increased mortality, while high-temperature BCs significantly reduced it (Fig. 3). By T2 and T3, *F. candida* mortality was generally similar across treatments and control (Fig. 4). BC effects on reproduction were inconsistent at T0 – T2. At these stages, a marked decrease in reproduction inhibition was observed in the SL500 (T0), SL700 (T1, T2), and WL500 (T2) variants. By T3, there were no significant differences in reproduction inhibition ($p > 0.05$) (Fig. 4) between the experiments without BC and those with BC addition.

Given the general tendency of all BC-enriched treatments to inhibit reproduction and increase mortality of *F. candida*, especially at the higher (5 %) soil additive dose, it cannot be ruled out that the observed inhibitory effect arises from an indirect impact on microbial communities. *F. candida* feeds primarily on soil microorganisms, particularly fungi and bacteria, and its growth and reproduction are strongly dependent on microbial biomass and community composition [72]. This indirect trophic effect is strongly driven by the matrix chemistry established by the specific BCs. The high salinity and pH fluctuations induced by SL-BCs (high ash) likely suppressed the fungal communities preferred by *F. candida*, shifting the microbiome toward less palatable bacterial biofilms [73]. In contrast, the organic-rich environment provided by WL-BCs (high DOC) favored fungal proliferation, sustaining the invertebrate food web and explaining the significantly lower reproductive inhibition observed in these variants.

It was observed that the effect of composted material on mortality and reproduction of *F. candida* varied depending on the application rate in context of the specific feedstock and pyrolysis temperature. BC feedstock exerted a greater effect on *F. candida* reproduction at 1 % application rate, while pyrolysis temperature influence was more visible when composted material was applied to soil at 5 % dose (Fig. 3). This first assumption is strongly supported by the dendrogram analysis (Fig. 5D), as at the end of the experiment variants enriched with BCs produced from the same feedstocks demonstrated the closest similarity, irrespective of the pyrolysis temperature.

Across all composting phases and applied doses, every treatment exhibited an inhibitory effect on *F. Candida* reproduction throughout the composting period, except for the variants containing WL-derived BCs (at T3 with a 1 % dose) (Fig. 3). Considering changes for a 1 % dose, composts enriched with WL-BCs demonstrated a lower level of *F. Candida* reproduction inhibition relative to SL-BCs produced at the same temperature (except for T0) (Fig. 3). This could be attributed to the higher amount of water-extractable Fe in composts made with WL-BCs than with SL-BCs (Table S6). Adequate, environmentally relevant Fe concentration is important because bioavailable Fe stimulates the growth of bacteria and fungi, which provide a food source for springtails [74]. Another reason for this could be the lower content of mineral fraction (ash content) in WL-BCs and composts enriched with WL-BCs compared to SL-derived counterparts (Table S1 and S3). The positive statistically significant correlation between *F. candida* reproduction (for a 1 % application rate) and ash content ($p \leq 0.1$) at the end of the experiment (T3) strongly supported this assumption (Fig. S5 D). In our study, the response of *F. candida* was distinctly governed by the trade-off between the mineral and organic fractions of the BCs. The negative correlation between ash content and reproduction suggests that the high salinity and potential pH fluctuations introduced by SL-BCs (high ash) created an unfavorable osmotic environment, outweighing any buffering benefits [75] [76]. Conversely, the higher DOC levels in WL-BCs, which were phytotoxic to *L. sativum*, proved beneficial for *F. candida*. This suggests a trophic-mediated mechanism where WL-BC-derived carbon stimulated the growth of the fungal community, thereby increasing the food availability for the collembolans and mitigating the direct chemical inhibition [79]. This divergence explains why the 'cleaner' SL-BCs (lower DOC) were less effective for invertebrates than the organic-rich WL-BCs.

Notably, the only non-toxic effect (reproduction inhibition < 20 %) was observed for the compost enriched with WL-BCs (in T2 and T3) (Fig. 3). This could be attributed to the higher DOC for the WL-BCs

treatments relative to SL-BCs and the provision of more soluble organic compounds necessary for the reproduction of springtails in the WL-BCs-enriched variants (Fig. S2). Additionally, high concentrations of DOC can chelate PTE ions, which may reduce their availability and therefore toxicity to springtails [54].

It was also observed that during the later stages of composting (T2, T3), the toxicity of a 5 % dose of composted material to *F. candida* increased, showing very high negative impact on mortality (Fig. 3). It can be explained by the complex changes occur in the structure of organic matter, including its decomposition and partial mineralization [77]. Simultaneously, especially for waste composting, levels of certain persistent pollutants, such as pharmaceuticals, microplastics, polychlorinated biphenyls, per- and polyfluoroalkyl substances, dioxins, phthalates, and pesticides, are observed to persist or increase [78–80]. Due to their diverse chemical nature, these pollutants can be released or concentrated during the composting process [79]. *F. candida*, exposed to residual pharmaceuticals or pesticides, may exhibit reduced reproductive capacity, reduced metabolism, or extended development time [81, 82]. Moreover, other authors proved that invertebrates can be seriously sensitive to PAHs and metals [83,84]. The high mortality of individuals (60 – 80 %), irrespective of the type of BC added, could be also related to the increasing EC level during composting (from 3.32 to 3.90 mS/cm in T0 to 5.09 – 6.61 mS/cm in T3, depending on the type of treatment, Fig. S2)), which, combined with the higher application rate, resulted in such a detrimental effect (Fig. 3). In the literature, there is no strictly defined safe level of soil salinity for *F. candida* life-cycle, however Owojori et al. [40] examined the range from 0.08 to 1.62 mS/cm and observed a substantial negative impact on juvenile production at 1.03 mS/cm and higher. Additionally, at the level of 1.62 mS/cm an absolute cessation of *F. candida* reproduction was presented. On the other hand, BC feedstock typically exerted no effect on mortality rate for a 5 % application rate, irrespective of evaluation time point (Fig. 3). For a 5 % soil application dose, *F. candida* reproduction was strongly inhibited, with reductions ranged from 50 % to 100 %, irrespective of the experimental variant and composting stage (Fig. 3). This may indicate that, regardless of BC presence, compost applied at excessively high doses is detrimental to soil invertebrates [85].

4. Conclusions

Biochar feedstock and pyrolysis conditions significantly shaped the ecotoxicity of composted sewage sludge, with effects varying by trophic level and composting stage. High-temperature BCs generally reduced toxicity toward bacteria and plants, making them ideal for yield-focused application. Conversely, willow-derived BCs better supported invertebrate reproduction, essential for restoring soil structure in degraded lands. Among all treatments, SL700 showed the strongest reduction in bacterial toxicity and the greatest stimulation of plant growth.

Our findings underscore that chemical analysis and single-trophic tests are insufficient for safety assessments and commercial composting must employ multi-level bioassays. Furthermore, results are context-dependent and cannot be generalized across different feedstocks, necessitating pilot studies for industrial scaling. Application strategy is equally critical. Reported in the literature, compost application rates range widely from 0.5 % to 20 %, with 1 – 5 % being the most commonly applied range, and typically providing comparable or superior outcomes. In line with this, our results proved the same: lower amendment (1 %) was more effective than higher dose (5 %). Finally, adequate composting time is vital to allow for the full integration of BC into the matrix. Based on the opposing effects of ash and DOC, we propose a divergent application strategy where mineral-rich BCs (e.g., sludge-derived at 700°C) are optimal for phytostabilization and promoting plant growth due to nutrient supply, whereas organic-carbon-rich BCs (e.g., willow-derived) are superior for ecological restoration aimed at rebuilding soil invertebrate communities. Future industrial applications must therefore select BC feedstock not just for waste volume reduction, but specifically targeted to the desired trophic endpoint.

CRediT authorship contribution statement

Aleksandra Rombel: Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Monika Raczkiewicz:** Methodology, Investigation. **Bo Pan:** Writing – review & editing, Formal analysis, Data curation. **Patryk Oleszczuk:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Formal analysis, Conceptualization.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2026.121924.

Data availability

Data will be made available on request.

References

[1] M. Wasserman, A. Moretti, D. Goi, M. Mainardis, Integrating renewable energy in sewage sludge treatment through greenhouse solar drying: a review, Sci. Total Environ. 965 (2025) 178634, https://doi.org/10.1016/J.SCITOTENV.2025.178634.
[2] D. Hariyani, P. Hariyani, S. Mishra, M.K. Sharma, A literature review on waste management treatment and control techniques, Sustain. Futur. 9 (2025) 100728, https://doi.org/10.1016/J.SFTR.2025.100728.
[3] K.C. Maturi, I. Haq, A.S. Kalamdhad, A. Gupta, A glance over current status of waste management and landfills across the globe: a review, Biodegrad. Detoxif. Micro Ind. Wastewater (2022) 131–144, https://doi.org/10.1016/B978-0-323-88507-2.00001-4.
[4] T. Raphela, N. Manqele, M. Erasmus, The impact of improper waste disposal on human health and the environment: a case of Umgungundlovu District in KwaZulu Natal Province, South Africa, Front. Sustain. 5 (2024) 1386047, https://doi.org/10.3389/FRSUS.2024.1386047.
[5] R.S. Noor, A.N. Shah, M.B. Tahir, M. Umair, M. Nawaz, A. Ali, S. Ercisli, N. R. Abdelsalam, H.M. Ali, S.H. Yang, S. Ullah, M.A. Assiri, Recent trends and advances in additive-mediated composting technology for agricultural waste resources: a comprehensive review, ACS Omega 9 (2024) 8632–8653, https://doi.org/10.1021/ACSOMEGA.3C06516.
[6] N. Zhu, J. Gao, D. Liang, Y. Zhu, B. Li, H. Jin, Thermal pretreatment enhances the degradation and humification of lignocellulose by stimulating thermophilic bacteria during dairy manure composting, Bioresour. Technol. 319 (2021) 124149, https://doi.org/10.1016/J.BIORTECH.2020.124149.
[7] S. Albert, E. Bloem, Antibiotic contamination of fresh organic fertilizers and processed bio-based fertilizer products, Agrosyst. Geosci. Environ. 8 (2025) e70059, https://doi.org/10.1002/AGG2.70059.
[8] Y. Yang, Z. Yang, J. Kang, Z. Wu, Y. Sun, X. Cao, Y. Guo, X. Tu, L. Mao, S. Li, W. Yao, J. Ge, W. Ping, Using quantitative evaluation model to assess the environmental benefits of metabolites in flax retting wastewater aerobic compost: The trade-offs of core species build the profiles of beneficial and harmful metabolites converted from lignocellulose, Chem. Eng. J. 513 (2025) 162571, https://doi.org/10.1016/J.CEJ.2025.162571.
[9] C. Lin, N.K. Cheruiyot, X.-T. Bui, H. Huu, N. Ngo, H.H. Kiprotich Cheruiyot, Ngo, Composting and its application in bioremediation of organic contaminants, Bioengineered 13 (2022) 1073–1089, https://doi.org/10.1080/21655979.2021.2017624.
[10] F. Okori, J. Lederer, A.J. Komakech, T. Schwarzböck, J. Fellner, Plastics and other extraneous matter in municipal solid waste compost: a systematic review of sources, occurrence, implications, and fate in amended soils, Environ. Adv. 15 (2024) 100494, https://doi.org/10.1016/J.ENVADV.2024.100494.

[11] J. O'Connor, B.S. Mickan, K.H.M. Siddique, J. Rinklebe, M.B. Kirkham, N.S. Bolan, Physical, chemical, and microbial contaminants in food waste management for soil application: A review, Environ. Pollut. 300 (2022) 118860, https://doi.org/10.1016/J.ENVPOL.2022.118860.
[12] C. Parab, K.D. Yadav, A review on green waste composting, role of additives and composting methods for process acceleration, Environ. Sci. Pollut. Res. 31 (2024) 63473–63500, https://doi.org/10.1007/S11356-024-35429-6.
[13] Z. Li, Global research progress on land application of sewage sludge: A comprehensive bibliometric review, Waste Biomass. Valoriz. (2025) 1–21, https://doi.org/10.1007/S12649-025-03084-8.
[14] S. Qian, X. Zhou, Y. Fu, B. Song, H. Yan, Z. Chen, Q. Sun, H. Ye, L. Qin, C. Lai, Biochar-compost as a new option for soil improvement: Application in various problem soils, Sci. Total Environ. 870 (2023) 162024, https://doi.org/10.1016/J.SCITOTENV.2023.162024.
[15] M.K. Nguyen, C. Lin, H.G. Hoang, P. Sanderson, B.T. Dang, X.T. Bui, N.S. H. Nguyen, D.V.N. Vo, H.T. Tran, Evaluate the role of biochar during the organic waste composting process: A critical review, Chemosphere 299 (2022) 134488, https://doi.org/10.1016/J.CHEMOSPHERE.2022.134488.
[16] A. Rombel, K. Różyło, Y.S. Ok, P. Oleszczuk, Influence of biochar characteristics on polycyclic aromatic hydrocarbons content during co-composting of sewage sludge, Bioresour. Technol. 423 (2025) 132220, https://doi.org/10.1016/J.BIORTECH.2025.132220.
[17] A. Rombel, K. Różyło, P. Oleszczuk, The high dose of biochar reduces polycyclic aromatic hydrocarbons losses during co-composting of sewage sludge and wheat straw, J. Environ. Manag. 351 (2024) 119628, https://doi.org/10.1016/J.JENVMAN.2023.119628.
[18] Z. Ji, L. Zhang, Y. Liu, X. Li, Z. Li, Evaluation of composting parameters, technologies and maturity indexes for aerobic manure composting: A meta-analysis, Sci. Total Environ. 886 (2023) 163929, https://doi.org/10.1016/J.SCITOTENV.2023.163929.
[19] Y. Kong, J. Zhang, X. Zhang, X. Gao, J. Yin, G. Wang, J. Li, G. Li, Z. Cui, J. Yuan, Applicability and limitation of compost maturity evaluation indicators: A review, Chem. Eng. J. 489 (2024) 151386, https://doi.org/10.1016/J.CEJ.2024.151386.
[20] E. Abban-Baidoo, D. Manka'abusi, L. Apuri, B. Marschner, K.A. Frimpong, Biochar addition influences C and N dynamics during biochar co-composting and the nutrient content of the biochar co-compost, Sci. Rep. 14 (2024) 1–12, https://doi.org/10.1038/s41598-024-67884-z.
[21] F. Carraturo, A. Siciliano, A. Giordano, F. Di Capua, F. Barone, E. Casaletta, F. Cicotti, M. Guida, F. Adani, Ecotoxicological assessment of waste-derived organic fertilizers and long-term monitoring of fertilized soils using a multi-matrix and multi-species approach, Sci. Total Environ. 912 (2024) 169341, https://doi.org/10.1016/J.SCITOTENV.2023.169341.
[22] K.J. Puddephatt, L.H. McCarthy, B.M. Serre, Assessing the potential chronic, sublethal and lethal ecotoxicity of land-applying biosolids on Folsomia candida and Lumbricus terrestris, 2022 3110, Ecotoxicol 31 (2022) 1520–1535, https://doi.org/10.1007/S10646-022-02606-7.
[23] O. Roques, J.P. Bedell, J. Le Maux, L. Wiest, S. Nélieu, C. Mougin, N. Cheviron, O. Santini, V. Lecomte, R. Bayard, Assessing the potential ecotoxicological risk of different organic amendments used in agriculture: Approach using acute toxicity tests on plants and earthworms, Arch. Environ. Contam. Toxicol. 84 (2023) 248–266, https://doi.org/10.1007/S00244-023-00979-2.
[24] R. Tao, M. Cui, Y. Li, J. Wang, W. He, Y. Zhao, X. Wenping, Y. Shen, Y. Feng, J. C. White, Nanoscale biochar for fertilizer quality optimization in waste composting: Microbial community regulation, Bioresour. Technol. 414 (2024) 131571, https://doi.org/10.1016/J.BIORTECH.2024.131571.
[25] N. Wang, X. Bai, D. Huang, M. Shao, Q. Chen, Q. Xu, Insights into the influence of digestate-derived biochar upon the microbial community succession during the composting of digestate from food waste, Chemosphere 316 (2023) 137786, https://doi.org/10.1016/J.CHEMOSPHERE.2023.137786.
[26] H. Jia, D. Chu, X. You, Y. Li, C. Huang, J. Zhang, X. Zeng, H. Yao, Z. Zhou, Biochar improved the composting quality of seaweeds and cow manure mixture and altered the microbial community, Front. Microbiol. 13 (2022) 1064252, https://doi.org/10.3389/fmicb.2022.1064252.
[27] A.C. Bastos, F.G.A. Verheijen, A. Amaro, M. Prodana, D.N. Cardoso, R.G. Morgado, M.J. Santos, A.M.V.M. Soares, J.J. Keizer, S. Loureiro, Screening the habitat function of biochar-amended vineyard soils at field plot-scale, based on invertebrate avoidance behaviour, Appl. Soil Ecol. 177 (2022) 104526, https://doi.org/10.1016/J.APSOIL.2022.104526.
[28] M. Prodana, A.C. Bastos, A. Amaro, D. Cardoso, R. Morgado, A.L. Machado, F.G. A. Verheijen, J.J. Keizer, S. Loureiro, Biomonitoring tools for biochar and biochar-compost amended soil under viticulture: Looking at exposure and effects, Appl. Soil Ecol. 137 (2019) 120–128, https://doi.org/10.1016/J.APSOIL.2019.01.007.
[29] M. Kopeć, A. Baran, M. Mierzwa-Hersztek, K. Gondek, M.J. Chmiel, Effect of the addition of biochar and coffee grounds on the biological properties and ecotoxicity of composts, Waste Biomass. Valoriz. 9 (2018) 1389–1398, https://doi.org/10.1007/S12649-017-9916-Y.
[30] W.J. Chung, S.W. Chang, D.K. Chaudhary, J.Du Shin, H. Kim, N. Karmegam, M. Govarthanan, M. Chandrasekaran, B. Ravindran, Effect of biochar amendment on compost quality, gaseous emissions and pathogen reduction during in-vessel composting of chicken manure, Chemosphere 283 (2021) 131129, https://doi.org/10.1016/J.CHEMOSPHERE.2021.131129.
[31] SDI, SDI Microtox Manual, Microbics Corp. (1992).
[32] EC, EN 12457-2 protocol Council Decision of 19 December 2002 Establishing criteria and procedures for the acceptance of waste at landfills Pursuant to Article 16 of and Annex II to Directive 1999/31/EC, Off. J. Eur. Communities. L 11/27 (2003).
[33] International Organization for Standardization, ISO 18763 Soil quality - Determination of the toxic effects of pollutants on germination and early growth of higher plants, 2016.
[34] International Organization for Standarization, ISO 11267 Soil quality - Inhibition of reproduction of Collembola (Folsomia candida) by soil contaminants, 2023. ⟨https://www.iso.org/standard/79816.html⟩ (accessed January 18, 2025).
[35] B. Ravindran, N. Karmegam, M.K. Awasthi, S.W. Chang, P.K. Selvi, R. Balachandar, S. Chinnappan, N.I.W. Azelee, G. Munuswamy-Ramanujam, Valorization of food waste and poultry manure through co-composting amending saw dust, biochar and mineral salts for value-added compost production, Bioresour. Technol. 346 (2022) 126442, https://doi.org/10.1016/J.BIORTECH.2021.126442.
[36] C. Tibu, T.Y. Annang, N. Solomon, D. Yirenya-Tawiah, Effect of the composting process on physicochemical properties and concentration of heavy metals in market waste with additive materials in the Ga West Municipality, Ghana, Int. J. Recycl. Org. Waste Agric. 8 (2019) 393–403, https://doi.org/10.1007/s40093-019-0266-6.
[37] M.K. Awasthi, Q. Wang, H. Chen, M. Wang, X. Ren, J. Zhao, J. Li, D. Guo, D. sheng Li, S.K. Awasthi, X. Sun, Z. Zhang, Evaluation of biochar amended biosolids co-composting to improve the nutrient transformation and its correlation as a function for the production of nutrient-rich compost, Bioresour. Technol. 237 (2017) 156–166, https://doi.org/10.1016/j.biortech.2017.01.044.
[38] A.A. Mohammed, S.M. Younis, A.E. Ghaly, M.M. Ibrahim, Mitigating greenhouse gas emissions and enhancing composting efficiency using biochar, used oil, and compost inoculum amendments, Sci. Rep. 15 (2025) 35020, https://doi.org/10.1038/s41598-025-21144-w.
[39] M. Feng, X. Wu, X. Qiu, H. Wang, Influence of peat and biochar on gas emissions and microbial metabolism during co-composting of chicken manure and maize straw, Waste Biomass. Valoriz. 14 (2022) 197–208, https://doi.org/10.1007/s12649-022-01857-z.
[40] O.J. Owojori, A.J. Reinecke, P. Voua-Otomo, S.A. Reinecke, Comparative study of the effects of salinity on life-cycle parameters of four soil-dwelling species (Folsomia candida, Enchytraeus doerjesi, Eisenia fetida and Aporrectodea caliginosa), Pedobiol. (Jena.) 52 (2009) 351–360, https://doi.org/10.1016/J.PEDOBI.2008.12.002.
[41] B. Wang, W. Li, N. Xue, R. Xi, Y. Wang, L. Fang, Q. Wang, X. Liang, Y. Xiao, X. Yang, X. Wu, Co-application of biochar and compost enhanced soil carbon sequestration in urban green space, Front. Microbiol. 16 (2025), https://doi.org/10.3389/fmicb.2025.1707894.
[42] K.M. Wichuk, D. McCartney, Compost stability and maturity evaluation - a literature review, Can. J. Civ. Eng. 37 (2010) 1505–1523, https://doi.org/10.1139/L10-101.
[43] L. Wu, L.Q. Ma, G.A. Martinez, Comparison of Methods for Evaluating Stability and Maturity of Biosolids Compost, J. Environ. Qual. 29 (2000) 424–429, https://doi.org/10.2134/jeq2000.00472425002900020008x.
[44] M. Marcińczyk, P. Krasucka, W. Duan, B. Pan, A. Siatecka, P. Oleszczuk, Ecotoxicological characterization of engineered biochars produced from different feedstock and temperatures, Sci. Total Environ. 861 (2022) 160640, https://doi.org/10.1016/J.SCITOTENV.2022.160640.
[45] K. Gondek, A. Baran, M. Mierzwa-Hersztek, M. Kopeć, Impact of thermal treatment of mixtures of sewage sludge and plant material on selected chemical properties and Vibrio fischeri response, Ecol. Chem. Eng. S. 24 (2017) 443–455, https://doi.org/10.1515/ECES-2017-0030.
[46] X. Guo, L. Yang, Z. Du, H. Zhou, L. Li, W. Zhu, L. Dai, Co-effects from inorganic and organic fractions in dissolved components of biochar on its adsorption behavior: Taking uranium adsorption as an example, Colloids Surf. A Physicochem. Eng. Asp. 713 (2025) 136546, https://doi.org/10.1016/J.COLSURFA.2025.136546.
[47] A.J. Lewis, X. Yun, D.E. Spooner, M.J. Kurz, E.R. McKenzie, C.M. Sales, Exposure pathways and bioaccumulation of per- and polyfluoroalkyl substances in freshwater aquatic ecosystems: Key considerations, Sci. Total Environ. 822 (2022) 153561, https://doi.org/10.1016/J.SCITOTENV.2022.153561.
[48] H. Lyu, H. Zhang, J. Dong, B. Shen, Z. Cheng, J. Yu, R. Li, N. Shao, J. Tang, Pyrolysis temperature matters: Biochar-derived dissolved organic matter modulates aging behavior and biotoxicity of microplastics, Water Res 250 (2024) 121064, https://doi.org/10.1016/J.WATRES.2023.121064.
[49] H. Wu, X. Dong, H. Liu, Evaluating fluorescent dissolved organic matter released from wetland-plant derived biochar: Effects of extracting solutions, Chemosphere 212 (2018) 638–644, https://doi.org/10.1016/J.CHEMOSPHERE.2018.08.110.
[50] H. Liu, B. Zhao, X. Zhang, L. Li, Y. Zhao, Y. Li, K. Duan, Investigating biochar-derived dissolved organic carbon (DOC) components extracted using a sequential extraction protocol, Mater. (Basel) 15 (2022) 3865, https://doi.org/10.3390/MA15113865.
[51] C. Lønborg, F. Baltar, M.L. Calleja, X.A.G. Morán, Heterotrophic bacteria respond differently to increasing temperature and dissolved organic carbon sources in two tropical coastal systems, J. Geophys. Res. Biogeosciences. 127 (2022) e2022JG006890, https://doi.org/10.1029/2022JG006890.
[52] M. Saebelfeld, L. Minguez, J. Griebel, M.O. Gessner, J. Wolinska, Humic dissolved organic carbon drives oxidative stress and severe fitness impairments in Daphnia, Aquat. Toxicol. 182 (2017) 31–38, https://doi.org/10.1016/J.AQUATOX.2016.11.006.
[53] R.E. Reitsema, P. Meire, J. Schoelynck, The future of freshwater macrophytes in a changing world: Dissolved organic carbon quantity and quality and its interactions with macrophytes, Front. Plant Sci. 9 (2018), https://doi.org/10.3389/FPLS.2018.00629.
[54] A. Al-Amin, R.J. Ryan, E.R. McKenzie, Effects of dissolved organic carbon on potentially toxic element desorption in stormwater bioretention systems, Sci. Total

Environ. 912 (2024) 168651, https://doi.org/10.1016/J.SCITOTENV.2023.168651.
[55] M. Wu, B. Pan, D. Zhang, D. Xiao, H. Li, C. Wang, P. Ning, The sorption of organic contaminants on biochars derived from sediments with high organic carbon content, Chemosphere 90 (2013) 782–788, https://doi.org/10.1016/J.CHEMOSPHERE.2012.09.075.
[56] Y.A. Yousif Abdellah, Z.J. Shi, Y.Sen Luo, W.T. Hou, X. Yang, R.L. Wang, Effects of different additives and aerobic composting factors on heavy metal bioavailability reduction and compost parameters: A meta-analysis, Environ. Pollut. 307 (2022) 119549, https://doi.org/10.1016/J.ENVPOL.2022.119549.
[57] K. Doe, P. Jackman, R. Scroggins, D. McLeay, G. Wohlgeschaffen, Solid-phase test for sediment toxicity using the luminescent bacterium, Vibrio Fischeri, SmallScale Freshw. Toxic. Investig. 1 (2005) 107–136, https://doi.org/10.1007/1-4020-3120-3_3.
[58] Y. Li, M. Kumar Awasthi, R. Sindhu, P. Binod, Z. Zhang, M.J. Taherzadeh, Biochar preparation and evaluation of its effect in composting mechanism: A review, Bioresour. Technol. 384 (2023) 129329, https://doi.org/10.1016/J.BIORTECH.2023.129329.
[59] H. Yan, C. Liu, W. Yu, X. Zhu, B. Chen, The aggregate distribution of Pseudomonas aeruginosa on biochar facilitates quorum sensing and biofilm formation, Sci. Total Environ. 856 (2023) 159034, https://doi.org/10.1016/J.SCITOTENV.2022.159034.
[60] M.M. Mian, W. Ao, S. Deng, Sludge-based biochar adsorbent: pore tuning mechanisms, challenges, and role in carbon sequestration, Biochar 5 (2023) 1–23, https://doi.org/10.1007/S42773-023-00288-W.
[61] M. Fan, C. Li, Y. Shao, S. Zhang, M. Gholizadeh, X. Hu, Pyrolysis of cellulose: Correlation of hydrophilicity with evolution of functionality of biochar, Sci. Total Environ. 825 (2022) 153959, https://doi.org/10.1016/J.SCITOTENV.2022.153959.
[62] X. Jia, B. Zhang, Y. Han, J. Guan, H. Gao, P. Guo, Role of reactive oxygen species (ROS) on biochar enhanced chromium phytoremediation in the soil–plant system: Exploration on detoxification mechanism, Environ. Int. 199 (2025) 109471, https://doi.org/10.1016/J.ENVINT.2025.109471.
[63] M. Abbas, M. Adil, S. Ehtisham-ul-Haque, B. Munir, M. Yameen, A. Ghaffar, G. A. Shar, M. Asif Tahir, M. Iqbal, Vibrio fischeri bioluminescence inhibition assay for ecotoxicity assessment: A review, Sci. Total Environ. 626 (2018) 1295–1309, https://doi.org/10.1016/J.SCITOTENV.2018.01.066.
[64] L.H. Mortensen, C. Cruz-Paredes, J. Qin, R. Rønn, M. Vestergård, Effect of ash application on the decomposer food web and N mineralization in a Norway spruce plantation, Sci. Total Environ. 715 (2020) 136793, https://doi.org/10.1016/J.SCITOTENV.2020.136793.
[65] Y. Sun, X. Xiong, M. He, Z. Xu, D. Hou, W. Zhang, Y.S. Ok, J. Rinklebe, L. Wang, D. C.W. Tsang, Roles of biochar-derived dissolved organic matter in soil amendment and environmental remediation: A critical review, Chem. Eng. J. 424 (2021) 130387, https://doi.org/10.1016/J.CEJ.2021.130387.
[66] J. Hu, J. Chen, W. Wang, L. Zhu, Mechanism of growth inhibition mediated by disorder of chlorophyll metabolism in rice (Oryza sativa) under the stress of three polycyclic aromatic hydrocarbons, Chemosphere 329 (2023) 138554, https://doi.org/10.1016/J.CHEMOSPHERE.2023.138554.
[67] M.S. Kiremit, H.M. Osman, H. Arslan, Response of yield, growth traits, and leaf nutrients of garden cress to deficit saline irrigation waters, J. Plant Nutr. 46 (2023) 1050–1065, https://doi.org/10.1080/01904167.2022.2072333.
[68] Y. Hu, R. He, X. Mu, Y. Zhou, X. Li, H. Wang, W. Xing, D. Liu, Cadmium toxicity in plants: from transport to tolerance mechanisms, Plant Signal. Behav. 20 (2025) 2544316, https://doi.org/10.1080/15592324.2025.2544316.
[69] S. Bolan, D. Hou, L. Wang, L. Hale, D. Egamberdieva, P. Tammeorg, R. Li, B. Wang, J. Xu, T. Wang, H. Sun, L.P. Padhye, H. Wang, K.H.M. Siddique, J. Rinklebe, M. B. Kirkham, N. Bolan, The potential of biochar as a microbial carrier for agricultural and environmental applications, Sci. Total Environ. 886 (2023) 163968, https://doi.org/10.1016/J.SCITOTENV.2023.163968.
[70] C. Fan, Y. Cui, Q. Zhang, N. Yin, X. Cai, X. Yuan, S. Senadheera, Y. Cho, Y.S. Ok, A critical review of the interactions between rhizosphere and biochar during the remediation of metal(loid) contaminated soils 5 (2023), https://doi.org/10.1007/S42773-023-00278-Y.
[71] S.B. Baloch, S. Ali, J. Bernas, J. Moudrý, P. Konvalina, Z. Mushtaq, Y. T. Murindangabo, E.F. Onyebuchi, F.B. Baloch, M. Ahmad, Q. Saeed, A. Mustafa, Wood ash application for crop production, amelioration of soil acidity and contaminated environments, Chemosphere 357 (2024) 141865, https://doi.org/10.1016/J.CHEMOSPHERE.2024.141865.
[72] Q. Xiang, D. Zhu, Q.L. Chen, M. Delgado-Baquerizo, J.Q. Su, M. Qiao, X.R. Yang, Y. G. Zhu, Effects of diet on gut microbiota of soil collembolans, Sci. Total Environ. 676 (2019) 197–205, https://doi.org/10.1016/J.SCITOTENV.2019.04.104.
[73] Z. Chen, A. Kumar, Y. Fu, B.P. Singh, T. Ge, H. Tu, Y. Luo, J. Xu, Biochar decreased rhizodeposits stabilization via opposite effects on bacteria and fungi: diminished fungi-promoted aggregation and enhanced bacterial mineralization, Biol. Fertil. Soils 2021 574. 57 (2021) 533–546, https://doi.org/10.1007/S00374-020-01539-9.
[74] L. Comensoli, S. Bindschedler, P. Junier, E. Joseph, Iron and fungal physiology: A review of biotechnological opportunities, Adv. Appl. Microbiol. 98 (2017) 31–60, https://doi.org/10.1016/BS.AAMBS.2016.11.001.
[75] S. Das, R. VishnuRadhan, Effect of trace metals on aquatic invertebrates: Dynamics and repercussions. in: Handb. Environ. Chem., Springer, Berlin, 2024, pp. 1–40, https://doi.org/10.1007/698_2024_1185.
[76] J.L. Johansen, M.L. Nielsen, M. Vestergård, L.H. Mortensen, C. Cruz-Paredes, R. Rønn, R. Kjøller, M. Hovmand, S. Christensen, F. Ekelund, The complexity of wood ash fertilization disentangled: effects on soil pH, nutrient status, plant growth and cadmium accumulation, Environ. Exp. Bot. 185 (2021) 104424, https://doi.org/10.1016/J.ENVEXPBOT.2021.104424.
[77] S. Xie, H.T. Tran, M. Pu, T. Zhang, Transformation characteristics of organic matter and phosphorus in composting processes of agricultural organic waste: research trends, Mater. Sci. Energy Technol. 6 (2023) 331–342, https://doi.org/10.1016/J.MSET.2023.02.006.
[78] M. Hrčka, T. Hřebečková, A. Hanč, A. Grasserová, T. Cajthaml, Changes in the content of emerging pollutants and potentially hazardous substances during vermi/composting of a mixture of sewage sludge and moulded pulp, Environ. Pollut. 348 (2024) 123736, https://doi.org/10.1016/J.ENVPOL.2024.123736.
[79] H. Lü, X.H. Chen, C.H. Mo, Y.H. Huang, M.Y. He, Y.W. Li, N.X. Feng, A. Katsoyiannis, Q.Y. Cai, Occurrence and dissipation mechanism of organic pollutants during the composting of sewage sludge: a critical review, Bioresour. Technol. 328 (2021) 124847, https://doi.org/10.1016/J.BIORTECH.2021.124847.
[80] M. Vráblová, K. Smutná, K. Chamrádová, D. Vrábl, I. Koutník, J. Rusín, M. Bouchalová, A. Gavlová, H. Sezimová, M. Navrátil, R. Chalupa, B. Tenklová, J. Pavlíková, Co-composting of sewage sludge as an effective technology for the production of substrates with reduced content of pharmaceutical residues, Sci. Total Environ. 915 (2024) 169818, https://doi.org/10.1016/J.SCITOTENV.2023.169818.
[81] D.N. Cardoso, M. Oliveira, A.M.V.M. Soares, S. Loureiro, Susceptibility of Folsomia candida to agrochemicals after multigenerational exposure to human pharmaceuticals, Environ. Toxicol. Chem. 41 (2022) 592–600, https://doi.org/10.1002/ETC.5013.
[82] S. Fernandes, K. Buskermolen, D. Ilyaskina, R. Bakker, C.A.M. van Gestel, Effects of life stage on the sensitivity of Folsomia candida to four pesticides, Environ. Toxicol. Chem. 42 (2023) 1782–1790, https://doi.org/10.1002/ETC.5682.
[83] A. Gainer, O.J. Owojori, M. Maboeta, Use of soil invertebrate avoidance tests as an emerging tool in soil ecotoxicology, Rev. Environ. Contam. Toxicol. 260 (2022) 1–18, https://doi.org/10.1007/S44169-021-00004-4.
[84] H. Jeong, E. Byeon, D.H. Kim, P. Maszczyk, J.S. Lee, Heavy metals and metalloid in aquatic invertebrates: a review of single/mixed forms, combination with other pollutants, and environmental factors, Mar. Pollut. Bull. 191 (2023) 114959, https://doi.org/10.1016/J.MARPOLBUL.2023.114959.
[85] M. Renaud, S. Chelinho, P. Alvarenga, C. Mourinha, P. Palma, J.P. Sousa, T. Natal-da-Luz, Organic wastes as soil amendments – Effects assessment towards soil invertebrates, J. Hazard. Mater. 330 (2017) 149–156, https://doi.org/10.1016/J.JHAZMAT.2017.01.052.

Supplementary information

Stage-dependent effects of willow- and sewage sludge-derived biochar on compost ecotoxicity across multiple trophic levels

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1. Materials and methods

1.1. Pyrolysis

To obtain biochars, slow pyrolysis was used in a horizontal tubular retort furnace PRS 168 × 380/90G (Czylok, Poland). The initial furnace heating was 10 °C/min, and the final pyrolysis temperature was maintained for 3 hours. An oxygen-free atmosphere was ensured by a continuous nitrogen flow (3 L/min). Pyrolysis conditions were optimized in previous studies (Siatecka et al., 2021). The four biochars used in the experiments were prepared from two feedstocks: willow and sewage sludge, at two pyrolysis temperatures: 500 °C and 700 °C. The sewage sludge was obtained from the Municipal Sewage Treatment Plant in Zamość (50°44'9.39" N, 23°14'14.92" E). The sewage sludge was obtained by anaerobic fermentation and initially mechanically dewatered on a belt press. Before pyrolysis, the sewage sludge was air-dried and ground, and the willow stems were ground in a laboratory knife mill (TESTCHEM, Radlin).

1.2. Physico-chemical characterization of samples

Dissolved organic carbon (DOC), electrical conductivity (EC), and pH were determined in water solutions according to the methods previously described in (Rombel et al., 2024). The pH and EC values were assessed using a HQ430D universal laboratory multi-parameter meter (HACH, Loveland, Colorado, USA). The total organic carbon (TOC) and DOC were investigated using TOC-L Analyzer equipped with SSM5000 furnace (Shimadzu, Kyoto, Japan). The ash content was analyzed after the 6 h residence of the material in the furnace (Magma Therm, Istanbul, Turkey) at 760 °C. To determine the moisture content, representative sample of the material was dried in a laboratory dryer (POL-EKO, Wodzisław Śląski, Poland) at 105 °C for 6 h until a constant mass. The porous structure of BCs was analyzed using low-

temperature (-195.8 °C) nitrogen adsorption-desorption isotherms (ASAP 2420 V2.09, Micromeritics, USA). The specific surface area (S_{BET}), total pore volume (V_p), and average pore width (d_{BET}), were analyzed based on the nitrogen desorption data (Michot and Villiéras, 2013). The composition of elements (C, H, N) was examined using an elemental analyzer (CHN Analyzer EuroEA3000, EuroVector, Italy). The results from three measurements were reported. The total content of O was calculated by the subtracting the sum of C, H, N and ash content from 100%. The total (C_{tot}) and freely dissolved (C_{free}) concentration of PAHs were determined following the protocols outlined in (Rombel et al., 2024). The analyses of PAHs were conducted using a Trace 1300 gas chromatograph (ThermoFisher Scientific, Waltham, Massachusetts, USA) equipped with an Rxi-5 ms column (length 30 m, id 0.25 mm, and 0.25 µm film thickness, Restek, Glastron, France).

1.3. Determination of metals and ions concentration

Determination of the pseudo-total content of metals was carried after digestion of 500 mg of BC using a mixture of nitric acid (65% pure p.a., POCH, Poland) and hydrochloric acid (35 – 38%, pure p.a., POCH, Poland) (3:1, v/v) for 1.5 hours at 200 °C in a microwave oven (Start D, Microwave Digestion System, Milestone, ETHOS EASY, Italy).

The bioavailability of potentially toxic elements (Cr, Cu, Mn, Ni, Zn, Co, Cd, Pb, As, Fe) in compost materials at different stages was assessed using an aqueous extraction procedure (the same as for pH, DOC, and EC determination, please see section 1.2). Following extraction, the supernatant was carefully decanted, after which the samples were centrifugated at 5000 rpm for 15 minutes. The obtained extracts were subsequently filtered through a 0.45 µm membrane filters (Lab Unlimited, Dublin, Ireland) to eliminate fine particles. Then for bioavailability determination, each extract was acidified with 1 mL of 65% HNO_3 and diluted with ultrapure water to a final volume of 12 mL.

The content of metals (both pseudo-total and water-extractable) was determined using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (iCAP 7400 Duo Thermo Scientific, USA). Argon (99.9999%, AirLiquide, Poland) was used for the plasma generation and sample nebulization at flow rates of 12 L/min and 0.5 L/min, respectively. The quantification of metals was performed based on the six-point calibration curve prepared for all metals in the range from 0.01 to 5 mg/L prepared by diluting a multi-element standard solution (1 g/L, Merck, Germany) with ultrapure water acidified with 65% HNO_3 (0.5 mL HNO_3 per 50 mL of solution).

2. Figures and Tables

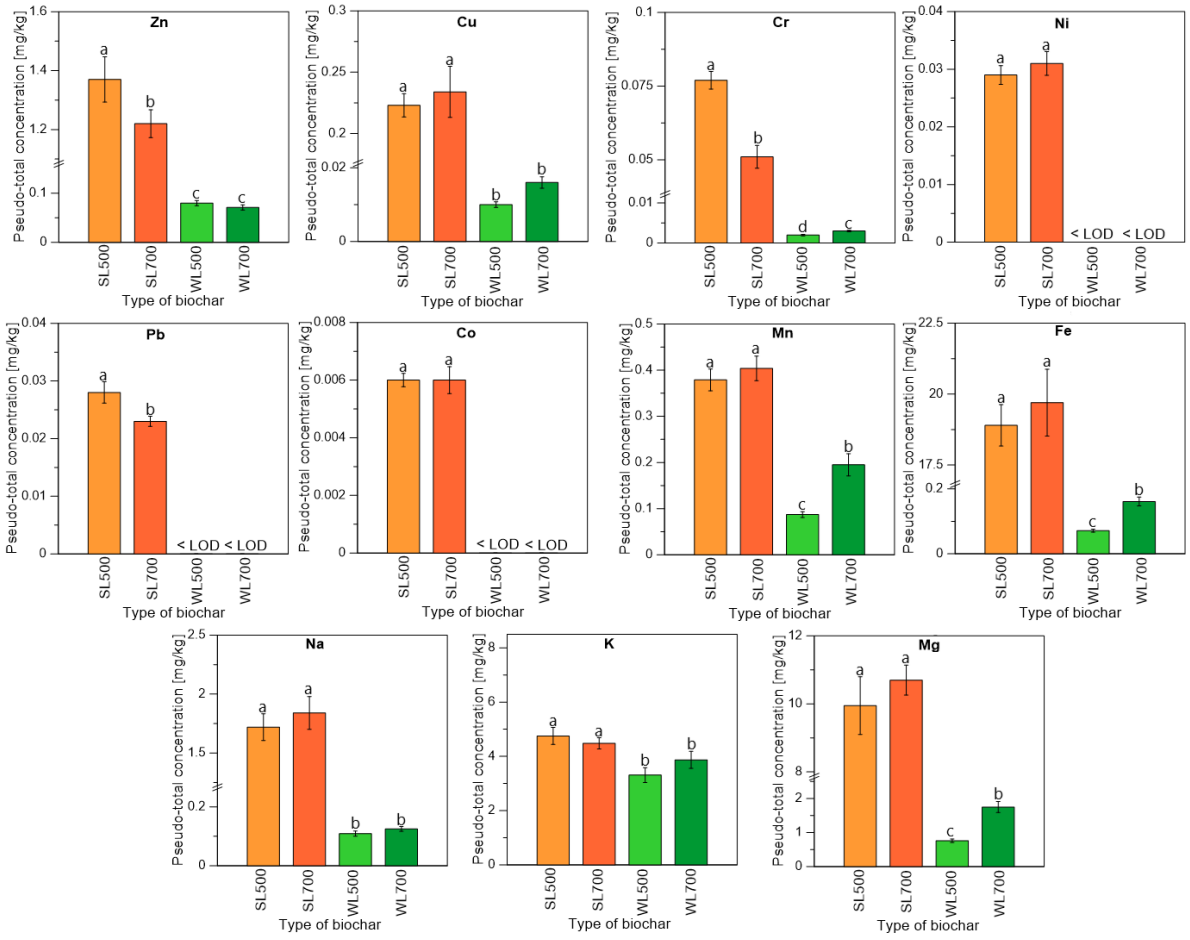
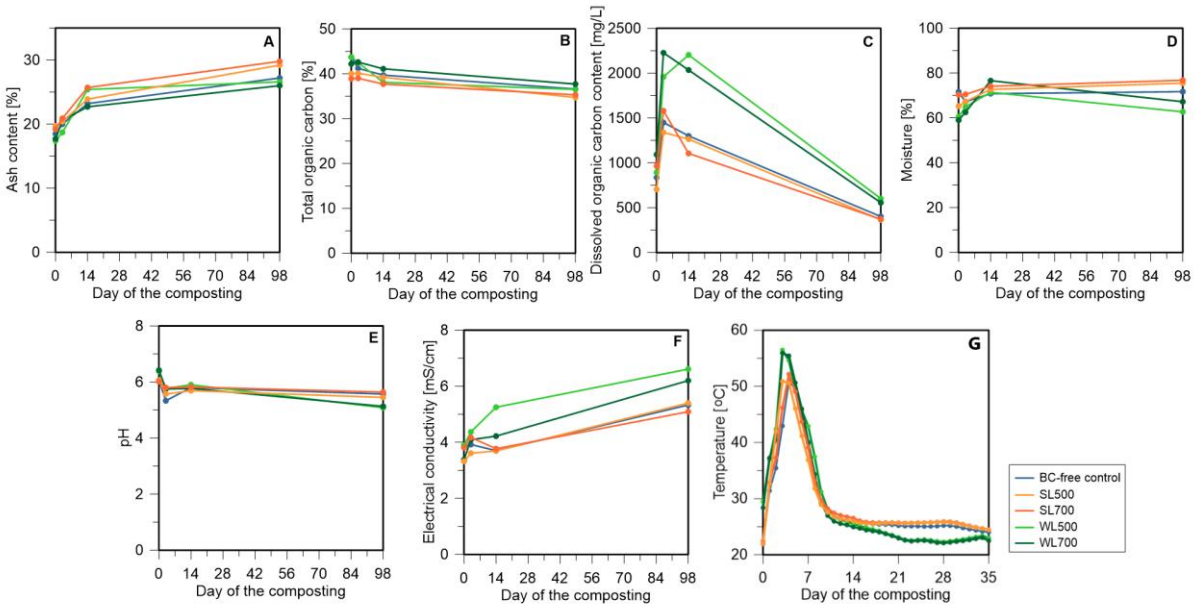


Fig. S1. Pseudo-total concentration [mg/kg] of metals present in biochars under study. Error bars mean standard deviation error (in triplicate) and different letters on bars indicate a significant difference between biochars ($p \leq 0.05$) according to the HSD Tukey test for $\alpha = 0.05$. Where: SL – sewage sludge, WL – willow, 500, 700 – pyrolysis temperature [°C], LOD – limit of detection.



81

82 **Fig. S2**. Changes in physico-chemical properties of the composted material during composting:
83 A – ash (mineral) content, B – total organic carbon, C – dissolved organic carbon content, D –
84 moisture, E – pH, F – electrical conductivity; and G – temperature changes profile during
85 composting in bioreactors. Where: SL – sewage sludge, WL – willow, and 500, 700 – pyrolysis
86 temperature [°C].

87

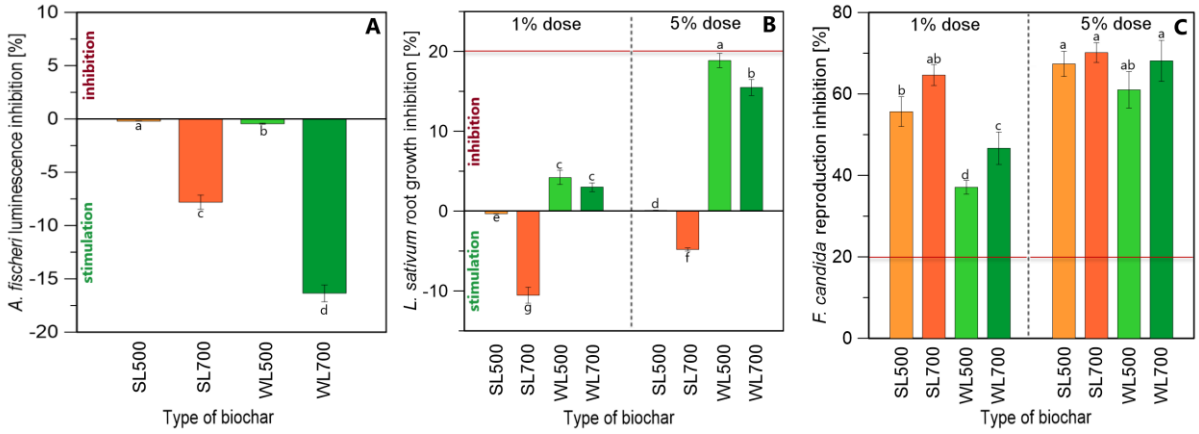


Fig. S3. *Aliivibrio fischeri* luminescence inhibition (%) after 15 minutes of exposure (A), *Lepidium sativum* root growth inhibition for a 1% and 5% dose (%) (B), and *Folsomia candida* reproduction inhibition for a 1% and 5% dose (%) (C) of biochars under the study. The 20% level marked with a dashed line represents the maximum level for non-toxic material. Error bars mean standard deviation error (in triplicate) and different letters on bars indicate a significant difference between biochars ($p \leq 0.05$) according to the HSD Tukey test for $\alpha = 0.05$. Where: SL – sewage sludge, WL – willow, and 500, 700 – pyrolysis temperature [°C].

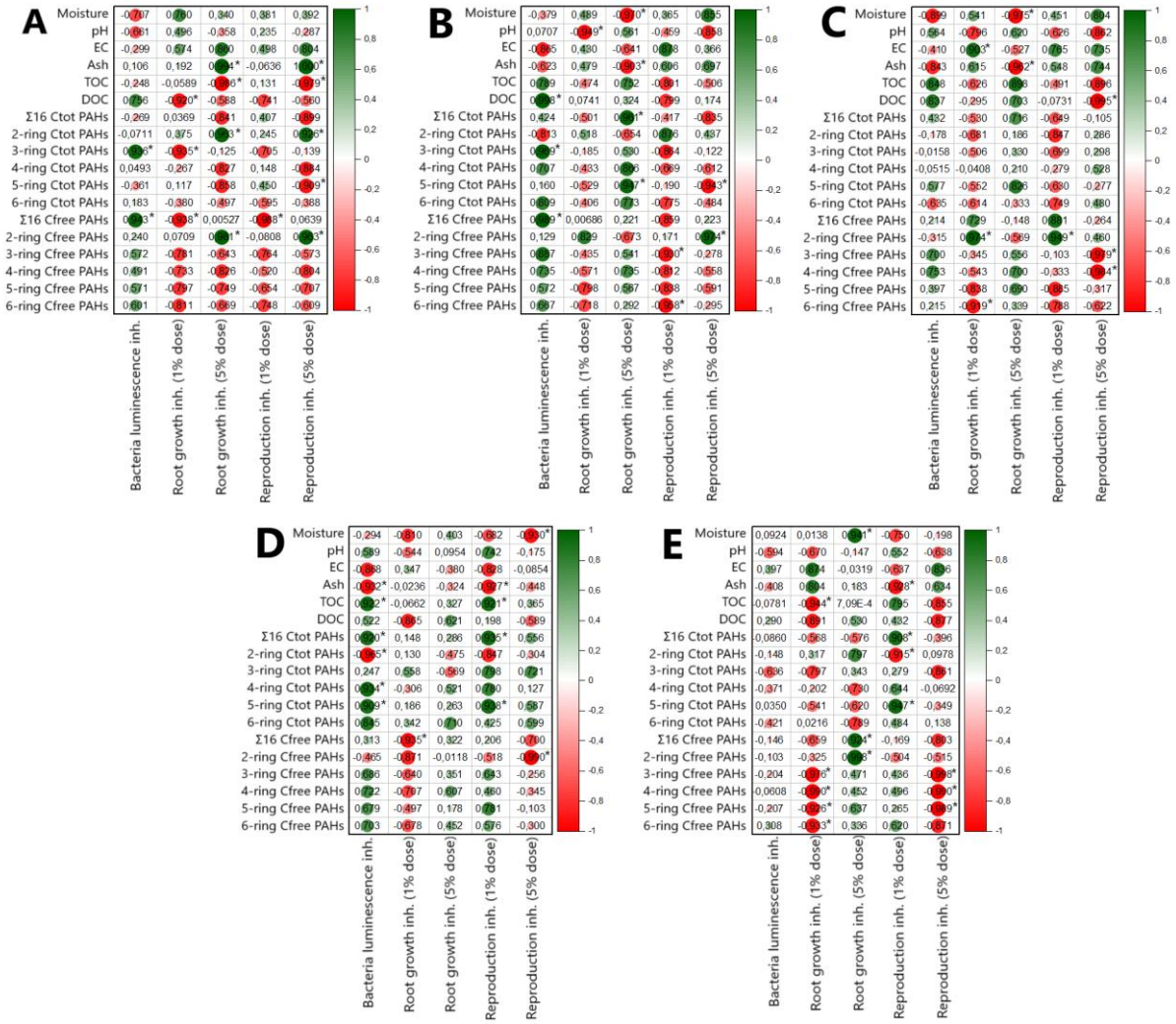


Fig. S4. Correlation plots demonstrating the values of Pearson correlation factors between physico-chemical characteristics of composted materials and bioassays endpoints for variants of the experiment with different additives: BC-free control (A), SL500 (B), SL700 (C), WL500 (D), and WL700 (E). Where: SL – sewage sludge, WL – willow, 500, 700 – pyrolysis temperature [°C], moisture [%], EC – electrical conductivity [mS/cm], ash – mineral fraction content [%], TOC – total organic carbon [%], DOC – dissolved organic carbon [mg/L], Σ16 C_{tot} PAHs – solvent extractable content of 16 PAHs [µg/kg] in composts, Σ16 C_{free} PAHs – freely dissolved content of 16 PAHs [ng/L] in composts, inh. – inhibition, * indicates statistically significant correlation ($p \leq 0.1$).

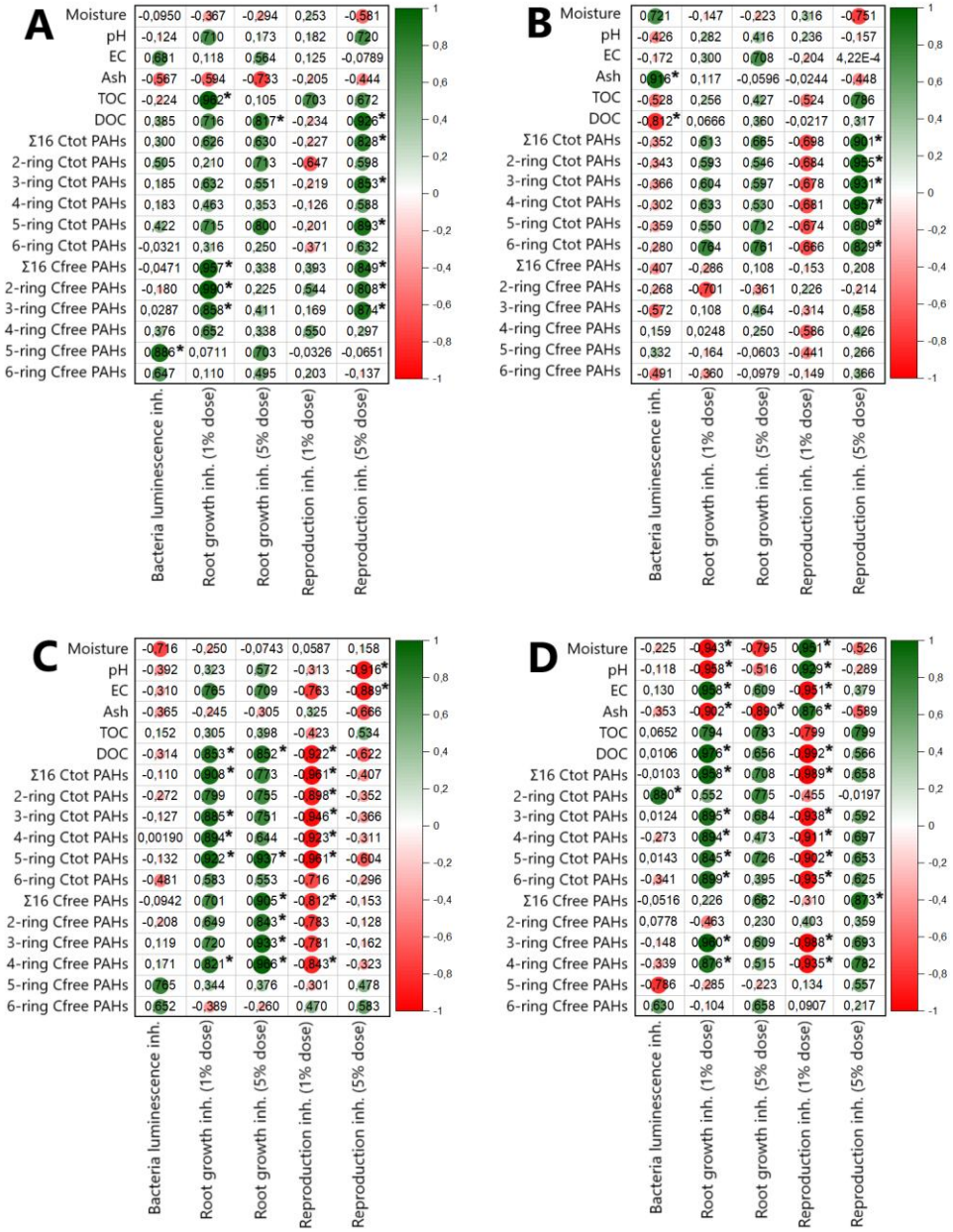


Fig. S5. Correlation plots demonstrating the values of Pearson correlation factors between physico-chemical characteristics of composted materials and bioassays endpoints in the different sampling terms: 0 day (A), 3 day (B), 14 day (C), and 98 day (D). Where: moisture [%], EC – electrical conductivity [mS/cm], ash – mineral fraction content [%], TOC – total organic carbon [%], DOC – dissolved organic carbon [mg/L], Σ16 C_{tot} PAHs – solvent extractable content of 16 PAHs [µg/kg] in composts, Σ16 C_{free} PAHs – freely dissolved content of 16 PAHs [ng/L] in composts, inh. – inhibition, * indicates statistically significant correlation ($p \leq 0.1$).

Table S1. Characteristics of biochars employed in the composting (EC – electrical conductivity [mS/cm], TOC – total organic carbon content [%], DOC – dissolved organic carbon [mg/L], ash – mineral fraction content [%], H/C and O/C and (O+N)/C – molar ratios, S_{BET} – specific surface area [m^2/g], d_{BET} – pore diameter [nm], V_p – total volume of pores [cm^3/g]. All values are the average of three measurements.

Property / **Biochar**	**Physico-chemical**								**Surface**		
	EC	**pH**	**TOC**	**DOC**	**Ash**	**H/C**	**O/C**	**(O+N)/C**	**S_{BET}**	**d_{BET}**	**V_p**
SL500	0.73	10.6	21.0	2.43	72.3	0.433	0.14	0.240	41.6	5.27	0.05
SL700	4.48	11.9	19.9	0.85	77.3	0.209	0.01	0.066	71.4	4.69	0.08
WL500	0.73	9.93	81.8	8.97	6.19	0.476	0.05	0.064	236.2	1.85	0.11
WL700	2.53	12.2	85.0	5.88	6.97	0.222	0.04	0.055	275.0	1.18	0.12

Table S2. Contaminants content in biochars used in the composting process (presented with standard deviation)

Biochar	Zn	Cu	Cr	Ni	Pb	Co	Mn	Fe	Na	K	Mg	Σ16 C_{tot} PAHs	Σ16 C_{free} PAHs
	pseudo-total concentration [mg/kg]											µg/kg	ng/L
SL500	1.37 ± 0.077	0.22 ± 0.0095	0.077 ± 0.0030	0.029 ± 0.0016	0.028 ± 0.0018	0.0060 ± 2.3E-4	0.38 ± 0.024	18.9 ± 0.73	1.72 ± 0.11	4.75 ± 0.31	9.95 ± 0.85	594 ± 31.2	138 ± 7.21
SL700	1.22 ± 0.047	0.23 ± 0.021	0.051 ± 0.0039	0.031 ± 0.0020	0.023 ± 8.9E-4	0.0057 ± 4.7E-4	0.40 ± 0.027	19.7 ± 1.18	1.84 ± 0.14	4.48 ± 0.21	10.7 ± 0.44	503 ± 22.3	155 ± 9.58
WL500	0.080 ± 0.0053	0.010 ± 0.00078	0.0025 ± 1.9E-4	nd	nd	nd	0.087 ± 0.0065	0.071 ± 0.0047	0.11 ± 0.0085	3.31 ± 0.27	0.76 ± 0.050	1098 ± 80.1	135 ± 4.98
WL700	0.071 ± 0.0054	0.016 ± 0.0015	0.0032 ± 1.7E-4	nd	nd	nd	0.20 ± 0.024	0.16 ± 0.014	0.13 ± 0.0082	3.87 ± 0.31	1.75 ± 0.16	685 ± 42.1	143 ± 5.16

Table S3. Temperature profiles of the composting material and gas concentrations in the exhaust mixture during composting. All values are the average of three measurements (nd – not detected).

Day of the composting	Average temperature [°C]	Aeration [L/h]	O_2 [%]	NO [ppm]	CH_4 [ppm]	CO_2 [%]	CO [ppm]
BC-free control							
0	21.9	60	14.6	7	nd	5.80	2
3	43.0	120	13.9	1	160	7.32	3
7	39.9	90	15.3	1	nd	6.25	7
14	25.9	30	19.1	nd	310	1.80	nd
21	25.2	30	19.3	nd	nd	1.10	nd
28	25.2	30	19.4	nd	20	1.09	nd
35	24.0	30	19.2	nd	200	1.15	nd
SL500							
0	22.4	60	15.0	4	nd	5.34	2
3	46.2	120	12.4	2	290	8.76	8
7	39.1	90	15.3	1	nd	5.50	5
14	26.5	30	19.1	nd	340	1.70	nd
21	25.7	30	19.2	nd	10	1.36	nd
28	25.9	30	19.4	nd	210	1.20	nd
35	24.5	30	19.2	nd	190	1.24	nd
SL700							
0	22.0	60	14.8	6	nd	5.67	2
3	50.9	120	12.0	2	280	9.08	11
7	36.9	90	16.1	1	10	4.70	5
14	26.0	30	18.9	nd	440	1.90	nd
21	25.6	30	18.8	nd	100	1.87	nd
28	25.8	30	19.2	nd	400	1.57	nd
35	24.5	30	19.4	nd	230	1.16	nd

WL500							
0	29.5	60	14.0	4	290	6.30	11
3	56.5	120	4.40	3	160	16.7	19
7	42.9	90	17.3	nd	250	3.44	1
14	25.5	30	19.6	1	210	1.06	nd
21	23.1	30	19.7	2	110	0.87	nd
28	22.3	30	20.2	5	nd	0.59	nd
35	21.8	30	20.0	9	150	0.70	nd
WL700							
0	28.4	60	11.4	8	920	8.83	14
3	55.9	120	2.29	14	nd	19.1	13
7	40.0	90	15.9	nd	20	4.73	1
14	24.9	30	20.0	3	30	0.57	nd
21	23.0	30	19.0	4	150	1.51	nd
28	22.1	30	20.1	5	nd	0.56	nd
35	21.8	30	19.9	12	50	0.66	nd

Table S4. Solvent extractable (C_{tot}) PAHs content [µg/kg] in the material during composting (presented with standard deviation).

Day of the composting	0					3					14					98				
Variant	BC-free	WL500	WL700	SL500	SL700	BC-free	WL500	WL700	SL500	SL700	BC-free	WL500	WL700	SL500	SL700	BC-free	WL500	WL700	SL500	SL700
NAP	49.8 ± 2.76	79.7 ± 6.26	71.4 ± 6.00	65.1 ± 3.21	65.6 ± 2.79	58.4 ± 2.14	79.7 ± 3.39	72.5 ± 5.46	65.7 ± 4.89	42.7 ± 3.65	59.3 ± 5.05	86.2 ± 5.39	94.3 ± 5.86	65.7 ± 2.26	50.9 ± 3.38	94.1 ± 5.22	89.4 ± 3.19	87.4 ± 3.65	83.4 ± 2.50	50.8 ± 3.79
ACY	2.99 ± 0.17	4.85 ± 0.11	5.76 ± 0.49	3.94 ± 0.22	3.75 ± 0.18	3.65 ± 0.15	4.39 ± 0.11	3.94 ± 0.26	3.85 ± 0.16	2.46 ± 0.18	2.97 ± 0.18	3.62 ± 0.17	6.58 ± 0.49	3.25 ± 0.20	2.85 ± 0.24	4.67 ± 0.45	5.05 ± 0.21	4.11 ± 0.14	4.08 ± 0.15	4.54 ± 0.17
ACE	9.24 ± 0.51	17.3 ± 0.95	17.1 ± 0.83	11.9 ± 1.00	13.2 ± 0.73	11.6 ± 0.30	15.7 ± 0.42	14.8 ± 0.34	13.6 ± 1.07	8.85 ± 0.24	12.7 ± 0.54	16.9 ± 1.26	18.5 ± 1.58	14.7 ± 1.25	9.76 ± 0.34	11.7 ± 0.28	22.6 ± 1.77	14.9 ± 0.35	8.53 ± 0.20	11.4 ± 0.51
FLO	19.1 ±1.88	39.6 ± 3.10	37.1 ± 2.91	24.1 ± 1.17	11.3 ± 0.95	24.5 ± 1.10	36.2 ± 2.38	32.7 ± 0.83	25.7 ± 1.16	16.9 ± 0.71	22.7 ± 0.61	34.2 ± 1.99	35.5 ± 1.97	26.7 ± 2.01	17.7 ± 0.97	16.9 ± 0.78	33.3 ± 1.50	25.5 ± 1.42	14.0 ± 0.64	16.9 ± 0.98
PHE	111.3 ± 5.42	214.3 ± 9.84	183.3 ± 9.02	123.5 ± 7.20	122.9 ± 7.68	130.5 ± 10.2	195.0 ± 8.04	173.3 ± 7.15	148.1 ± 6.11	95.8 ± 7.51	119.5 ± 8.99	188.7 ± 10.5	183.2 ± 4.93	141.9 ± 3.82	96.0 ± 5.96	118.4 ± 4.95	194.9 ± 14.7	150.5 ± 5.51	87.6 ± 6.88	100.9 ± 4.63
ANT	12.4 ± 0.97	22.2 ± 0.60	20.7 ± 1.77	13.4 ± 0.31	13.8 ± 0.67	15.0 ± 0.47	19.9 ± 0.97	17.0 ± 0.53	16.0 ± 0.50	10.2 ± 0.67	15.5 ± 1.53	16.3 ± 1.28	18.2 ± 1.06	13.3 ± 0.57	10.0 ± 0.74	9.07 ± 0.41	24.1 ± 1.59	19.3 ± 1.51	10.4 ± 0.89	10.7 ± 0.44
FLA	127.1 ± 4.54	180.1 ± 17.8	179.9 ± 9.88	158.9 ± 9.93	121.8 ± 6.76	137.4 ± 6.31	183.7 ± 4.34	167.8 ± 7.70	157.8 ± 10.4	104.7 ± 2.67	108.7 ± 5.35	156.2 ± 4.86	155.7 ± 15.4	141.7 ± 7.78	94.5 ± 2.19	121.8 ± 4.46	136.2 ± 3.66	152.3 ± 6.87	96.5 ± 4.35	110.9 ± 8.70
PYR	108.6 ± 6.75	163.6 ± 4.17	161.6 ± 10.1	154.0 ± 5.50	112.1 ± 8.44	127.0 ± 8.34	166.6 ± 7.51	144.3 ± 6.14	144.2 ± 3.68	95.1 ± 4.29	99.5 ± 5.80	148.5 ± 8.24	141.1 ± 11.9	127.1 ± 7.94	92.0 ± 9.08	92.7 ± 7.28	125.8 ± 2.97	144.3 ± 10.9	95.2 ± 3.98	108.4 ± 3.25
BaA	35.3 ± 2.21	39.0 ± 1.21	38.7 ± 2.41	30.9 ± 0.83	31.4 ± 1.72	30.4 ± 0.70	22.9 ±1.03	37.1 ± 2.91	36.9 ± 0.87	25.8 ± 0.80	32.5 ± 1.58	37.0 ± 3.15	36.5 ± 1.09	33.7 ± 1.64	25.3 ± 1.58	28.7 ± 2.13	37.0 ± 0.86	39.6 ± 1.01	31.1 ± 2.44	32.2 ± 1.35
CHR	57.8 ± 4.94	71.4 ± 3.48	67.0 ± 2.08	54.0 ± 5.33	54.9 ± 5.42	47.2 ± 2.01	82.0 ± 3.43	65.4 ± 2.95	61.7 ± 2.83	44.2 ± 1.05	57.6 ± 3.16	62.8 ± 2.67	58.5 ± 4.59	52.1 ± 2.90	41.8 ± 2.32	47.9 ± 1.49	53.7 ± 1.37	65.1 ± 2.02	46.4 ± 1.65	51.8 ± 3.40
BbF	35.4 ± 0.95	40.4 ± 2.52	41.4 ± 2.42	30.7 ± 2.31	34.3 ± 0.92	25.2 ± 2.12	48.6 ± 4.09	41.6 ± 1.48	35.4 ± 1.29	27.1 ± 1.58	32.9 ± 1.82	37.9 ± 2.08	34.8 ± 1.70	32.9 ± 0.76	28.2 ± 0.76	30.3 ± 1.25	49.7 ± 2.11	40.7 ± 1.68	23.9 ± 1.57	34.8 ± 1.24

BkF	39.0 ± 1.92	41.7 ± 1.88	41.5 ± 4.10	33.3 ± 2.07	37.5 ± 1.60	23.5 ± 0.55	50.8 ± 1.18	39.7 ± 1.07	38.6 ± 2.14	30.1 ± 1.38	33.7 ± 1.16	38.2 ± 1.15	43.1 ± 3.21	34.7 ± 2.92	18.0 ± 1.00	30.0 ± 2.35	54.1 ± 2.23	42.2 ± 1.94	26.0 ± 1.07	35.2 ± 2.62
BaP	427.7 ± 36.4	652.8 ± 42.9	499.1 ± 27.7	438.6 ± 18.7	442.9 ± 10.3	372.1 ± 15.6	560.4 ± 20.0	467.6 ± 17.1	290.2 ± 22.8	232.5 ± 9.59	100.4 ± 3.58	150.2 ± 5.17	123.9 ± 11.8	79.5 ± 5.27	88.5 ± 7.44	114.3 ± 2.91	159.7 ± 7.78	116.7 ± 7.66	74.2 ± 1.89	83.1 ± 2.12
IcdP	11.0 ± 0.82	25.5 ± 0.60	33.6 ± 1.86	18.0 ± 0.99	17.0 ± 1.45	12.5 ± 0.94	36.4 ± 2.74	25.1 ± 1.05	22.3 ± 1.48	7.64 ± 0.27	19.9 ± 1.24	23.7 ± 1.17	22.4 ± 1.23	20.2 ± 2.00	18.4 ± 1.38	7.50 ± 0.49	23.9 ± 1.10	25.4 ± 0.59	8.90 ± 0.28	14.9 ± 1.17
DahA	1.57 ± 0.15	1.44 ± 0.084	4.44 ± 0.29	1.41 ± 0.048	7.67 ± 0.48	2.90 ± 0.23	3.16 ± 0.20	4.38 ± 0.10	1.71 ± 0.073	3.19 ± 0.12	8.83 ± 0.26	5.74 ± 0.30	7.13 ± 0.30	7.24 ± 0.36	3.49 ± 0.17	0.86 ± 0.064	3.03 ± 0.11	4.37 ± 0.19	3.77 ± 0.28	3.63 ± 0.18
BghiP	24.5 ± 2.09	30.2 ± 1.25	28.8 ± 2.43	26.8 ± 2.29	24.9 ± 0.86	19.6 ± 1.09	35.8 ± 2.81	28.9 ± 2.77	24.1 ± 2.06	20.8 ± 1.63	18.8 ± 1.86	22.3 ± 2.20	27.6 ± 1.72	22.3 ± 1.67	21.8 ± 0.93	22.1 ± 1.45	28.2 ± 1.60	28.6 ± 1.90	20.7 ± 1.21	22.5 ± 0.53

Where: NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene).

Table S5. Freely dissolved (C_{free}) PAHs content [ng/L] in the material during composting (presented with standard deviation).

Day of the composting	0					3					14					98				
Variant	**BC-free**	**WL500**	**WL700**	**SL500**	**SL700**	**BC-free**	**WL500**	**WL700**	**SL500**	**SL700**	**BC-free**	**WL500**	**WL700**	**SL500**	**SL700**	**BC-free**	**WL500**	**WL700**	**SL500**	**SL700**
NAP	52.4 ± 3.30	55.5 ± 3.42	50.4 ± 4.26	40.9 ± 3.50	39.3 ± 1.22	61.2 ± 5.50	54.0 ± 1.97	58.9 ± 2.10	51.6 ± 4.12	56.2 ± 4.18	63.8 ± 2.88	66.3 ± 3.71	81.9 ± 3.51	52.7 ± 3.44	48.9 ± 1.60	75.1 ± 2.52	55.1 ± 2.49	56.6 ± 4.43	53.7 ± 2.68	66.1 ± 4.31
ACY	0.60 ± 0.027	1.73 ± 0.12	1.82 ± 0.081	0.46 ± 0.041	0.60 ± 0.051	0.90 ± 0.076	1.37 ± 0.071	0.56 ± 0.037	0.58 ± 0.013	0.91 ± 0.057	0.41 ± 0.015	0.50 ± 0.021	0.57 ± 0.028	0.46 ± 0.015	0.48 ± 0.040	0.45 ± 0.028	0.63 ± 0.021	0.69 ± 0.049	0.43 ± 0.037	0.57 ± 0.044
ACE	4.21 ± 0.18	6.69 ± 0.35	6.35 ± 0.27	3.63 ± 0.16	3.92 ± 0.10	5.95 ± 0.22	5.64 ± 0.13	6.36 ± 0.50	4.80 ± 0.41	5.37 ± 0.45	7.47 ± 0.74	6.45 ± 0.54	7.37 ± 0.38	5.82 ± 0.50	5.51 ± 0.13	3.06 ± 0.11	5.38 ± 0.27	5.49 ± 0.46	2.46 ± 0.12	3.48 ± 0.16
FLO	7.50 ± 0.64	9.62 ± 0.46	8.65 ± 0.54	6.12 ± 0.28	5.24 ± 0.36	8.56 ± 0.20	8.86 ± 0.75	9.27 ± 0.21	6.71 ± 0.34	7.09 ± 0.18	8.69 ± 0.39	8.19 ± 0.21	9.49 ± 0.43	6.22 ± 0.22	5.73 ± 0.56	2.52 ± 0.078	5.02 ± 0.17	5.01 ± 0.13	2.02 ± 0.073	2.57 ± 0.11
PHE	14.7 ± 0.50	19.9 ± 0.51	17.1 ± 0.73	14.3 ± 1.41	11.4 ± 0.26	15.3 ± 0.78	18.4 ± 0.63	18.9 ± 1.30	13.7 ± 0.46	14.7 ± 0.66	20.0 ± 1.12	19.7 ± 1.24	19.5 ± 0.88	14.8 ± 0.93	13.8 ± 0.95	9.59 ± 0.81	12.7 ± 0.83	13.0 ± 0.40	7.38 ± 0.17	8.50 ± 0.31
ANT	1.76 ± 0.041	1.66 ± 0.085	1.43 ± 0.075	1.37 ± 0.062	1.21 ± 0.10	1.94 ± 0.065	1.82 ± 0.18	1.70 ± 0.061	1.47 ± 0.095	1.70 ± 0.083	1.72 ± 0.085	1.49 ± 0.053	1.67 ± 0.14	1.19 ± 0.069	1.27 ± 0.11	0.29 ± 0.0075	1.02 ± 0.088	1.06 ± 0.090	0.68 ± 0.035	0.71 ± 0.025
FLA	6.60 ± 0.65	7.13 ± 0.24	6.23 ± 0.21	6.65 ± 0.57	5.45 ± 0.54	7.92 ± 0.57	7.33 ± 0.17	6.88 ± 0.58	6.30 ± 0.43	6.28 ± 0.53	6.94 ± 0.59	7.06 ± 0.35	6.94 ± 0.35	5.87 ± 0.14	5.75 ± 0.21	3.53 ± 0.082	4.43 ± 0.40	4.34 ± 0.11	3.10 ± 0.13	3.60 ± 0.16
PYR	5.52 ± 0.29	5.86 ± 0.38	5.25 ± 0.26	5.65 ± 0.24	4.91 ± 0.18	6.53 ± 0.34	6.11 ± 0.52	5.79 ± 0.57	5.33 ± 0.12	5.42 ± 0.28	6.04 ± 0.42	6.03 ± 0.39	5.84 ± 0.20	5.36 ± 0.23	5.06 ± 0.21	3.17 ± 0.17	3.79 ± 0.14	3.95 ± 0.14	3.00 ± 0.21	3.47 ± 0.19
BaA	0.22 ± 0.015	0.20 ± 0.0067	0.18 ± 0.0041	0.23 ± 0.0081	0.16 ± 0.0055	0.28 ± 0.022	0.24 ± 0.0062	0.21 ± 0.015	0.20 ± 0.010	0.20 ± 0.0067	0.23 ± 0.0097	0.22 ± 0.019	0.21 ± 0.014	0.18 ± 0.010	0.18 ± 0.014	0.11 ± 0.0066	0.13 ± 0.0058	0.11 ± 0.0048	0.11 ± 0.0055	0.12 ± 0.0042
CHR	0.43 ± 0.024	0.41 ± 0.022	0.36 ± 0.013	0.44 ± 0.037	0.35 ± 0.016	0.52 ± 0.019	0.44 ± 0.038	0.41 ± 0.021	0.40 ± 0.031	0.38 ± 0.025	0.43 ± 0.036	0.42 ± 0.029	0.42 ± 0.036	0.35 ± 0.015	0.35 ± 0.0080	0.23 ± 0.020	0.26 ± 0.0059	0.25 ± 0.021	0.23 ± 0.019	0.28 ± 0.014

BbF	0.11 ± 0.0038	0.10 ± 0.0047	0.089 ± 0.0032	0.11 ± 0.0028	0.079 ± 0.0029	0.13 ± 0.011	0.11 ± 0.0045	0.10 ± 0.0068	0.094 ± 0.0079	0.099 ± 0.0084	0.12 ± 0.0039	0.11 ± 0.0065	0.10 ± 0.0045	0.11 ± 0.0036	0.096 ± 0.0034	0.069 ± 0.0038	0.061 ± 0.0027	0.064 ± 0.0031	0.065 ± 0.0045	0.070 ± 0.0025
BkF	0.081 ± 0.0053	0.069 ± 0.0016	0.058 ± 0.0049	0.081 ± 0.0056	0.071 ± 0.0016	0.097 ± 0.0023	0.080 ± 0.0055	0.071 ± 0.0040	0.071 ± 0.0037	0.065 ± 0.0028	0.095 ± 0.0080	0.078 ± 0.0039	0.082 ± 0.0074	0.080 ± 0.0036	0.073 ± 0.0031	0.047 ± 0.0020	0.047 ± 0.0017	0.047 ± 0.0040	0.049 ± 0.0022	0.052 ± 0.0012
BaP	0.055 ± 0.0047	0.071 ± 0.0022	0.042 ± 0.0033	0.056 ± 0.0020	0.041 ± 0.0032	0.066 ± 0.0028	0.054 ± 0.0019	0.052 ± 0.0023	0.048 ± 0.0043	0.047 ± 0.0026	0.058 ± 0.0015	0.048 ± 0.0022	0.053 ± 0.0034	0.047 ± 0.0017	0.045 ± 0.0026	0.027 ± 0.0012	0.031 ± 0.0010	0.033 ± 0.0017	0.035 ± 0.0030	0.049 ± 0.0041
IcdP	0.020 ± 0.0017	0.022 ± 0.0018	0.015 ± 6.2E-4	0.017 ± 0.0017	0.022 ± 0.0011	0.022 ± 0.0013	0.019 ± 0.0015	0.015 ± 7.3E-4	0.015 ± 0.0013	0.021 ± 7.4E-4	0.026 ± 0.0012	0.018 ± 8.2E-4	0.019 ±6.9E-4	0.024 ± 0.0011	0.021 ± 0.0015	0.015 ± 0.0010	0.012 ± 0.0010	0.0090 ± 3.9E-4	0.0086 ± 3.9E-4	0.014 ± 8.5E-4
DahA	0.017 ± 7.9E-4	0.054 ± 0.0014	0.026 ± 0.0015	0.032 ± 0.0020	0.075 ± 0.0032	0.015 ± 0.0013	0.0035 ± 1.6E-4	0.0066 ± 5.5E-4	0.011 ± 2.9E-4	0.0015 ± 1.2E-4	0.024 ± 0.0010	0.0033 ± 2.8E-4	0.017 ± 0.0011	0.020 ± 9.2E-4	3.7E-4 ± 1.9E-5	0.024 ± 0.0018	0.029 ± 7.3E-4	0.019 ± 9.2E-4	6.4E-4 ± 6.3E-5	0.022 ± 0.0015
BghiP	0.021 ± 0.0010	0.020 ± 0.0013	0.017 ± 8.3E-4	0.022 ± 0.0011	0.016 ± 0.0015	0.024 ± 0.0011	0.020 ± 0.0010	0.033 ± 8.3E-4	0.017 ± 0.0014	0.018 ± 0.0012	0.024 ± 8.2E-4	0.020 ± 0.0010	0.020 ± 0.0017	0.020 ± 8.7E-4	0.018 ± 8.1E-4	0.011 ± 6.0E-4	0.011 ± 6.9E-4	0.011 ± 4.8E-4	0.012 ± 5.8E-4	0.012 ± 5.6E-4

Where: NAP - naphthalene, ACY - acenaphthylene, ACE - acenaphthene, FLO - fluorene, PHE - phenanthrene, ANT - anthracene, FLA - fluoranthene, PYR - pyrene, BaA - benz(a)anthracene, CHR - chrysene, BaF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, BaP - benzo(a)pyrene, IcdP - indeno(1,2,3-cd)pyrene, DahA - dibenz(a,h)anthracene, BghiP - benzo(ghi)-perylene).

Table S6. Concentrations of selected metals in the water-soluble fraction [mg/L] in the materials during the composting (presented with standard deviation). Where: nd – not detectable.

Day of the composting	Cr	Cu	Mn	Ni	Zn	Co	Cd	Pb	As	Fe
BC-free control										
0	0.024 ± 0.00026	0.34 ± 0.00015	1.19 ± 0.00052	0.17 ± 0.0011	1.52 ± 0.0083	0.019 ± 3.3E-5	0.0024 ± 1.3E-5	0.013 ± 0.0011	0.051 ± 0.00023	10.6 ± 0.037
3	0.013 ± 9.5E-5	0.29 ± 0.00059	1.76 ± 0.0062	0.11 ± 0.00015	1.27 ± 0.00067	0.019 ± 2.3E-5	0.0029 ± 1.6E-6	0.0087 ± 0.00063	0.056 ± 0.0014	7.29 ± 0.049
14	0.019 ± 0.00022	0.47 ± 0.0018	0.84 ± 0.0023	0.13 ± 6.5E-5	1.59 ± 0.0053	0.023 ± 0.00030	0.0031 ± 4.3E-5	0.012 ± 0.00057	0.074 ± 0.0012	10.2 ± 0.062
98	nd	0.12 ± 0.0078	1.90 ± 0.0073	0.048 ± 0.00020	0.68 ± 0.00095	0.012 ± 2.8E-5	0.0021 ± 7.8E-5	0.0026 ± 0.00049	0.048 ± 0.00043	1.17 ± 0.012
SL500										
0	0.026 ± 0.00011	0.33 ± 5.8E-5	1.17 ± 0.0022	0.16 ± 0.00034	1.38 ± 0.0016	0.019 ± 0.00011	0.0024 ± 6.6E-5	0.012 ± 0.00023	0.063 ± 0.00022	9.30 ± 0.123
3	0.019 ± 0.00021	0.35 ± 0.0017	1.70 ± 0.0014	0.12 ± 0.00026	1.48 ± 0.0015	0.020 ± 6.8E-5	0.0028 ± 2.4E-5	0.011 ± 0.00011	0.073 ± 0.00068	8.43 ± 0.023
14	0.016 ± 0.00079	0.39 ± 0.0016	1.31 ± 0.00027	0.11 ± 5.1E-5	1.12 ± 0.0042	0.019 ± 7.2E-5	0.0025 ± 0.00010	0.0104 ± 0.00063	0.068 ± 0.00034	7.76 ± 0.0074
98	nd	0.15 ± 0.00095	2.37 ± 0.013	0.056 ± 5.3E-5	0.92 ± 4.5E-6	0.014 ± 0.00033	0.0028 ± 1.1E-5	0.0042 ± 0.00033	0.064 ± 0.0013	1.46 ± 0.025
SL700										
0	0.023 ± 3.3E-5	0.36 ± 0.0013	1.47 ± 0.0034	0.18 ± 0.00033	1.40 ± 0.0020	0.020 ± 4.8E-5	0.0024 ± 4.3E-5	0.013 ± 0.00011	0.062 ± 0.00040	8.68 ± 0.032
3	0.025 ± 7.3E-5	0.49 ± 0.00018	1.55 ± 0.00036	0.14 ± 5.4E-5	1.48 ± 0.00073	0.024 ± 2.3E-5	0.0028 ± 3.8E-5	0.015 ± 0.00033	0.069 ± 0.0012	10.8 ± 0.185
14	0.0075 ± 0.00013	0.33 ± 0.0011	1.28 ± 0.0013	0.11 ± 9.5E-5	0.80 ± 0.0016	0.021 ± 0.00029	0.0024 ± 4.1E-6	0.0088 ± 0.00049	0.068 ± 0.0018	5.21 ± 0.022
98	nd	0.15 ± 0.00027	2.09 ± 0.0068	0.059 ± 0.00026	0.81 ± 0.0024	0.013 ± 4.2E-5	0.0027 ± 0.00013	0.0050 ± 0.00028	0.065 ± 0.00071	1.43 ± 0.017
WL500										
0	0.054 ± 0.00046	0.38 ± 0.0037	1.01 ± 0.0019	0.21 ± 0.0014	2.02 ± 0.018	0.026 ± 3.0E-5	0.0032 ± 0.00013	0.027 ± 0.00084	0.066 ± 0.00035	20.4 ± 0.056
3	0.050 ± 0.00018	0.59 ± 0.0061	0.77 ± 0.0042	0.19 ± 0.0012	2.26 ± 0.014	0.031 ± 9.1E-5	0.0032 ± 3.4E-5	0.025 ± 0.00032	0.073 ± 0.00046	17.2 ± 0.415
14	0.020 ± 0.00048	0.47 ± 0.0035	1.19 ± 0.0085	0.12 ± 7.9E-5	1.45 ± 0.00037	0.022 ± 0.00018	0.0027 ± 0.00013	0.012 ± 0.00019	0.071 ± 0.00032	9.92 ± 0.056
98	nd	0.17 ± 0.00077	2.59 ± 0.00027	0.067 ± 9.6E-5	1.45 ± 0.00038	0.012 ± 0.00031	0.0032 ± 7.4E-5	0.0036 ± 0.00052	0.076 ± 0.0017	2.80 ± 0.0021

WL700										
0	0.041 ± 0.00017	0.29 ± 0.00065	0.88 ± 0.00049	0.22 ± 0.00068	1.58 ± 0.0029	0.026 ± 0.00021	0.0027 ± 2.6E-6	0.021 ± 0.00053	0.067 ± 0.0018	16.0 ± 0.357
3	0.046 ± 0.00059	0.46 ± 0.00056	0.82 ± 0.0042	0.18 ± 0.0019	2.26 ± 0.023	0.029 ± 7.7E-5	0.0032 ± 5.0E-5	0.023 ± 0.00038	0.068 ± 0.0015	16.4 ± 0.121
14	0.034 ± 0.00053	0.63 ± 0.0028	1.02 ± 0.0050	0.18 ± 0.00062	2.36 ± 0.00046	0.027 ± 1.5E-5	0.0038 ± 4.2E-6	0.020 ± 0.00051	0.095 ± 0.00061	14.2 ± 0.441
98	nd	0.16 ± 0.00059	2.66 ± 0.015	0.068 ± 0.00016	1.52 ± 0.0011	0.011 ± 3.0E-6	0.0033 ± 0.00016	0.0041 ± 0.00055	0.075 ± 0.00017	1.99 ± 0.021

Table S7. Pearson correlation coefficients describing the relationship between concentrations of water-extractable metals [mg/L] and bioassay endpoints at T0, T1, T2, and T3 (days 0, 3, 14, and 98 of the composting). Green and red boxes represent positive and negative statistically significant correlations, respectively ($p \leq 0.1$).

Bioassay	Cr	Cu	Mn	Ni	Zn	Co	Cd	Pb	As	Fe
BC-free control										
Root growth inhibition – 1% dose	-0.182	-0.573	0.247	-0.078	-0.441	-0.626	-0.962	-0.349	-0.755	-0.359
Root growth inhibition – 5% dose	-0.890	-0.613	0.437	-0.894	-0.813	-0.704	-0.402	-0.829	-0.128	-0.855
Bacteria luminescence inhibition	-0.118	0.354	-0.062	-0.224	0.166	0.388	0.845	0.066	0.691	0.070
Springtails reproduction inhibition – 1% dose	-0.179	-0.681	0.510	-0.071	-0.463	-0.659	-0.897	-0.379	-0.950	-0.365
Springtails reproduction inhibition – 5% dose	-0.830	-0.519	0.325	-0.840	-0.738	-0.623	-0.351	-0.755	-0.029	-0.786
SL500										
Root growth inhibition – 1% dose	-0.671	-0.413	0.804	-0.779	-0.220	-0.309	0.965	-0.578	0.527	-0.569
Root growth inhibition – 5% dose	0.801	0.470	-0.499	0.795	0.953	0.674	-0.127	0.740	0.334	0.744
Bacteria luminescence inhibition	0.575	0.905	-0.579	0.367	0.620	0.899	-0.137	0.726	0.832	0.731
Springtails reproduction inhibition – 1% dose	-0.701	-0.953	0.867	-0.572	-0.439	-0.831	0.652	-0.806	-0.379	-0.804
Springtails reproduction inhibition – 5% dose	-0.721	-0.203	0.536	-0.850	-0.621	-0.323	0.488	-0.569	0.306	-0.566
SL700										
Root growth inhibition – 1% dose	-0.412	-0.352	0.828	-0.767	-0.234	-0.468	0.900	-0.413	0.350	-0.399
Root growth inhibition – 5% dose	0.991	0.844	-0.419	0.880	0.987	0.756	0.044	0.961	-0.134	0.948
Bacteria luminescence inhibition	0.950	0.921	-0.363	0.686	0.948	0.824	0.313	0.957	0.200	0.959
Springtails reproduction inhibition – 1% dose	-0.323	-0.167	0.654	-0.733	-0.191	-0.263	0.921	-0.288	0.577	-0.264
Springtails reproduction inhibition – 5% dose	-0.802	-0.976	0.769	-0.627	-0.657	-0.995	0.007	-0.880	-0.509	-0.899
WL500										

Root growth inhibition – 1% dose	-0.181	-0.607	0.591	-0.228	0.140	-0.409	0.927	-0.178	0.392	-0.246
Root growth inhibition – 5% dose	0.433	0.878	-0.642	0.403	0.572	0.738	-0.243	0.420	0.171	0.352
Bacteria luminescence inhibition	0.942	0.741	-0.820	0.918	0.986	0.922	0.284	0.937	-0.455	0.891
Springtails reproduction inhibition – 1% dose	0.859	0.224	-0.545	0.861	0.758	0.573	0.510	0.866	-0.798	0.874
Springtails reproduction inhibition – 5% dose	0.256	-0.303	0.201	0.209	0.527	-0.010	0.993	0.259	0.062	0.190
WL700										
Root growth inhibition – 1% dose	-0.966	-0.810	0.976	-0.888	-0.744	-0.992	-0.032	-0.981	-0.094	-0.969
Root growth inhibition – 5% dose	0.081	0.808	-0.185	0.068	0.734	0.245	0.900	0.154	0.967	0.143
Bacteria luminescence inhibition	-0.090	-0.036	0.188	-0.392	0.294	-0.129	0.184	-0.110	-0.281	-0.179
Springtails reproduction inhibition – 1% dose	0.751	0.075	-0.657	0.623	0.151	0.639	-0.615	0.703	-0.720	0.686
Springtails reproduction inhibition – 5% dose	-0.893	-0.902	0.936	-0.856	-0.788	-0.956	-0.198	-0.924	-0.322	-0.920

References

Michot, L.J., Villiéras, F., 2013. Surface Area and Porosity. Dev. Clay Sci. 5, 319–332. https://doi.org/10.1016/B978-0-08-098259-5.00012-3

Rombel, A., Różyło, K., Oleszczuk, P., 2024. The high dose of biochar reduces polycyclic aromatic hydrocarbons losses during co-composting of sewage sludge and wheat straw. J. Environ. Manage. 351, 119628. https://doi.org/10.1016/J.JENVMAN.2023.119628

Siatecka, A., Różyło, K., Ok, Y.S., Oleszczuk, P., 2021. Biochars ages differently depending on the feedstock used for their production: Willow- versus sewage sludge-derived biochars. Sci. Total Environ. 789, 147458. https://doi.org/10.1016/J.SCITOTENV.2021.147458