



# Both Sides of Coin: Benefits and Potential Negative Consequences of Biochar in Sediment Remediation

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## Abstract

Biochar has been widely used for in situ remediation of sediments in recent years because of its advantages including suitable surface area, pore structure, and abundant surface oxygen-containing functional groups. Nevertheless, leaching of some hazardous components of biochar, e.g., potentially toxic elements (PTEs), polycyclic aromatic hydrocarbons, persistent free radicals, dioxins-like compounds, etc., can pose ecological risks to the water–sediment system. In this review, the applications and associated mechanisms of biochar in the remediation of PTEs- and organic pollutants contaminated sediment systems have been illustrated and critically discussed. Additionally, the potentially hazardous constituents in biochar were summarized and the effects of biomass and production conditions on their bioavailability were reviewed. Furthermore, the effects of biochar addition on water/sediment eutrophication, phytotoxicity, benthic damage, and microbial community changes were discussed. On this basis, the monitoring and assessment measures of the potential risks of biochar were summarized, and the corresponding avoidance strategies for different risks were proposed. This paper aims to provide a baseline reference and guidance implications for the biochar selection, toxicity detection, and evaluation in the field of sediment remediation.

## Introduction

Intense industrialization has led to increased effluent discharges and atmospheric deposition, and high concentrations of nutrients, PTEs, and organic pollutants (OPs) have been detected in many river sediments (Huang et al. 2018). Sediments serve both as reservoirs for accumulating pollutants and, in turn, as sources of pollutants discharged into the water environment. The ever-increasing accumulation of these pollutants in sediments has a potential negative consequences on the aquatic environment and ecology (Dietrich et al. 2021). The use of absorbents to immobilize pollutants is an innovative and effective approach for the in situ sediment remediation. Among them, biochar is widely considered as an environmentally friendly sediment amendment due to its large specific area, rich porous structure, and high structural stability (Gu et al. 2022). In recent years, biochar research has been in a period of dramatic growth worldwide (Fig. 1), with the amount of literature related to biochar increasing approximately 1000-fold from 2007 to 2021, showing a wide appeal and irreversible heat. However, most of the studies focus on water pollution treatment, soil amendment, greenhouse gas reduction, etc. (Wu et al. 2021; Chen et al. 2022), and as of August 2022, biochar has only few studies in the direction of Sediment.

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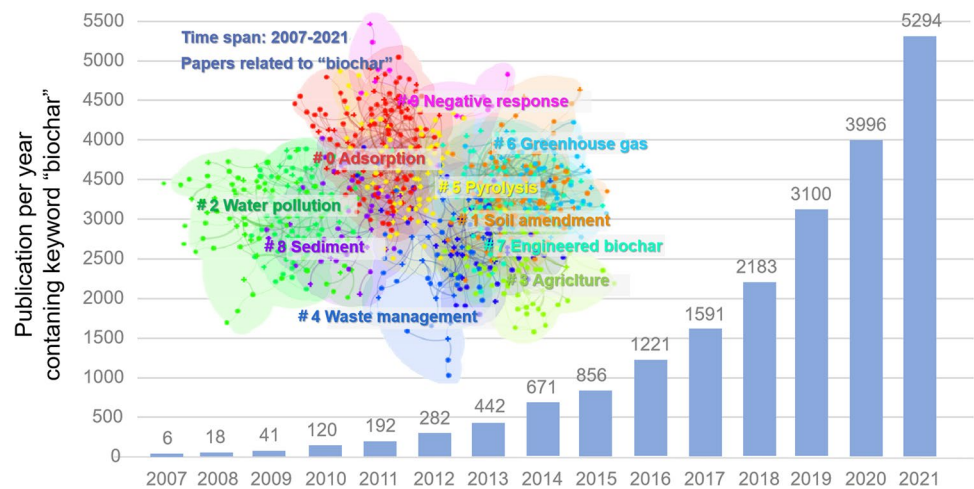
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**Fig. 1** Publications containing the keyword "biochar" published in indexed journals for each year between 2007 and 2021. 0–9 represent the clustering of 10 research directions in the biochar field. 0 represents the largest number of studies and 9 represents the smallest number. The data are based on the search results from Web of Science



In addition, although some of these studies have demonstrated the effectiveness of biochar for the immobilization of PTEs, OPs, and other inorganic contaminants ( $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , and  $\text{NO}_3^-$ ) in sediments (Hung et al. 2021a, b), harmful components (PTEs, PAHs, environmentally persistent free radicals (EPFRs), etc.) may be generated by biochar due to improper selection of biomass, preparation conditions and methods (Wang et al. 2019b, 2021). For instance, slowly pyrolyzed biochar typically produces low concentrations of PAHs, while biochar from gasification processes is typically associated with high PAHs concentrations (Zhou et al. 2022a). Wang et al. (2019a, b, c) also found the bioavailability of Zn in sewage sludge biochar pyrolyzed at 300 °C was 2.7 times higher than that of biochar pyrolyzed at 700 °C. Furthermore, the leaching of these contaminants into the water–sediment system after biochar application may pose potential risks (e.g., phytotoxicity, ecotoxicity, and cytotoxicity) to the environment and human health (Zhang et al. 2019a, b). For instance, PTEs have been shown to be introduced to biochar from feedstock and produce significant inhibition of watercress seedlings after dosing (Buss et al. 2016). Gu et al. (2022) found that PAHs produced in biochar at 250–900 °C could reach concentrations of up to 45 mg/kg, even higher than in some contaminated sediments/soils. Nevertheless, there were very few reviews on the potential risks and potential negative consequences of biochar, and a literature search in the web of science showed that potential negative consequences is one of the least researched and reviewed sections in the field of biochar (Fig. 1). Zhang et al. (2019a) briefly mentioned the environmental risks of biochar in their review. Nevertheless, the detailed information and mechanisms involved need further documentation. Xiang et al. reviewed the potential potential negative consequences of biochar application, while did not propose corresponding risk avoidance strategies. Several studies have proposed various strategies to mitigate the formation of contaminants and eliminate potential risks, including high pyrolysis temperatures (Qin et al. 2017), co-pyrolysis (Fakayode et al. 2020), heat

treatment (Kołtowski et al. 2015). There is not much systematic summary of monitoring methods and avoidance measures for specific contaminants in biochar. Therefore, it is essential to systematically discuss the potential negative environmental impacts of biochar and to find measures to avoid potential risks.

This review provided a comprehensive review of the application of biochar, the generation of potential pollutants, the potential negative consequences of biochar application on the environment, risk detection and assessment tools, and avoidance strategies. The mechanism and effectiveness of biochar in removing contaminants from sediments were described, and the effects of different feedstocks, pyrolysis temperatures, and other production conditions on the formation of contaminants (PTEs, PAHs, EPFRs) were compared. In addition, eutrophication, biotoxicity, and the changes of microbial community in water/sediment after biochar incorporation into sediments were systematically analyzed, and the means of risk detection and assessment and corresponding avoidance measures were proposed. This paper innovatively proposes a complete system of pollution remediation effects of biochar, its own harmful components, environmental changes after biochar application, risk monitoring means and avoidance measures, and the changes of sediment microorganisms after biochar application are also included in the paper to provide a reference from a microscopic perspective.

## Biochar Application for Contaminated Sediments Remediation

Biochar has shown the ability to absorb both organic and inorganic contaminants through a series of physical/chemical processes (Liu et al. 2017) and reduce the mobility and bioavailability of contaminants (Hung et al. 2021b). For instance, the magnetized coal bitumen biochar working in conjunction with  $\text{Fe}^{2+}$  to degrade persulphate in

PAH-contaminated sediments and is able to increase the removal of PAHs to 80% (Dong et al. 2019). The gasification biochar prepared from palm sawdust can significantly improve the stability of copper and lead (Wang et al. 2019a). The removal mechanisms of biochar for different pollutants in sediments vary and are closely related to the nature and characteristics of pollutants (Huang et al. 2018). In addition, the removal effectiveness and adsorption mechanism also depend on various properties of biochar, including surface functional groups, specific surface area, pore structure, and mineral fraction (Palansooriya et al. 2019) (Fig. 2).

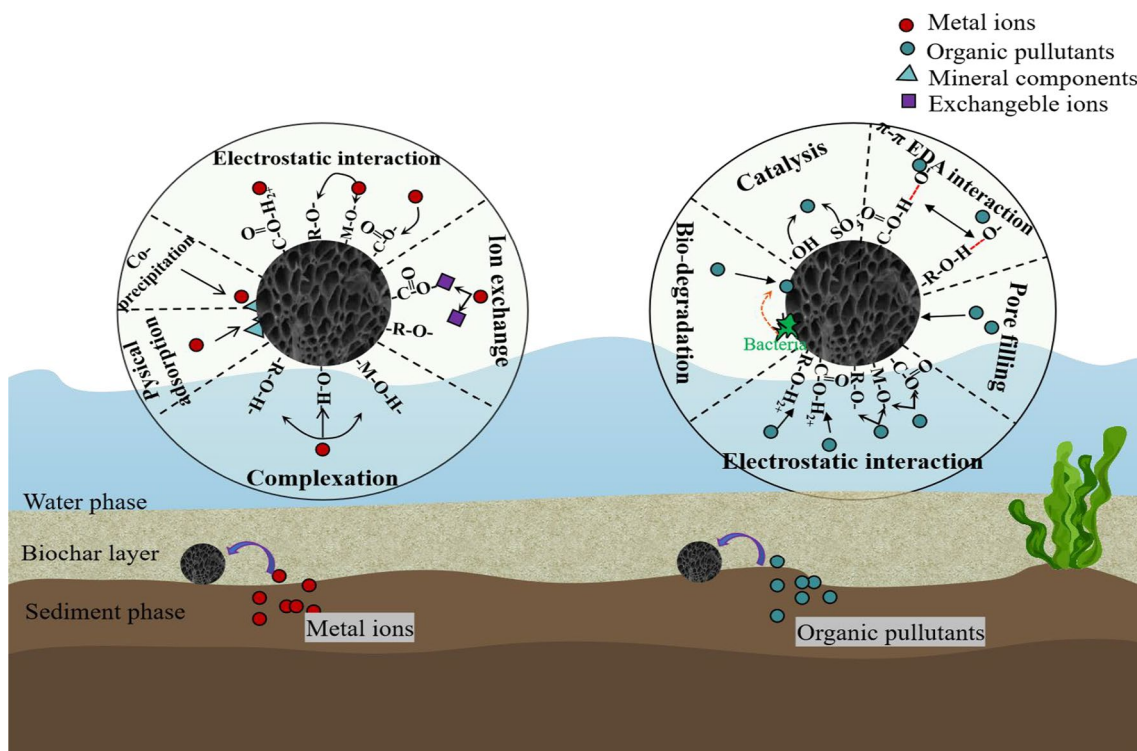
## Metal(loid)s Contaminated Sediments Remediation

### Sorption

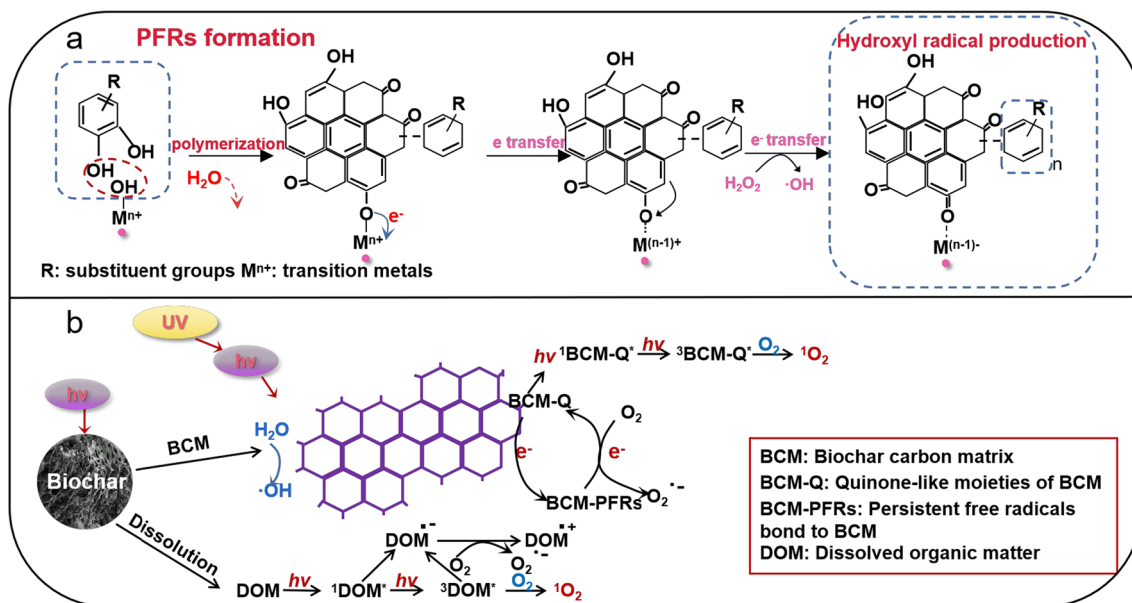
Cu(II), Cd(II), Pb(II), and Zn(II) are common metal cations in sediments, usually in the form of divalent ions or compounds/complexes with similar behavior and characteristics (Beesley and Dickinson 2011; Dong et al. 2014). Surface precipitation is one of the major ways in which biochar stabilizes metal cations, and its effect is mainly related to the pore structure, specific surface area, and oxygen-containing functional groups of biochar (Fig. 3). Wang et al. (2019a) used palm sawdust biochar to remove PTEs from sediments and found that 5% dosage decreased

the concentrations of Cu and Pb in pore water to 19% and 32% of the control group, respectively. The minerals (e.g., phosphate,  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}$ , etc.) of biochar acted as additional adsorption sites for metals through electrostatic reactions, ion exchange, surface complexation, and precipitation of mineral-metals (Li et al. 2017). Zhou et al. (2013) found that biochar produced from sugarcane showed effective immobilization of Pb, Cd, and Cu, with removal rates of 51.5, 48.5 and 54.3%, respectively. The removal processes were mainly governed by pore filling, surface complexation and ion exchange.

Mercury (Hg) is significantly more toxic in the ecosystem than the above four metals, and its Geo-chemical characteristics in sediments mainly include redox reactions and methylation (Yu et al. 2022). Liu et al. (2017) found that the Hg concentration in sediment decreased to 21.7% of the initial concentration after 120 d amendment using willow branch biochar produced at 600 °C. The interaction of Hg(II) with oxygen-containing functional groups on the biochar surface dominated the Hg(II) removal process (Yang et al. 2021b). In addition, the biochar-induced formation of  $(-\text{COO})_2\text{Hg}(\text{II})$  and  $(-\text{O})_2\text{Hg}(\text{II})$  enhanced the immobilization of Hg, while the  $\pi$  electrons derived from  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  triggering Hg- $\pi$  interaction was also another key factor affecting the immobilization of Hg (Liu et al. 2019).



**Fig. 2** Proposed mechanisms of using biochar for remediation of sediments contaminated with heavy metals and organic pollutants. Reproduced from Yang et al. (2022)



**Fig. 3** Mechanisms of environmentally persistent free radicals (EPFR) formation and  $H_2O_2$  activation by biochar synthesized via pyrolysis process (a); proposed framework for reactive oxygen species (ROS) formation from biochar suspension under light (b)

In addition, the improvement of sediment pH by carbonates and functional groups (e.g.,  $-\text{COOH}$  and  $-\text{OH}$ ) of biochar aided in enhancing the removal of PTEs in the sediment (Dong et al. 2014). The reason may be that the amount of  $H^+$  in sediments under alkaline conditions is lower than in acidic environments, and the competition between  $H^+$  and metal cations in sediments for ligands (e.g.,  $\text{CO}_2-3$ ,  $\text{SO}_2-4$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ , etc.) is less intense, resulting in more metal ions binding to ligands and reducing their concentration in sediments (Ojeda et al. 2016).

### PTEs Fraction Transformation

The bioavailability and biotoxicity of PTEs are closely related to their fractions present in the environment, which are affected by the addition of biochar (Liu et al. 2018). The species of PTEs in sediment/soil are generally divided into four categories: weakly acid-extractable fraction (F1), reducible fraction (F2), oxidation fraction (F3), and residual fraction (F4) (Huang et al. 2018), of which  $F1 + F2 + F3$  are considered as potential bio-available forms for PTEs. F1 and F2 are considered as the weakly bound fractions, capable of causing direct toxicity to the organisms. Biochar dosing has been shown to promote the conversion of the active chemical forms of PTEs (F1, F2 and F3) into a stable fraction (F4). Wang et al. (2019b) applied rice straw biochar composites for As and Cd immobilization in sediments, and they found that after 60 days of treatment, the F1 of As and Cd decreased by 43% and 11%, respectively, while F4 increased

by 17% and 6%, respectively. The shift in sediment properties (e.g., total organic carbon, pH, and clay content) caused by biochar addition may be the main reason for the change in PTEs species. For instance, the percentage of available fraction ( $F1 + F2 + F3$ ) of Cd decreased more in sandy soils/sediments (27.4%) and accordingly, its residual fraction (F4) percentage increased more in sandy soils (30.6%) (Brazauskienė et al. 2008). This may be because sandy soils/sediments contain less organic carbon and clay minerals compared to clayey soils/sediments, and therefore have a lower sorption of PTEs. In addition, Yang et al. (2019) found that the average decrease of  $F1 + F2 + F3$  fraction in alkaline sediments was 35.0%, 12.4%, and 42.4% for Cd, Cu and Pb, respectively. Therefore, the addition of biochar can improve the acidic environment of sediments and promote the transition of PTEs to residual fraction in the meantime.

## Organic Pollutants Contaminated Sediments Remediation

### Sorption

The adsorption of OPs from sediments by biochar consists mainly of physical and chemical absorption processes (Fig. 3). Physical absorption is due to the high specific surface area of biochar, which binds the pollutants by intermolecular attraction. In addition, the special pore structure of biochar blocks the adsorbed macro-molecular pollutants. Zhou et al. (2022b) found that biochar adsorbed hydrophobic

organic compounds with irreversible expansion of pores, leading to an irreversible phenomenon of adsorption–desorption, verifying the role of pore filling in the adsorption process of biochar. Chemical absorption is the chemical interaction of biochar and OPs to form chemical bonds (e.g.,  $\pi$ -bonds, coordination bonds, ion-coupled bonds, etc.). Ding et al. (2021) investigated the mechanism of antibiotic adsorption from marine sediments by algal biochar. They found that biochar is highly aromatic and contains many  $\pi$ -electrons on its surface, which can act as an electron donor and strongly form  $\pi$ – $\pi$  bonds with antibiotics through a special donor–acceptor interaction and adsorption on biochar. In addition, biochar can also be used as an electron shuttle to accelerate electron transfer and thus enhance the adsorption of organic matter. Moreover, the surface of biochar is rich in hydroxyl, carboxyl, carbonyl, and other functional groups, and OPs can easily form stable chemical bonds with these functional groups, resulting in a strong complexation (Isakovski et al. 2020). In addition, there are differences in the adsorption mechanisms of polar and non-polar organic compounds on biochar, with polar organic compounds being hydrogen bonded to the O-containing portion of the biochar and non-polar compounds being adsorbed on the biochar by entering hydrophobic sites on the surface of the biochar (Li et al. 2020a; Li et al. 2022).

### Catalysis

Besides sorption, biochar acts as an electron transfer medium to stimulate electron transfer and acts as a catalyst to promote the redox of pollutants (Yuan et al. 2017). Dong et al. (2017) used biochar and  $\text{Fe}^{2+}$  synergistic persulfate to remove PAHs from sediments and found that persulfate alone,  $\text{Fe}_3\text{O}_4$  + bamboo biochar, and  $\text{Fe}_3\text{O}_4$  + bamboo biochar + persulfate had removal efficiencies of 14%, 21%, and 78% for PAHs, respectively. The marked increase in removal efficiency after the addition of biochar is mainly due to the fact that the biochar promoted the activation of persulfate to generate  $\text{SO}_4 \cdot^-$ , which enhanced the efficiency of chemical oxidation of PAHs. Hung et al. (2021b) used sludge biochar coupled with sodium percarbonate (SPC) to remove refractory organic matter in estuary sediments, the SPC was activated by the biochar to produce sufficient  $\cdot\text{OH}$  and  $\text{CO}_3 \cdot^-$  through electron transfer interactions on Fe–Mn redox pairs. The reaction efficiency was up to 73% for 4-nonylphenol removal at pH = 9 for 12 h. Moreover, the persistent free radicals (PFRs) contained in the biochar itself are captured by the reducing agent and more active free radicals are involved in the reduction of OPs. Fang et al. (2014) used electron paramagnetic resonance (EPR) and salicylic acid (SA) capture techniques to clarify that the continuous production of  $\cdot\text{OH}$  during the synergistic removal of hydrogen peroxide from

2-chlorobiphenyl (2-CB) by biochar was responsible for the significant reduction in the concentration of EPFRs. The linear correlation between PFRs concentration and captured  $\cdot\text{OH}$  confirms redox-induced process.

### Bio-Degradation

Regulation of microbial communities in sediments by biochar is also a factor in OPs degradation (Sopeña et al. 2012). Biochar is porous and rich in C, N, and P elements, providing habitats and nutrients for microbes to enhance microbial biomass and/or microbial activity in the sediment (Chen et al. 2012; Hung et al. 2021a). Cheng et al. (2017) found that biochar addition significantly increased the biomass and relative abundance of the genera *Pseudomonas* and *Sphingomonas*. Both microbes used nonylphenol (NP) as an energy and carbon source to biodegrade NP at high and low concentrations, respectively. The promotion of microbes in sediments by biochar is poorly studied, while it can be assumed from similar effects and mechanisms in other carbonaceous materials that this approach for biochar-induced remediation is feasible. For instance, Jin et al. (2017b) found that the genera *Pseudomonas* immobilized in the pores of cinder and chitosan beads had a significant effect in explaining benzo(a)pyrene degradation in wetland sediments. Bonaglia et al. (2020) found a sharp increase in the relative abundance of the genera *Geobacter*, *Thiobacillus*, *sulicurvum*, and *methanogenic archaea* amended by activated carbon (AC) under anaerobic conditions, with the degradation efficiency of naphthalene in the sediment reaching 93%. It probably results from the AC particles facilitating direct interspecies electron transfer (DIET) between microorganisms involved in the PAH degradation pathway. Although similar experiments were not conducted around biochar, considering the structure and properties of biochar AC types, perhaps biochar could also facilitate electron transfer from microbes involved in OPs degradation.

### Potential Potential Negative Consequences of Biochar in Sediments Remediation

Several potential potential negative consequences exist with the application of biochar to sediment remediation. These risks may be related to the components of the biochar itself and the inverse modification of the sediment system caused by the biochar injection.

## Harmful Components of Biochar

### Heavy Metals

In the case of biomass with high metal content, the pyrolysis process concentrates and retains these elements on the biochar, resulting an ecological risk. However, biochar produced from plant feedstock tends to have a lower PTEs content than biomass like compost and sewage sludge. For instance, Yang et al. (2021c) found that Cu, Cd, and Pb in rice straw biochar could reach 41.92 mg/kg, 1.44 mg/kg, and 10.70 mg/kg, respectively. Assirey et al. (2021) found the concentrations of PTEs in corn-based biochar were at a low level, with a maximum of 11.53 mg/kg for Pb, and Oleszczuk et al. (2013) also confirmed that the major PTEs in wicker-based biochar were 60 mg/kg for Zn and 32.90 mg/kg for Pb. Yet, PTEs in plant-based biochar were mainly Zn and Hg, which were weakly adsorbed on the biochar matrix and may also be released to the environment under mild conditions (von Gunten et al. 2017). Meanwhile, the high proportion of acid-soluble fraction and exchange fraction (even more than 50%) of plant-based biochar may lead to a generally high bioavailability of PTEs (Wang et al. 2020). Conversely, the concentration of Zn in textile dyeing sludge-based biochar can reach 2000 mg/kg (Wang et al. 2019b), and that in municipal sewage sludge-based biochar even exceeds 10,000 mg/kg (Wang et al. 2021a). Nevertheless, the bioavailability of PTEs in such biomass is relatively low. In addition, the biochar produced from animal manure also contains a large quantity of PTEs, primarily Zn, Cu, and Mn, which may be due to the excretion of the inadequately absorbed Cu and Zn additives in the feed along with the manure (Zeng et al. 2018). Pyrolysis temperature is an essential factor affecting heavy metal concentration and bioavailability. Heavy metal concentration tends to increase with increasing pyrolysis temperature, Yang et al. (2021b) found that the concentrations of Zn, Cu, and Cr in sewage sludge-based biochar increased by 37%, 33%, and 36%, respectively, at pyrolysis temperatures from 300 to 700 °C, the reason may be that the high temperature decomposes a large amount of OM in the biomass, and the PTEs originally bound to it were released (Zhang et al. 2021). On the contrary, the bioavailability of PTEs in biochar decreased with the increase in pyrolysis temperature (Zeng et al. 2018; Wang et al. 2019b).

### PAHs

During the pyrolysis of biochar, OM (e.g., lignin, cellulose) undergoes cyclization, dealkylation, dehydrogenation, and aromatization. Then, the disappearance of the main compounds in the biomass (water, carbon dioxide, methane and hydrogen sulfide) during this process is accompanied by the

production of PAHs. There are more than 150 known PAHs, while 16 PAHs (e.g., phenanthrene, fluorene, benzo(a)pyrene, etc.) specified by the U.S. Environmental Protection Agency (USEPA) are usually used as indicators to assess the ecological risk of PAHs in the environment (Shahhoseini et al. 2020; Kumar et al. 2021). During the formation of PAHs, the number of rings of PAHs increases from 1 to 5 rings as  $E_a$  (activation energy) increases from 50 to 110 kcal/mol (Hao et al. 2021). Generally, low molecular weight PAHs (2 rings or 3 rings) are formed at pyrolysis temperatures below 500 °C, while high temperatures (> 500 °C) cause the reorganization of highly reactive radicals (e.g.,  $H_2C=CH-CH=C.H$ ) in biochar, and low molecular weight PAHs transform into high molecular weight PAHs (4, 5, 6 rings) (Lin et al. 2022). Nevertheless, Devi et al. (2015) found that chrysene (4-ring) was the dominant PAHs among 16 PAHs in the biochar derived from cracking paper mill effluent sludge at 200 °C, and the dominant PAHs changed to naphthalene (2-ring) when the temperature increased to 400 °C. Previous studies have shown opposing views on the effect of pyrolysis temperature on PAH concentrations in biochar, suggesting that PAHs concentrations increased/decreased with increasing pyrolysis temperature (Table 1). For instance, Dunnigan et al. (2017) found that the concentration of PAHs in rice husk-based biochar increased consistently from  $1.022 \pm 0.212$  µg/g to  $11.284 \pm 0.877$  µg/g as the pyrolysis temperature increased from 400 to 800 °C, with an exponential increase occurring especially at 800 °C. Nakajima et al. (2007) also found that the concentration of PAHs in cypress-based biochar was positively correlated with temperature increase. Yet, Konczak et al. (2019) produced sewage sludge-based biochar at 500, 600, and 700 °C, respectively, and found that the concentration of total PAHs decreased from 2.325 to 1.505 µg/g. The reason may be that the  $\pi-\pi$  bond between biochar and PAHs break with the increase of pyrolysis temperature. In addition, the high temperature leads to the release of Ca, Al, and Ba from the biochar, which facilitates the leaching of PAHs (Hale et al. 2012). For instance, the concentration of PAHs in food waste-based biochar increased continuously from 0.373 to 0.645 µg/g between 300 and 500 °C, but decreased significantly to 0.105 µg/g at 600 °C (Hale et al. 2012). The peak concentration of PAHs in most studies occurred at 500 °C (Hale et al. 2012; Devi et al. 2015; Kończak et al. 2019), while their bioavailability decreased with increasing pyrolysis temperature.

### Environmental Persistent Free Radicals (EPFRs)

EPFRs were detected abundantly in biochar produced by various feedstocks (typically  $10^{18}$  unpaired spins per gram of biochar) (Yuan et al. 2022). EPFRs induce the production of  $\bullet OH$  and cause oxidative damage to cell

**Table 1** Total and bioavailable PAHs contents in biochars derived from different biomass and operating conditions

Biomass	Temperature (°C)	Production conditions	Residence time	Dominant PAHs	Total PAHs concentration (µg/g)	Bioavailable PAHs	Reference
Sewage sludge	500	Atmosphere: N <sub>2</sub> /CO <sub>2</sub>	180 min	3-ring (Phenanthrene)	2.325	44 ng/L	Kościak et al. (2019)
	600				1.711	51 ng/L	
	700				1.505	46 ng/L	
Cypress	400	Atmosphere: N <sub>2</sub> , Production reactor: muffle furnace	16 h	3-ring (Fluorene)	0.723	N/D	Nakajima et al. (2007)
	600				2.332		
	800				3.817		
	1000				3.851		
Vegetable waste	200	Modern slow pyrolysis	6 h	2-ring (Naphthalene)	3.3	N/D	Yang et al. (2019)
	500			3-ring (Fluorene)	3.4		
Food waste	400	Rotary kiln	20–240 min	-	0.80–6.36	N/D	José et al. (2019)
	500						
	600						
Food waste	300	Modern slow pyrolysis	30 min	3-ring (Phenanthrene)	0.373	2.242 ng/L	Hale et al. (2012)
	400				0.448	4.849 ng/L	
	500				0.649	1.063 ng/L	
	600				0.105	0.404 ng/L	
Corn stover	350	Modern slow pyrolysis	30 min	3-ring (Phenanthrene)	1.611	1.620 ng/L	
	450			2-ring (Naphthalene)	1.961	1.410 ng/L	
	550			2-ring (Naphthalene)	1.772	1.303 ng/L	
Poplar wood	1200	Gasification	-	4-ring (Pyrene)	15.6619	N/D	Visioli et al. (2016)
Dairy manure	300	Modern slow pyrolysis	30 min	2-ring (Naphthalene)	0.332	3.604	Hale et al. (2012)
	400			2-ring (Naphthalene), 3-ring (Phenanthrene)	0.234	2.528	
	500			2-ring (Naphthalene)	0.343	2.542	
	600			2-ring (Naphthalene)	0.189	0.830	
Rice husk	400	Atmosphere: N <sub>2</sub>	16 min	2-ring (Naphthalene)	1.022 ± 0.212	0.91 ± 0.35 ng/L	Dunnigan et al. (2017)
	500			3-ring (Acenaphthylene)	3.250 ± 0.499	1.87 ± 0.03 ng/L	
	600			3-ring (Acenaphthylene)	7.829 ± 2.380	3.54 ± 0.17 ng/L	
	700			3-ring (Acenaphthylene)	6.185 ± 1.664	83.17 ± 33.60 ng/L	
	800			3-ring (Acenaphthylene)	11.284 ± 0.877	1112.68 ± 50.99 ng/L	
Oak	250, 400, 650	Modern slow pyrolysis, Production reactor: Muffle furnace	3 h	2-ring (Naphthalene)	0.096	2.159 ng/L	Hale et al. (2012)
					0.141	0.358 ng/L	
					0.183	0.281 ng/L	
Grass			3 h	2-ring (Naphthalene)	0.132	1.251 ng/L	Hale et al. (2012)
					0.126	0.128 ng/L	
					0.291	0.228 ng/L	

**Table 1** (continued)

Biomass	Temperature (°C)	Production conditions	Residence time	Dominant PAHs	Total PAHs concentration (µg/g)	Bioavailable PAHs	Reference
Paper mill effluent sludge	200	–	–	4-ring (Chrysene)	0.323	N/D	Devi and Saroha (2015)
	300			4-ring (Chrysene)	0.321		
	400			2-ring (Naphthalene)	5.970		
	500			3-ring (Phenanthrene)	19.723		
	600			ring (Pyrene)	9.375		
	700			3-ring (Phenanthrene)	0.615		

membranes, and DNA (Bi et al. 2022). In addition, the steric hindrance between EPFRs and biochar particles enhances the stability of EPFRs, and their half-lives can even reach several months (Tao et al. 2020). The formation mechanism of the EPFRs in biochar may be that the high temperature causes the pyrolysis of OM in the biochar and the molecular precursors eliminate H<sub>2</sub>O. Then, the transition metal is transferred to the biomass by chemical adsorption, transferring an electron from the substituted aromatics to the metal center. Subsequently, the reduction of the metal and the production of EPFRs occur simultaneously (Fig. 3a) (Yang et al. 2017). Cellulose, hemicellulose, and lignin are the main molecular precursors in biochar. The first two are depolymerized to oligosaccharides by high temperature and then cleave glycosidic bonds to form different monomeric radicals (Li et al. 2020b). The formation of free radicals is easier due to the presence of two cleavage sites in the cellulose chain (Zhang et al. 2013). Nevertheless, the more compact structure of lignin leads to a more complex formation process of EPFRs. First, lignin undergoes C–C, C–O bonds,  $\alpha$ - and  $\beta$ -alkyl aryl ether fracture at high pyrolysis temperatures, resulting in the formation of free radicals. These radicals extract hydrogen from other molecules, and subsequently undergo sequential reactions (e.g., dehydration, decarboxylation, aromatization, etc.) (Odinga et al. 2020). In this process, transition metals transfer electrons to phenol lignin (Fig. 3a), resulting in numerous phenols or quinones, and EPFRs are formed on the surface of biochar (Fang et al. 2014). The  $\alpha$ -aryl ether bond of softwood lignin is more prone to fracture than hard and non-wood lignin, and softwood lignin contains more phenyl coumarin structures, and thus, has a higher yield of free radicals (Han et al. 2022). Careful consideration of softwoods (e.g., fir, poplar,

and silver fir) as biomass is necessary to hedge the risk the accumulation of EPFRs in biochar.

Pyrolysis temperature is another dominant factor affecting the concentration of EPFRs in biochar. Several studies had shown that the signal intensity of EPFRs elevated with the increase of pyrolysis temperature (Jiang et al. 2020; Hu et al. 2022). For instance, Fang et al. (2014) investigated the production of biochar pyrolysis by wheat straw and maize straw at 300–500 °C. The concentration of EPFRs in the former increased from  $16.5 \times 10^{18}$  spins/g at 400 °C to  $28.6 \times 10^{18}$  spins/g at 500 °C, and the concentration of EPFRs in the later increased from  $6.25 \times 10^{18}$  spins/g at 400 °C to  $30.2 \times 10^{18}$  spins/g at 500 °C. Nevertheless, some studies showed that the signal intensity of EPFRs started to weaken at pyrolysis temperatures above 600 °C and decreased sharply at 700 °C. For instance, Qin et al. (2017) compared biochar produced from rice husk (R) at 300–700 °C and found that the concentration of EPFRs from R-300 to R-500 °C increased from  $2.77 \times 10^{18}$  spins/g to  $17.20 \times 10^{18}$  spins/g, while the concentration of EPFRs decreased from  $17.20 \times 10^{18}$  spins/g at 500 °C to  $6.16 \times 10^{18}$  spins/g at 700 °C. The reason may be that the high temperature destroyed the structure of free radicals and hindered the production of EPFRs.

EPFRs sometimes act like a double-edged sword in that they can activate S<sub>2</sub>O<sub>8</sub><sup>2-</sup> or H<sub>2</sub>O<sub>2</sub> to generate reactive oxygen species (ROS) for effective degradation of organic/inorganic pollutants (Vejerano et al. 2018). In addition, photogeneration of ROS could be achieved by EPFRs in biochar under UV irradiation, resulting in the enhanced degradation of OPs (Fig. 3b). Fang et al. (2015) found that UV irradiation of 0.2 g/L biochar could remove 52.3–72.6% of ethyl phthalate (EP) after 2 h reaction. They concluded that biochar-derived quinone-like structure, dissolved organic matter (DOM), and



EPFRs produced OH and singlet oxygen through a series of reactions were key factors in the degradation of EP. Nevertheless, despite the positive effect of ROS in degrading organic/inorganic substances, there are environmental risks associated with their potential toxicity to plants and cells. Xiang et al. suggested that the semi-quinone radical anion in biochar reacts with molecular O to form super oxide, which subsequently reacts with bio-reductive equivalents to form peroxide hydroxyl groups. The biotoxicity may arise from the oxidative stress generated by EPFRs induced ROS.

### Dioxins, PFOS, and PFOA

In addition to the typical contaminants mentioned above, incomplete combustion of biomass can also produce Dioxin-like contaminants (e.g. polychlorinated, dibenzofurans, dibenzo-p-dioxins) (Khan et al. 2021). Dioxins and aryl hydrocarbon receptor reactions disrupt normal hormonal pathways, leading to reproductive and developmental disorders, and are often considered as “carcinogens”. Hale et al. (2012) investigated more than 50 types of biochar produced from different biomass and found that dioxin-like compounds were detected in 14 biochar in the pyrolysis temperature range of 250–900 °C, with concentrations ranging from  $8 \times 10^{-6}$  to  $12 \times 10^{-6}$  ng/g. Moreover, Kim et al. (2015) found total residual concentrations of 15.8–16.9 ng/g of perfluorooctane sulfonic acid (PFOS) and perfluorooctane acid (PFOA) in sludge-based biochar, exhibiting some environmental persistence. These contaminants are present in biochar at low concentrations and have not been reported to be harmful to humans, while their toxicity and environmental persistence exhibit environmental risks that are worthy of in-depth study.

## Potential Risks of Biochar to Water–Sediment Systems

### Aquatic Environment and Organisms

Some biochar (e.g., pig manure and cow manure derived biochar) may be enriched with nutrients (e.g., nitrogen and phosphorus). Inorganic nitrogen/phosphorus leached from biochar may cause endogenous pollution of rivers, leading to the risk of eutrophication (Fig. 3). Chen et al. (2017) found that biochar prepared from bamboo could release 0.30–4.92% of total  $\text{NH}_4^+$  and 2.63–5.09% of total  $\text{PO}_4^{3-}$  into the water within 2–88 h (Table 2). Cui et al. (2016) investigated the effect of biochar produced by 22 artificial wetland plants on nutrient release and found that 17 of them had increased phosphate release, with the largest release of 3.68 mg/g from *Pennisetum purpureum* Schum. Yao et al. (2012) researched on the effect of thirteen biochar on soil nutrient leaching and also showed that 9 of

them released  $\text{NO}_3^-$ , 4 of them released  $\text{NH}_4^+$ , and 8 of them released  $\text{PO}_4^{3-}$ . Hale et al. (2013) also found that the phosphate leaching from cacao shell and corn cob biochar reached 1.48 mg/g and 0.17 mg/g, respectively, after 60 d of continuous leaching. Ions in natural water/wastewater compete with  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$ , which not only reduce the adsorption effect of biochar, but even promote the desorption of nutrients from biochar itself (Yang et al. 2021a). Cations (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , etc.) compete significantly with  $\text{NH}_4^+$ , while anions (e.g.,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc.) also reduce the adsorption of  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$ . Wang et al. (2015) observed that maple biochar desorbed 90% of  $\text{NH}_4^+$  in KCl solution. Novais et al. (2018) compared the nutrient release behavior of poultry manure biochar in pure water and  $\text{NO}_3^-$  solution and found that after four rounds of extraction, only 20% of P was leached from biochar in pure water solution, while up to 90% of P was leached from  $\text{NO}_3^-$  solution, indicating that the ions in water did promote nutrient desorption in the biochar. Furthermore, pyrolysis temperature is one of the key factors affecting the nutrients leaching from biochar. Biochar produced at high temperatures tends to have more phosphate leaching. Yao et al. (2012) found no phosphate leaching from Peanut hull biochar produced at 300 °C and 350 °C, but 3.57% phosphate was released from biochar produced at 600 °C. Park et al. (2015) also reported that the leaching of phosphate from sesame straw biochar increased from 62.6 to 168.2 mg/g as the pyrolysis temperature increased from 300 to 600 °C. The reason may be due to the weaker affinity of phosphate for biochar with low Ca and Mg content, and the high temperature exacerbates the desorption of phosphate. Conversely, biochar produced at low temperature was observed to have more  $\text{NH}_4^+$  and  $\text{NO}_3^-$  leaching. Yao et al. (2012) compared the leaching behavior of nutrients in four different biochar (e.g., sugarcane, peanut hull, Brazilian pepper wood, and Bamboo) produced at 300 °C, 450 °C and 600 °C, respectively. They observed  $\text{NO}_3^-$  and  $\text{NH}_4^+$  leaching from all four biochars produced at 300 °C and 450 °C pyrolysis temperatures, while the leaching was inhibited when the pyrolysis temperature was increased to 600 °C. In addition, the initial concentration of nutrients in water is also considered to be one of the reasons affecting the leaching of nutrients from biochar. For instance, biochar tends to adsorb rather than release phosphate at a higher initial phosphorus concentration (Cui et al. 2022). Cui et al. (2016) found that as the initial phosphorus concentration increased from 6 to 10 mg/L, the phosphorus leaching from *Pennisetum purpureum* Schum biochar decreased from 3.68 to 2.91 mg/g, while the phosphorus leaching from miscanthus biochar decreased from 2.75 to 0.95 mg/g. Although theoretically it is possible that some nutrient-enriched biochar may contribute to nutrient release in sediments increasing the chances of eutrophication, the practical contributions from other anthropogenic nutrient sources such as fertilizers

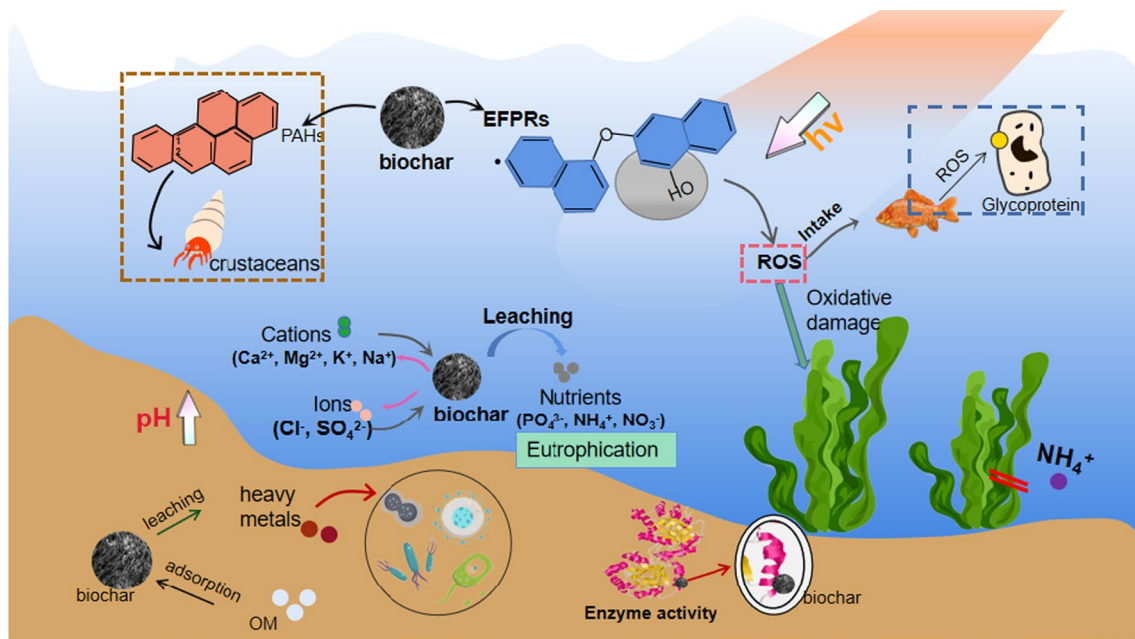
**Table 2** The amount/rate of nutrient release from biochar produced from different biomass and operating conditions

Biomass	Pyrolysis temperature (°C)	Types of nutrients	Operation conditions	Release amount/rate	Reference
Montmorillonite/bamboo	400	NH <sub>4</sub> <sup>+</sup> , PO <sub>4</sub> <sup>3-</sup>	–	0.30–4.92%, 2.63–5.09%	Chen et al. (2017)
Pennisetum purpureum Schum	500	PO <sub>4</sub> <sup>3-</sup>	Initial phosphorus concentration: 6 mg/L	3.68 mg/g	Cui et al. (2016)
			Initial phosphorus concentration: 8 mg/L	3.23 mg/g	
			Initial phosphorus concentration: 10 mg/L	2.91 mg/g	
Miscanthus	500	PO <sub>4</sub> <sup>3-</sup>	Initial phosphorus concentration: 6 mg/L	2.75 mg/g	Cui et al. (2016)
			Initial phosphorus concentration: 8 mg/L	1.88 mg/g	
			Initial phosphorus concentration: 10 mg/L	0.95 mg/g	
Sugarcane bagasse	300	NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup>	–	2.18%, 3.15%	Yao et al. (2012)
	450	NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>		3.74%, 2.61%	
	600	PO <sub>4</sub> <sup>3-</sup>		3.27%	
Peanut hull	300	NO <sub>3</sub> <sup>-</sup>	–	3.98%	Yao et al. (2012)
	450	NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>		3.04%, 23.2%	
	600	PO <sub>4</sub> <sup>3-</sup>		3.57%	
Brazilian pepperwood	300	NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup>	–	4.12%, 1.85%	Yao et al. (2012)
	450	NO <sub>3</sub> <sup>-</sup>		4.97%	
	600	–		–	
Bamboo	300	NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup>	–	1.98%, 2.21%	Yao et al. (2012)
	450	NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , PO <sub>4</sub> <sup>3-</sup>		2.39%, 16.72%, 5.52%	
	600	PO <sub>4</sub> <sup>3-</sup>		4.37%	
Cacao shell	300	PO <sub>4</sub> <sup>3-</sup>	60 d continuous leaching	1.48 mg/g	Hale et al. (2013)
Corn cob	350	PO <sub>4</sub> <sup>3-</sup>		0.17 mg/g	
Sesame straw	300, 600	PO <sub>4</sub> <sup>3-</sup>	Activated by ZnCl <sub>2</sub>	62.6, 168.2 mg/g	Park et al. (2015)

in agriculture are hundred and thousand times more than biochar. Even a nutrient-rich biochar may release nutrients slowly in the sediment–water system. Nevertheless, a systematic monitoring is needed following application of biochar in sediment system to check any potential chances of the above environmental issues.

In addition to the risk of leaching nutrients that may lead to eutrophication, PTEs, PAHs, EPFRs, dioxins, etc. in biochar may be toxic to aquatic/substrate organisms (Zhou et al. 2021) (Fig. 4). Oleszczuk et al. (2013) found that biochar might have potentially impact on plants (e.g., *Lepidium sativum*), microbes (e.g., *Vibrio fischeri*), protozoa (e.g., *Tetrahymena thermophila*), algae (e.g., *Selenastrum capricornutum*), and crustaceans (e.g., *Daphnia magna*). Among them, crustaceans were the most sensitive to biochar, and the amount of PAHs leached from biochar was significantly and positively correlated with the mortality of *D. magna*. Additionally, biochar had no effect on the germination of plant seeds, but a 10% dosing of willow biochar inhibited the root growth of *L. sativum* by up to 92%. The reason may

be that biochar absorbs substances necessary for symbiotic biochemical exchange, the bioavailability of nutrients is reduced, and the symbiotic relationship between microbes and plants is affected. Buss et al. (2016) also observed that 19 plant biochar barely affected germination of aquatic plants, but significantly inhibited early root growth, with healthy seedlings (roots > 5 mm) reduced to 0–60%. They concluded that biochar leaching of NH<sub>4</sub><sup>+</sup> was toxic to the root system of the plants. Moreover, the presence of large amounts of EPFRs in biochar has been mentioned in 3.1.3, and their production of hydroxyl radicals in the aqueous environment also induces the production of ROS in plant cells and causes oxidative damage to cells (Nidheesh et al. 2021). For instance, Zhang et al. (2019b) found that both *Pinus massoniana* Lamb biochar produced at 300–600 °C pyrolysis temperatures significantly promoted ROS generation in *Streptococcus obliquus* cells, especially the biochar produced at 400 °C induced 134% higher ROS levels than the control. In addition, superoxide dismutase (SOD) content of *Scenedesmus obliquus* was significantly increased when



**Fig. 4** Potential potential negative environmental impacts of biochar application on aquatic/sediment environments. EPFR: environmentally persistent free radicals; ROS: reactive oxygen species

the dosing amount exceeded 200 mg/L, indicating that the oxidative equilibrium of *S. obliquus* was disrupted. Meanwhile, they also noticed the inhibition of chlorophyll-a in *S. obliquus* by biochar prepared at 500 °C up to 89%. This can be explained by the formation of semi-quinone radicals in biochar that act as electron scavengers in humus and plants, thereby affecting the electron transfer chain and hindering plant photosynthesis (Odinga et al. 2020).

### Sediment Microbial Community and Enzyme Activity

Microbial community structure and enzyme activity are significant indicators of changes in sediment microbial ecosystems (Song et al. 2020). Biochar can directly or indirectly affect indigenous microbial community structure and enzymatic activity by altering the physicochemical properties and PTEs, and OPs concentration of the sediment (Fig. 3). Huang et al. (2021b) found that the genes encoding bacterial 16 s rRNA and fungal 18 s rRNA were reduced by 74% and 25%, respectively, in the sediment after 90 d of 50 mg/kg rice straw biochar incorporation. The results of RDA indicated that changes in sediment physicochemical properties, PTEs, and OPs concentrations explained 92% of the variation in microbial community structure. Wang et al. (2021a) investigated the impacts of PTEs on the top 20 dominant genera in urban river sediments and found that more than 50% of the microbes (e.g., *Rhizobium*, *Romboutsia*, *Caldisericum*, *Aeromonas*, etc.) were inhibited by PTEs, with the relative abundance of *Romboutsia* decreased from 5.7

to 2.3%. The potential negative consequences of biochar on sediment microbial communities are attributed to: (i) affecting material cell–cell communication and signaling between microbes (Zhang et al. 2011). (ii) altering the OM content in sediments, which directly affects microbial growth. (iii) leaching of PTEs from biochar inhibits microbes that do not possess PTEs resistance genes. Furthermore, the enzymatic activity in the sediment is sensitive to biochar. Bailey's study (Bailey et al. 2011) showed that the activity of  $\beta$ -glucosidase and the lipase assay decreased by about 20% after the addition of biochar. Huang et al. (2017) found that the activity of invertase and alkaline phosphatase in the sediment decreased to 75% of the control at a biochar concentration of 50 mg/kg. The decrease in enzyme activity could be attributed to: (i) biochar inhibited enzyme substrate reaction by blocking the reaction sites; and (ii) high concentration of biochar increased the pH of the sediment, which inhibited the enzyme activity. In a previous study by Chintala et al. (2014), pH was shown to be negatively correlated with invertase and alkaline phosphatase. Moreover, biochar may also increase the amount of harmful microbes in sediments, which compete with beneficial microbes for nutrients and habitats, thus making sediment remediation much less effective. To reduce the risk of biochar sediment microecology, further clarification of the mechanisms between various biochar and microbial communities and enzymes, specially by conducting long-term experiments, is needed.

## Circumvention Strategy for Mitigating the Potential Negative Consequences of Biochar

Potential adverse effects of biochar in the sediment–water system are possible to avoid or minimize through careful selection of biochar materials and appropriate implementation of remediation methods, risk assessment before application of biochar, follow up monitoring of risks, putting site- and time-specific mitigation strategies in place, and full life cycle assessment of a sediment remediation method. Development of test methods to rapidly assess the potential risks of biochar to plants and organisms in the sediment ecosystem is an area of priority research for sustainable implementation of biochar technologies for sediment remediation.

### Risk Detection and Assessment

#### Risk Detection and Assessment of Sediment Environments

Biochar incorporation might be toxic to some sensitive plants grown in sediments (Gong et al. 2019), thus quantitative phytotoxicity analysis is necessary to determine the safety of biochar. The ratio of organic carbon (OC) to elemental carbon (EC) in biochar was used by Ruzickova et al. to reflect the phytotoxicity caused by organic compounds in biochar.  $OC/EC > 0.1$  indicated the highest level of phytotoxicity, while  $OC/EC < 0.1$  indicated that biochar inhibited plants by less than  $< 30\%$ . Additionally, the ratio of aliphatic organic compounds to aromatic organic compounds (AL/AR) can also be used as an indicator of phytotoxicity (e.g., AL/AR values  $< 0.5$  indicate that aliphatic compounds dominate in biochar toxicity). Moreover, the phytotoxicity of biochar can also be evaluated from a metabolic point of view. Kong et al. (2019) found significant changes in the metabolic profile of wheat after sewage sludge-derived biochar incorporation, with a fourfold decrease in the metabolism of a dozen amino acids compared to the control. The main reason was the enhanced oxidative stress induced by biochar in plants, which led to a down-regulation of amino acid metabolism.

Furthermore, changes in the community structure of microbes, especially sensitive microbes, can be used as a signal for the potential negative consequences of biochar. The 16S/18S rRNA/rDNA sequence analysis technique mainly relies on nucleic acid amplification, cloning and sequencing to determine the direct sequence of 16S/18S rRNA/rDNA in samples to analyze the changes in microbial abundance and community structure (Rochelle et al.

1992). Its main components include phosphorus fatty acid polymorphic analysis (PLFA), polymerase chain-denaturing gradient gel electrophoresis (PCR-DGGE), PCR-SSCP, and fluorescence in situ hybridization (FISH) techniques (Harrison et al. 2021). Hung et al. (2021b) used 16 s rRNA to analyze the effect of sewage sludge biochar on sediment microbial communities, and they found that the abundance of the dominant phylum *Proteobacteria* increased with biochar addition, while the abundance of *Epsilonbacteraeota*, *Synergistetes*, *Planctomycetes*, *Bacteroidetes* had higher relative abundance in the control group than in the treated group. Although there is no quantitative relationship between biochar and microbial community changes, based on the positive response of microorganisms to PTEs and OM, it is promising to use microbial community changes as an indicator of the potential negative consequences of biochar.

#### Risk Detection and Assessment of Aquatic Environments

In contrast to sediment environments, microbial communities in aqueous environments are mobile and stochastic, and therefore the analysis of structure may not be deterministic. Nevertheless, some specific sensitive microbes can be used as indicators of biochar impacts. For instance, Zhang et al. (2019b) detected that the luminescence inhibition of luminescent bacteria (*Photobacterium phosphoreum*) increased with increasing biochar concentration. Fish and algae toxicity tests may be more intuitive indicators. For instance, Vyavahare et al. (2019) used a toxicity assessment of *Oreochromis niloticus* reflecting the effects of biochar treatment of dye wastewater. They observed an increase in intracellular vacuolation in the fish and found that contraction of cartilage support rods resulted in a reduction in gill size. They concluded that the gills of *Oreochromis niloticus* are sensitive to biochar toxicity and can be used as an indicator of toxicity, but quantitative relationships need to be further investigated. The leaching of PTEs and non-degradable organic matter from biochar can also be toxic to aquatic algae. Smith et al. (2013) found that pine wood-derived biochar inhibited both prokaryotes (e.g., *Synechococcus*) and eukaryotes (e.g., *Desmodesmus*), which are important members of aquatic ecological communities. Based on the toxicity of biochar to aquatic algae, Zhang et al. (2019a, b) proposed four quantitative indicators including cell growth (inhibition), ROS content (up-regulation), Chl-a (concentration reduction), and SOD content (up-regulation), through the acute toxicity test of *Chlamydomonas obliqua*. Finally, the biological toxicity of biochar to aquatic algae was determined by the comprehensive evaluation of these indicators.

## Life Cycle Assessment

Due to the benign restoration effects of biochar on sediments and its potential ecological risks, a systematic evaluation of its risks and benefits in complex ecological environments is necessary. Life cycle assessment (LCA) is a method used to assess the potential environmental impact of a commodity (e.g., biochar) throughout its life cycle from raw material acquisition, processing, manufacturing, use, and final disposal (Zhu et al. 2022). LCA is widely used in biochar-associated applications, such as quantitative analysis of carbon sequestration and emission reduction effects, comparative analysis of treatment and disposal options, ecotoxicity evaluation, etc. (Matuščík et al. 2022). It consists of four parts: goal definition and scope, life cycle inventory (LCI), life cycle impact assessment (LCIA), and interpretation (Miranda et al. 2021). The first part determines the purpose of conducting LCA, the depth of detail of the study, and the scope of the framework. The determination of functional units (FU) and system boundaries is critical in this part. The FU is the subject around which all parameters in the LCA revolve, and is usually defined as biomass or product depending on the use of the biochar system. As the purpose of the biochar system is to digest waste biomass, the FU is often defined as the feedstock for the preparation of biochar, while the purpose is to remediate contaminated sediments/soils, the FU is usually the biochar produced (Munoz et al. 2017). Another major aspect of the goal definition and scope is the determination of the system boundary. Although LCA is a start-to-finish process, the starting point differs from different biochar systems, as the feedstock is an energy crop grown for biochar production, then the agricultural process needs to be included in the LCA, but not if the feedstock is waste (Hamedani et al. 2019).

The second part is an iterative and objective quantification of energy and resource use (inputs) and pollutant emissions to the environment (outputs) for the entire LCA process (Chen et al. 2022). This portion of the data used to characterize the system determines the quality and effectiveness of the overall LCA. Although local and system-specific data should normally be preferred, it is practically impossible to collect such data for all the processes included (Puettmann et al. 2020). Therefore, LCA databases are often used to characterize back-end system processes.

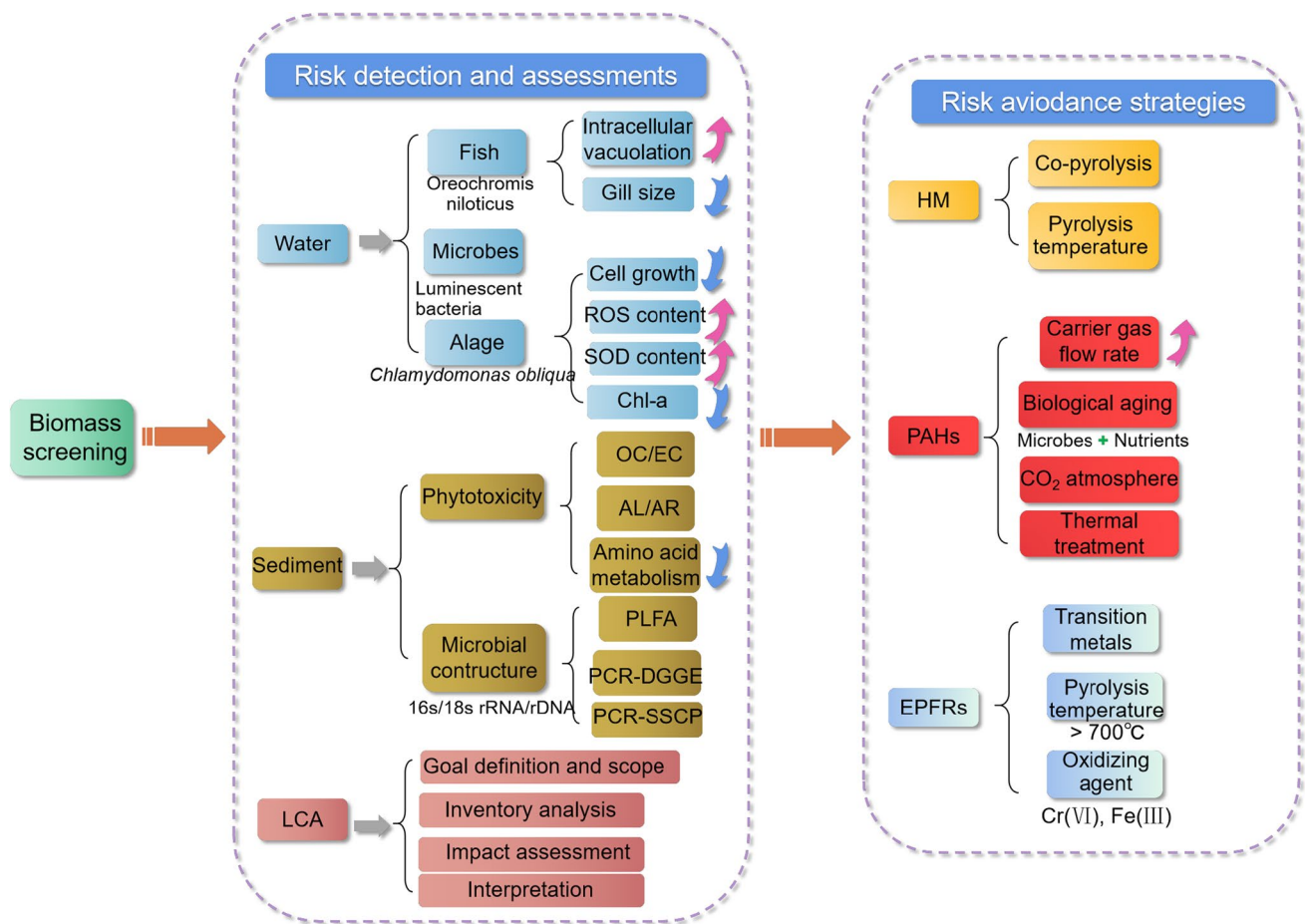
The third part is to analyze the relevance of the data to the environment by classifying, characterizing and normalizing the impact of biochar on human health, natural resources, climate change and ecology through a weighted approach to qualitatively or quantitatively measure the impact. Since the life cycle of different products varies greatly, LCIA is usually automated by LCA software for measurement (Huijbregts et al. 2017). In our search, SimaPro, GaBi and OpenLCA are the more commonly used LCA software, while

the assessment methods are mainly ReCiPe, CML or IPCC (Hamidani et al. 2019).

The last part means summarizing the environmental impact results based on the results of inventory analysis and impact evaluation, identifying the links with high impact, and analyzing the sensitivity and uncertainty (Miranda et al. 2021). Beni et al. (2017) applied the LCA to compare the environmental impacts of four types of sludge biochar (sludge incineration, sludge landfill, and sludge anaerobic digestion, and sludge pyrolysis). The results showed that the total environmental impact of biochar produced by sludge pyrolysis was the lowest, and the aquatic ecotoxicity was reduced by 85% due to the lower migration of PTEs in biochar. Peters et al. used LCA to evaluate the potential negative consequences of biochar on acidification and eutrophication, and the results showed that the degree of acidification and eutrophication increased with increasing biochar production and application. Inventory analysis can be seen as an increase in the amount of biomass to be transported and treated per hectare of water body, which is the main reason for the potential negative consequences of overall risk and benefits. If the assessment process finds that the environmental benefits do not offset the environmental impacts of biochar, then the LCA will produce a potential negative result. For instance, Song et al. (2019) found potentially significant potential negative environmental impacts from biochar in rural areas of the tropics, as LCA showed that high emissions of aerosols from the production process cannot be compensated by carbon sequestration. It is worth noting that although LCA has been widely used in the assessment of the environmental impact of biochar, it still has obvious drawbacks. The results of biochar life cycle depend on the chosen method and the choice of assumptions, but there is a wide range of methods for LCA (e.g., CML, EDIP, ILCD 2016, IPCC, Recipe Mind-point, TRACI, Eco-indicator EE, Ecological Scarcity, IMPACT 2002+, and Recipe End-point). The differences in results resulting from different assessment methods make it difficult to have a systematic and universal assessment system, and causality applicable to all or even most biochar systems require further research to prove (Fig. 5).

## Strategies to Reduce the Contaminant in Biochar

Biomass types and pyrolysis temperature are the key factors affecting the total PTEs concentration and bioavailability in biochar. The PTEs concentration in sewage sludge and animal manures biochar can reach tens or even hundreds of times higher than that in plant biochar (Table 3), and the PTEs bioavailability is also much higher than that in plant biochar. Furthermore, as mentioned in "Heavy Metals" section, the effect of pyrolysis temperature on total PTEs concentration and bioavailability showed a polarization, with a



**Fig. 5** Detection methods and avoidance strategies for potential risks in biochar remediation of sediments

significant increase in total PTEs concentration with increasing pyrolysis temperature, while bioavailability seemed to be higher in biochar pyrolyzed at low temperatures, and considering the balance between these two, we believe that the pyrolysis interval of 500–600 °C is more moderate. Moreover, co-pyrolysis of biomass with low PTEs levels (e.g., bamboo and rice straw) and high PTEs levels (e.g., animal manure and sewage sludge) is a reliable way to reduce the total PTEs load of biochar (Fakayode et al. 2020) (Fig. 6a). Meng et al. (2018) found that mix the rice husk with pig manure (3:1, w/w) via a co-pyrolysis process at 600 °C, in which the concentrations of Cu and Zn were reduced to 32.7% and 24.5% of the single pig manure biochar, respectively, and the bioavailability of Cu was reduced to 20% of the original. Jin et al. (2017a) mixed bamboo sawdust with sewage sludge (1:1, w/w) and pyrolysis at 400–600 °C, and they found that the total PTEs concentration in the co-pyrolyzed biochar was reduced by about 50%, especially at a pyrolysis temperature of 600 °C, which resulted in the highest stability of PTEs and the lowest ecological risk in the biochar. Therefore, mixing raw materials with low and

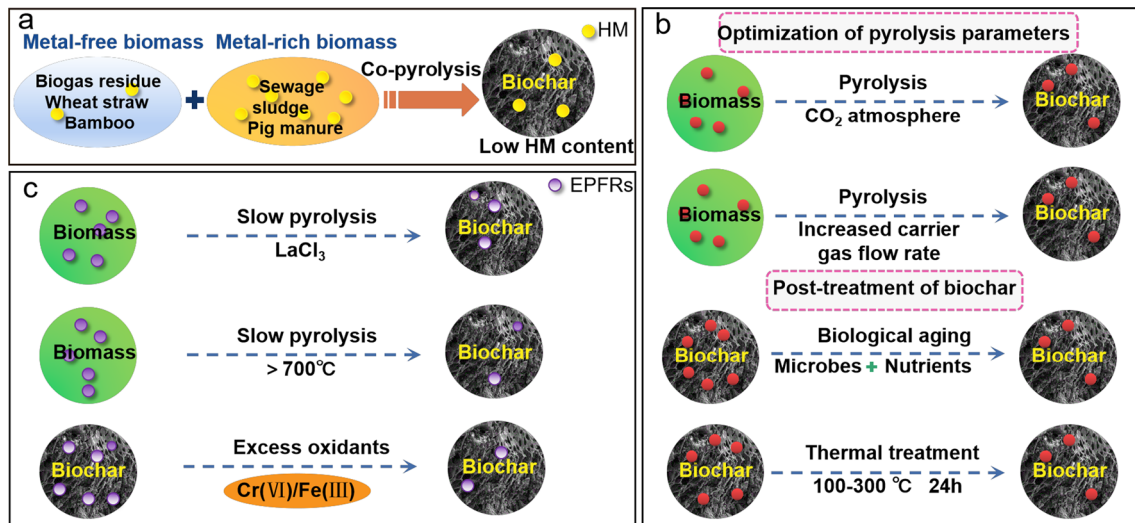
high PTEs contents is an effective method to reduce PTEs concentration and bioavailability of biochar.

Pyrolysis conditions and carrier gas flow rates are critical to control the concentration of PAHs (Fig. 6b). Hale et al. (2012) found that in a systematic study of more than 50 biochar, the concentration of PAHs in slow pyrolysis biochar was 0.07–3.27 mg kg<sup>-1</sup>, while that in biochar produced by fast pyrolysis was 23–45 mg kg<sup>-1</sup>. Fabbri et al. (2013) found that the introduction of 0.67 L/min of carrier gas (CO<sub>2</sub>) during biochar pyrolysis process reduced the PAHs in straw biochar by 92%.

Furthermore, post-treatment of biochar is another pathway that has a role in reducing the total concentration and bioavailability of PAHs (Fig. 6b). Kołtowski et al. (2015) conducted a thermal post-treatment of miscanthus, willow, and wheat straw biochar at 100–300 °C for 24 h, and the results showed a 33.8–100% reduction in the PAH concentration. Additionally, microbial degradation and photo-oxidation are natural processes that degrade PAHs in biochar. Nguyen and Lehmann (2009) found that aging of biochar in the presence of microbes and nutrients was

**Table 3** Dominant pollutants of biochar from different biomass and production temperatures

Biomass types	Biomass	Temperature (°C)	Dominant pollutants	Total concentration (mg/kg)	Leaching concentration (mg/kg)	Bioavailability	Reference
Plant	Rice straw	300	Cu, Cd, Pb	18.61±0.87, 1.09±0.1, 6.91±0.72	-	7.72±0.31, 0.67±0.03, 5.57±1.03	Xu et al. (2022)
		500		26.57±0.91, 1.44±0.14, 9.43±0.82		3.46±0.31, 0.76±0.03, 7.25±0.27	
	700		32.66±0.75, 0.62±0.02, 6.30±0.41		7.70±0.10, 0.16±0.02, 5.00±0.24		
	900		41.92±1.13, 0.19±0.01, 4.14±0.19		12.04±0.70, 0.07±0.01, 3.42±0.46		
Sewage sludge	Miscanthus	500	Zn, Pb, Cr	102.00, 22.30, 18.05	-	-	Oleszczuk et al. (2013)
	Wicker	350	Zn, Pb	21.60, 32.90	-	-	Assirey and Altamimi (2021)
	Corn	450	Pb	8.72, 11.53	-	-	Wang et al. (2019c)
Sewage	Textile dyeing sludge	300	Zn, Mn	10,400.17±97.21, 1859.43±20.75	1559.51, 715.92	41%, 42%	
		500		12,550.41±93.04, 2256.54±52.01		30%, 39%	
	700		14,109.92±91.39, 2525.01±72.13		16%, 23%		
	350	Zn, Cu, Cr	2059.72±18.75, 134.67±4.74, 110.59±5.79	401.21, 8.04, 1.01	-	Wang et al. (2021b)	
Sludge	Sewage	550		2602.93±17.58, 169.93±3.66, 142.90±3.89	208.16, 3.38, 0.02		
		750		2763.47±13.94, 178.91±2.55, 150.93±7.12	165.78, 7.12, 0.02		
Animal manures	Cow manure	500	Zn, Cu	434.90±4.27, 718.55±3.50	-	40%, 69%	Zhang et al. (2020)
	Swine manure	350	Zn, Cu, Mn	1052.16±20.92, 1200.66±25.71, 867.87±17.65	112.56, 285.12, 332.16	82%, 61%, 71%	Zeng et al. (2018)
Goat manure		500		1203.60±21.03, 1358.15±5.75, 1015.69±20.01		70%, 58%, 69%	
		700		1226.37±22.74, 1463.70±27.69, 1034.10±19.14		67%, 49%, 62%	
		500	Zn, Mn	181.32±6.91, 1077.81±15.32	15.28, 361.92	85%, 76%	
		700		200.56±8.52, 1271.54±10.13, 222.97±8.49, 1387.91±14.23		80%, 73%, 60%, 56%	



**Fig. 6** Co-pyrolysis of metal-rich biomass and metal-free biomass to reduce PTEs content in biochar (a). Strategies for the production of biochar with low-PAH levels through optimization of pyrolysis

parameters and post-treatment of biochar (b). Strategies for mitigating EPFRs in biochar (c)

able to reduce the total PAHs concentration by 12–100% and bioavailability by 30–100%. Oleszczuk et al. (2018) also found that aging wheat straw and elephant grass biochar at  $-20$  to  $70$  °C for 420 days reduced the total PAHs concentration and bioavailability by 25–50.2%. Overall, optimizing pyrolysis parameters and increasing biochar post-treatment are effective ways to reduce the risk of PAHs.

The stability and persistence of EPFRs in biochar are closely related to the transition metal. For instance, EPFRs can persist for several years when ZnO nanoparticles are used as transition metals (Vejerano et al. 2018). In contrast, lanthanum incorporation during the pyrolysis process was able to reduce the amount of EPFRs in the biochar thereby reducing phytotoxicity (Li et al. 2017). In addition, Zha et al. used high levels of oxidants (e.g., Cr(VI) and Fe(III)) to reduce the content of EPFRs in rice husk-derived biochar by about 34% due to the depletion of the synthesized EPFRs during the reduction of Cr(VI) and Fe(III).

Moreover, high pyrolysis temperatures ( $> 700$  °C) can destroy the precursors of EPFRs in biochar, thus reducing their content (Fig. 6c). Qi et al. found that the concentration of EPFRs in biochar increased from  $2.77 \times 10^{18}$  spins/g to  $17.20 \times 10^{18}$  spins/g when the pyrolysis temperature of rice husk was increased from  $300$  to  $500$  °C, but when the pyrolysis temperature was increased from  $500$  to  $700$  °C, the concentration of EPFRs increased from  $17.20 \times 10^{18}$  spins/g to  $6.16 \times 10^{18}$  spins/g. Overall, controlling transition metals, increasing pyrolysis temperature and dosing oxidants are effective ways to limit the content of EPFRs in biochar.

## Conclusions and Outlook

Biochar is capable of remediating contaminated sediments through a series of physicochemical actions such as electrostatic adsorption, ion exchange, surface complexation, and biodegradation. However, biochar prepared from some wastes has its environmental disadvantages, posing potential risks to water–sediment systems and affecting indigenous microbial communities when added. In view of the potential negative consequences of biochar, targeted monitoring and avoidance measures are being proposed for specific potential risks, with the aim of eliminating possible dangers while embracing the environmental benefits from biochar. To clarify the complex linkages and unpredictable chemistry that exist between biochar and contaminated sediments, further research is required with focus on the following areas.

Biochar produced from different biomass and pyrolysis temperatures has different physical–chemical properties and pollutant contents, and has different remediation effects on different types of sediments. To accurately and rapidly screen specific biochar for different types of contaminated sediments, a database of feedstocks, preparation conditions, physical–chemical properties, functions and types of contaminated sediments can be established.

The interactions of biochar with various environmental media in the biosphere and the overall potential negative environmental impacts of biochar on the entire ecosystem need to be further explored. The integrated mechanisms of the potential negative environmental impacts of biochar at the micro-cellular and molecular levels also need



to be further investigated to facilitate the use of sensitive microbes as indicators for predicting potential risks of biochar.

Clarifying the quantitative relationship between production factors and potential ecological risks in the process of biochar from feedstock selection to treatment and disposal is valuable for the application of biochar. LCA can be used to assess the potential environmental risks of biochar.

Most current experiments using biochar for sediment remediation are limited to laboratory or pilot-scale, and few studies consider field conditions. Thus, practical application of biochar to actual wastewater/sediments should be carried out so that data can be obtained to further explore the practicality and treatment costs of biochar.

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**Data availability** All the data and graphs presented in the article are quotable.

## Declarations

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