

1    **Potential hazards of biochar: the negative environmental impacts of biochar**  
2    **applications**

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## **Abstract**

Biochar has been widely used as an environmentally friendly material for soil improvement and remediation, water pollution control, greenhouse gas emission reduction, and other purposes because of its characteristics such as high surface area, porous structure, and abundant surface oxygen-containing functional groups. However, certain effects of surface properties (i.e., the composition of organic functional groups, content of inorganic composition, and changes in pH) as well as chemical reactions (e.g., aromatic carbon ring oxidation) that occur with biochar in its applied environment may result in the release of harmful components into the environment. In this study, biochars with a potential risk to the environment were classified according to their harmful components, surface properties, special structure, and particle size, and the potential negative environmental effects of these biochars and the mechanisms inducing these negative effects were reviewed. This article presents a comprehensive overview of the systemic negative environmental impacts of biochar on soil, water, and atmospheric environments. Moreover, this review summarizes various technical methods of environment-related risk detection and evaluation of biochar application, thereby providing a baseline reference and guiding significance for future biochar selection and toxicity detection, evaluation, and avoidance.

**Keywords:** Activated carbon; Negative impacts; Influence mechanisms; Risk detection; Life cycle assessment (LCA); Avoidance measures

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## 1. Introduction

With the ever-increasing global population, it is necessary to seek efficient, environmentally friendly, sustainable, and economically feasible solutions to solve the pressing global problems of environmental pollution, food security, and resource and energy shortages [1-3]. In recent years, biochar has been widely applied for soil improvement [4, 5], agricultural production [6, 7], greenhouse gas (GHG) reduction [8, 9], water pollution treatment [10, 11], waste management [12, 13] and other purposes (Fig. 1) because of its high surface area, rich pore structure, and relatively high structural stability. Although biochar has been widely regarded as an environmentally friendly soil amendment, harmful components (heavy metals, polycyclic aromatic hydrocarbons (PAHs), environmentally persistent free radical (EPFR), dioxins, and perfluorochemicals (PFCs)) may produce because of the improper selection of biomass feedstocks, preparation conditions, and preparation methods (Table 1). Recent studies have turned their attention to the negative environmental effects owing to its potentially harmful components and various interactions with the environment [14, 15].

Meanwhile, the evolution (aging) of biochar in environmental processes may produce negative effects in the media by changing its properties, which not only affects the media itself, but also has a certain impact on the media interface [16, 17]. A soil–water–gas cycle is possibly induced during biochar transportation [18]; that is, the following transport processes may occur with biochar: from soil to water due to migration and leaching, from water to soil due to runoff, from soil to atmosphere due

to wind erosion and weathering, and finally from atmosphere to soil or water due to free settlement and precipitation [19-21]. Therefore, it is imperative to systematically discuss the negative environmental effects of biochar from the perspective of the media to avoid possible risks.

Previous reviews and studies on biochar have mainly focused on the modification of biochar [22], reaction mechanisms [13], and the active role of biochar in environmental remediation [23]. However, the negative effects and potential risks of biochar have only recently been highlighted. For example, Zhang et al. [3] and Lian et al. [24] briefly mentioned certain environmental risks of biochar in their commentaries; however, the comprehensive phenomena and mechanisms require elucidation. Similarly, Godlewska et al. [25] reviewed the potential environmental risks of biochar in a single environmental media (soil); however, the potential hazards of biochar to water and the atmosphere, as well as the comprehensive effects between the different medium, must be investigated. Meanwhile, the utilization of life cycle assessment (LCA) to assess the negative impact of biochar has recently been focused on [26, 27], which should be summarized and reviewed for research guidance. Therefore, the overall potential risks of biochar application in soil, water, and the atmosphere remain to be comprehensively studied to determine the corresponding occurrence, detection, assessment, and avoidance measures of these risks.

## **2. Negative impact potential of biochar**

Considering the harmful components, structure, and particle size of biochar, the

negative effects of biochar application to the environment should not be ignored. In this section, the mechanisms that induce these negative effects are discussed.

## **2.1. Harmful components of biochar**

### **2.1.1 Internal harmful components of biochar**

Based on the information in existing studies [28-31], this section describes the primary environmentally harmful substances in biochar (heavy metals, PAHs, dioxins, EPFRs, PFCs, and volatile organic compounds [VOCs]). Most of the cited articles are laboratory-scale studies; however, the amount of biochar typically used in such experiments is close to the actual amount that would be used in environmental remediation; moreover, actual water or soil was used in the laboratory experiments or formulated by chemical reagents. It should be noted that, because of the experimental conditions, the application time in most studies was usually shorter than that in field experiments. Under laboratory conditions, although the actual remediation amount of biochar may have negative environmental impacts over a relatively short period of time and could be reduced or degraded in the long term [32], these phenomena are correlated with actual field remediation conditions. Therefore, these laboratory-scale studies have high field relevance.

#### **a) Heavy metals**

The content and bioavailability of heavy metals in biochar varies with biomass type. When biomass with high heavy metal content is used, the resulting biochar may increase the environmental heavy metal content because of processes such as leaching.

*Miscanthus*, an energy crop, is often growing in soils fertilized with sewage sludge or wastewater and shows a high accumulation of trace metals. Therefore, *Miscanthus*-derived biochar, if applied, shows higher hazardous metal content than others and potential high metal leaching to the environment [33]. von Gunten et al. [34] found that the heavy metals in wood biochar (derived from pin wood chips, bamboo, or oak) with higher heavy metal content (e.g., Zn and Mn) may mainly exist in the form of monovalent and divalent cations. Therefore, these heavy metals are weakly adsorbed in the biochar matrix and are easily released, even under mild conditions (such as irrigation) [35]. Meanwhile, wood-derived biochar possesses a high surface area (180–270 m<sup>2</sup>/g) and therefore a higher heavy metal concentration in the exchangeable/acid-soluble fraction (sometimes more than 50% of the total), thus leading to higher bioavailability of heavy metals [34]. In addition, controlling the pyrolysis temperature is important for the heavy metal content in biochar. For example, Devi and Saroha [36] found that the contents of Cu, Pb, and Zn in biochar increased significantly with an increase in temperature, and when the pyrolysis temperature increased from 200 to 700 °C, the contents of the three metals increased by 61%, 73%, and 65%, respectively. This is mainly because as the temperature increases, the organic matter present in the biomass decomposes, which in turn leads to the release of heavy metals bound to the organic matter. Regarding the relationship between pyrolysis temperature and the bioavailability of heavy metals, it has been found that the bioavailability of heavy metals in biochar may decrease with increasing pyrolysis temperature [36]. The

144 environmental risk of heavy metals in biochar not only depends on the heavy metal  
145 content and pyrolysis temperature, but also on other factors, including the Ph, existing  
146 forms of heavy metals, mineral structures, and the applied environment. Devi and  
147 Saroha [36] reported a contrasting effect of pH on the leaching capacity of heavy metals  
148 in sludge biochar. The heavy metals in biochar showed maximum leaching ability at  
149 pH 3, owing to the fact that low pH conditions generally enhance metal dissolution. As  
150 the pH of the solution increased from 3 to 7, the leaching amount decreased. A further  
151 increase in the solution pH from 7 to 13 led to an increase in the leaching of heavy  
152 metals, especially the enhanced leaching ability of Cr at higher pH values. This might  
153 be because the leached Cr reacted with CaO to form  $\text{CaCrO}_4$  after carbonate  
154 decomposition [37]. Meanwhile, the environmental media may change the forms of  
155 heavy metals in biochar, which may lead to changes in the potential risk degree of the  
156 biochar. Studies have shown that the environmental risks in different forms of heavy  
157 metals are in the order (from high to low) of: the carbonate-bound state, iron-manganese  
158 oxide-bound state, organic matter, sulfide bound state, and residue lattice state. When  
159 alkaline biochar with a high level of heavy metal content (higher content of acid-soluble  
160 or exchangeable parts) is used in acidic soil media, Cd, Zn, Pb, and Cu in the biochar  
161 may be activated and converted from a low-risk (e.g., residue state) to a high-risk  
162 binding state (e.g., carbonate binding state) [38]. This is mainly because with the  
163 decrease in soil pH, the free metal components of heavy metals in the soil, the reciprocal  
164 action, and the plant's contact and absorption toward heavy metals may all increase



[39]. Therefore, the type of biomass feedstock and pyrolysis temperature should be correctly selected when producing biochar to reduce the heavy metal content in biochar as much as possible (Table 1). If the application of biochar with a high heavy metal content in the environment cannot be avoided (Table 2), it is necessary to systematically consider the relationship between biochar and the environmental media, such as the soil pH mentioned above, to minimize the environmental risks of biochar due to the presence of heavy metals. It is true that there are some contradicting results. Changas et al. [40] reported that when using sludge biochar with a high amount of heavy metal components, heavy metal leaching in the environmental media was measured using diethylenetriamine pentaacetate, and it was found that the heavy metal leaching amount was lower than the highest limit of the international standard. This may be because the biomass component has a bonding reaction with the high-concentration metal component during the char formation process, resulting in the formation of a metal-carbon/metal-oxygen-carbon bond structure [41], which stabilizes the morphology of heavy metals and makes it more difficult for them to leach out. However, to review the potential risks of biochar as thoroughly as possible, it is worth noting that this relatively stable combination may also be a potentially risky environmental pollutant [42].

#### b) PAHs

Polycyclic aromatic hydrocarbons, with high biotoxicity, contained in biochar can influence the survival of plants and microorganisms in different environmental media. In the literature, the PAH content in biochar prepared from biomass was different under

different production conditions (such as temperature) (Table 3). Moreover, the PAH content in biochar from different feedstocks is naturally different; biochar obtained from hemp had a higher content of mutagens than did biochar from wood [43]. Since there are relatively few PAH precursors in plant biomass, light naphthalene primarily exists as PAHs in biochar produced from plant biomass-dominated feedstocks. In addition, Hale et al. [29] conducted a quantitative analysis of PAHs in more than 50 biochars by slow pyrolysis (characterized by slow heating on the order of minutes to hours of organic material to ~400 °C in the absence of oxygen, and with relatively long solids and gas residence times, typically several minutes to hours) between 250 and 900 °C. It was found that compared with the total concentration of PAHs in fast pyrolysis and gasification biochar, the total concentration of PAHs in slow pyrolysis biochar was lower. Flash evaporation also increased the PAHs content of biochar. Meanwhile, the content of PAHs in biochar generally decreases with an increase in pyrolysis time and temperature. Hale et al. [29] reported that the PAH concentration of pine wood at 900 °C was significantly lower than that at all other production temperatures (except at 600 °C). This is because the  $\pi$ - $\pi$  interactions between PAHs and biochar would be disrupted with an increase in pyrolysis time and temperature. Additionally, with the increase in pyrolysis temperature, the release of Ca, Al, and Ba in the biochar also increased, which was conducive to the leaching of PAHs. The leaching of PAHs occurs because of the destruction of hydrophobic organic compounds (HOCs)–(metal ion)–mineral bonds, thereby improving the release of HOCs and HOC-

bound PAHs; moreover, the extent of metal cross-linking in biochar is reduced during the leaching process, resulting in the diffusion of PAHs through the internal matrix, thereby accelerating the desorption of PAHs [44, 45]. Chen et al. [44] evaluated the leaching behavior of PAHs in biochar derived from sewage sludge pyrolyzed at different temperatures (300–700 °C). The total concentration of PAHs in the leachate reached its peak of 11.75 µg/L at 700 °C, which is equivalent to 15.9% of the total PAHs in the biochar. Rombolà et al. [46] proposed that almost 1 year after the last biochar application, the total PAH concentrations in the amended soils ( $153 \pm 38$  ng/g) were significantly higher than those in the control soil ( $24 \pm 3$  ng/g). Similarly, Quilliam et al. [32, 47] found that the concentration of 16 United States Environmental Protection Agency (US EPA)-priority PAHs in a three-year soil amended with wood-based biochar (50 t/ha) was 1,953 µg/kg, which was observably higher than that of the control soil (1,131 µg/kg). This phenomenon occurs because plants actively or passively release root secretions, which enhance the release of PAHs in biochar by changing the surface structure of biochar or dissolving solid organic matter combined with PAHs [48]. For the environmental risk of PAHs, its bioavailability is more important and is mainly affected by the pyrolysis temperature and biomass of the raw materials. Some researches reported that biochar produced at low pyrolysis temperatures may contain a high content and bioavailability of PAHs [29] (Table 3). Moreover, other studies found that among various biomasses, the PAHs (mainly 3-ring PAHs) produced from sludge have the highest bioavailability (37–126 ng/L) and generally appear at 500–600 °C [29].

### c) Dioxins

Harmful components, such as dioxins, may also be produced during the preparation of biochar [49]. Therefore, the preparation conditions are the key factors affecting the amount of dioxins in biochar. Hale et al. [29] quantitatively studied the dioxins (130 toxic and non-toxic dioxins) of more than 50 types of biochars (derived from food waste, digested milk fertilizer, pine wood, and pine) through slow pyrolysis between 250 and 900 °C, with concentrations ranging from 84 to 92 ng/kg. Food waste, which often has a high salt content, has been shown to contain significant amounts of dioxins [50]. Additionally, the selection of the pyrolysis temperature of biochar has a certain influence on the formation of dioxins. Although the dioxins will be destroyed when the production temperature is >1000 °C, the energy consumption will increase significantly. Therefore, the initial biomass feedstocks should have sufficiently low Cl contents to prevent the formation of detectable levels of dioxins [51]. However, the use of dioxin concentrations alone is not a direct indication of the environmental risk of dioxins, as such risk is usually expressed by the toxicity equivalency quotient (TEQ). The limits established by the International Biochar Initiative and European Biochar Certificate for dioxins in biochar were 17 and 20 ng/kg TEQ, respectively. Lyu et al. [30] discovered that the concentration of dioxins was 50–610 pg/g in wood-chip-derived biochar produced at 250–700 °C, and the TEQ concentrations were significantly lower (1.79.6. Hale et al. also observed the highest TEQ concentration (1.2 pg/g TEQ) in biochar derived from food residues at 300 °C [29]. The bioavailable

content of dioxins was below the detection limit; therefore, the dioxins in biochar generally have a low level of pollution. However, it should be acknowledged that environmental contamination can still occur under circumstances with repeated application of biochar containing these compounds.

#### d) EPFR

A very strong EPFR signal can be detected in biochar, which is usually  $10^{18}$  unpaired spins per gram [52]. These EPFRs are widely involved in environmental processes during the production and large-scale application of biochar [53]. During pyrolysis, the organic components of biomass are thermally decomposed, and both the type of raw materials and carbonization conditions contribute to the formation of EPFRs in the process. Lignin, cellulose, and hemicellulose are the main precursors of EPFR formation in biochar (Fig. 2a) [42]. Since there are two possible cleavage positions in the cellulose chain, free radicals may be formed through the uniform cleavage reaction of the chain [54]. Compared with cellulose hemicellulose, lignin has a tighter structure. Thus, cellulose undergoes a strong decomposition reaction, in which the gradual reaction of EPFR is included [55]. Compared with non-wood and hardwood lignin, softwood lignin contains more G-type subunits and a phenylcoumaran structure, which contains a weak  $\alpha$ -aryl ether bond, leading to the production of more free radicals under the same conditions [56]. Therefore, more attention should be paid to the potential environmental risks of EPFR in the application of biochar, especially softwood-derived (e.g., *Douglas fir*) biochar. In addition, EPFRs can be produced from

270 biochar residues in the environment. This process occurs mainly because of the  
271 presence of transition metals, such as  $\text{Fe}^{2+}$  [57]. Transition metals are usually transferred  
272 onto biomass through chemical adsorption during pyrolysis and then continue to  
273 transfer electrons from the polymer to the metal center, leading to the formation of  
274 EPFRs [58]. Lignin and cellulose in biomass may be decomposed to form aromatic  
275 molecular precursors during pyrolysis and converted into EPFRs after exposure to air.  
276 In addition, a stable EPFR could be generated directly without precursors at high  
277 pyrolysis temperatures (Fig. 2a) [59]. In addition to the influence of the type of biomass  
278 on the EPFR content in biochar, the EPFR signal intensities increased with an increase  
279 in pyrolysis temperature [60]. This indicated that the increase in pyrolysis temperature  
280 (200–500 °C) caused the formation of EPFRs in the biochar. When the pyrolysis  
281 temperature was further increased to 600 °C, the organic compounds in the biomass,  
282 which are the main components required for forming EPFRs, were found to decompose  
283 [31, 61]. Moreover, the concentration of EPFRs in the biochar increased at higher  
284 temperatures. Considering the binding ability of environmental media (especially soils  
285 with high complexing/binding capacity), the total concentration of EPFR cannot  
286 directly represent its toxicity index; however, the bioavailability of EPFR should be  
287 used as an index for toxicity assessment. In addition, Maskos et al. [59] found that the  
288 free radicals produced by the biochar obtained at a high temperature of 450 °C had a  
289 stronger environmental sustainability than those produced by biochar obtained at  
290 320 °C. This suggests that the pyrolysis temperature not only affects the free radical

content in biochar, but also affects the environmental sustainability of free radicals. Accordingly, the importance of pyrolysis temperature in biochar production should be determined.

Through a study of relatively persistent free radicals similar to EPFRs, it was found that the stability of the properties of biologically active free radicals is due to their long-term presence on the surface of particulate matter in the atmosphere [62], which is the result of redox reactions under atmospheric conditions [63]. Hence, EPFRs in biochar are stable on the surface of transition metals and can persist in the atmosphere [42]. Environmentally persistent free radicals in biochar may pose a potential environmental risk because they can induce the formation of reactive oxygen species (ROS) with high phytotoxicity and cytotoxicity within the environmental media (Fig. 2c) [64]. The internal mechanism of ROS production induced by EPFRs can be explained by the semiquinone hypothesis, which states that semiquinone radical anions react with molecular oxygen to form superoxide, which then reacts with biological reduction equivalents (such as nicotinamide adenine dinucleotide phosphate and ascorbate) to form disproportionation to hydroxyl peroxide [65]. Moreover, the biotoxicity and cytotoxicity of EPFRs may be related to induced oxidative stress, which leads to cell cancer and even death [60, 66]. Balakrishna et al. [67] found that EPFRs significantly increased ROS production in BEAS-2B cells and reduced cellular antioxidants, ultimately leading to cell death. In this way, the ratio of oxidants and antioxidants may become imbalanced owing to the ROS content induced by EPFRs,

thereby leading to cell death [66, 68]. Meanwhile, the ROS induced by EPFRs may also react with macromolecules (e.g., glycoproteins), leading to membrane instability, which further results in cell apoptosis [42]. Zhang et al. [31] used pine needle-derived biochar to explore its biotoxicity to aquatic algae. The results showed that EPFRs in the biochar induced not only the production of acellular ROS (e.g.,  $\cdot\text{OH}$ ) in water (Fig. 2b), but also the production of intracellular ROS in aquatic organisms. Therefore, the levels of ROS and superoxide dismutase (SOD) activity in algae cells were both upregulated, leading to oxidative damage.

#### e) Other contaminants

In addition to the typical pollutants mentioned above, which are often noticed and discussed, there may be other environmentally harmful substances in biochar due to the different types of raw materials. For example, PFCs are persistent pollutants with high resistance to both chemical and thermal degradation [69]. Kim et al. [70] studied the pollution of perfluorooctane sulfonic acid (PFOS) and perfluorooctane acid (PFOA) on plant residues and biochar of sewage sludge. It was found that the total residual concentration of PFOA and PFOS in the sludge biochar was 15.8-16.9 ng/g, and the total residual concentration of PFOA and PFOS did not decrease significantly after pyrolysis. On the other hand, these perfluorocarbons are not found in plant-derived biochar. Additionally, bio-toxic VOCs are potential environmental pollutants in biochar. For instance, Spokas et al. [71] tested the VOC content in biochar produced from more than 30 material types under different conditions and found that acetone, benzene,



333 methyl ethyl ketone, toluene, and methyl acetate were identified in more than half of  
334 the biochars. Buss et al. [72] also observed that the re-condensation of VOCs occurred  
335 during the preparation of biochar from pyrolyzed cork, which in turn resulted in a higher  
336 VOC content.

### 337 **2.1.2 External pollutants adsorbed onto biochar**

338 After biochar is applied to the environmental media, it undergoes physical,  
339 chemical, and biological actions during contact with various parts of the media to  
340 promote aging, which causes the characteristics of biochar to change significantly [73].  
341 The physical aging process of biochar mainly refers to the fact that it is affected by  
342 various physical factors after entering the environment. For example, owing to wear,  
343 impact, or wind effects, biochar may shrink in size after entering the environment.  
344 Compared to woody plant biochar, herbaceous plant biochar is more susceptible to such  
345 physical forces [74]. Under the action of these physical conditions, large pieces of  
346 biochar may be broken, thus exposing more surface area, which is beneficial to both  
347 the chemical and biological aging processes [75]. Chemical aging mainly refers to the  
348 process in which the chemical structure (property) of biochar changes due to chemical  
349 oxidation after application within the environment [76]. Through the analysis and  
350 summary of the literature, it was found that oxidants could violently oxidize biochar,  
351 which causes its surface structure to change and oxygen-containing functional groups  
352 (hydroxyl, nitro, and carboxyl) to be generated [77]. Biological aging mainly refers to  
353 the process by which microorganisms use biochar as a substrate for oxidative

respiration and other life activities [78]. During this process, extracellular enzymes are secreted from microorganisms, which leads to the breakage of the C-C bonds of the aromatic structure of biochar, resulting in the degradation of biochar [79].

Notably, the aging process of biochar is extremely complex. In the natural environment, due to the synergistic effects of physical, chemical, and biological aging effects, the physical and chemical properties of biochar as well as its influence on the environmental media change dynamically. The three main points of this process are described here:

(1) Theoretically, the increase in oxygen-containing functional groups on the surface of the aged biochar strengthens the ion exchange with heavy metals [76, 80]. However, the surface functional groups of biochar under low pH conditions are easier to dissociate than under high pH conditions, and this effect is more obvious in aged biochar. Meanwhile, in the relatively low pH range (3.3–5.0), the more easily dissociated functional groups (such as carboxyl) play a major role in the adsorption of certain heavy metals (such as Cu) on biochar, which weakens the adsorption capacity of heavy metals [81]. Therefore, it is necessary to comprehensively consider the pH of the media and the internal mechanism of the adsorption of different heavy metals by the biochar when determining the changes in the adsorption capacity of the aged biochar for heavy metals. In addition, under the acidic conditions formed by aging, some heavy metal ions (such as Cr) undergo a reduction reaction and exist in the form of precipitates [82], thereby reducing the amount of biochar adsorbed;

375 (2) PAHs are adsorbed onto biochar through the  $\pi$ - $\pi$  interaction between the benzene  
376 ring of PAHs and the aromatic carbon structure of biochar. However, during the aging  
377 process of biochar, aromatic carbon rings rich in  $\pi$ - $\pi$  electrons become oxidized [17].  
378 Therefore, aged biochar may also cause the release of organic pollutants originally  
379 adsorbed onto the biochar, causing secondary environmental pollution;

380 (3) Aged biochar is more prone to biodegradation or physical decomposition, resulting  
381 in the release of a series of biochar components (e.g., dissolved organic matter and  
382 soluble carbon black) and endogenous pollutants (e.g., heavy metals) [83-86]. For  
383 example, Cui et al. [15] found that aging can activate heavy metals in biochar, which  
384 could improve the leaching rate and bioavailability of heavy metals, with potential  
385 environmental risks. In that study, biochars with high, medium, and low heavy-metal  
386 contents were aged using dry-wet and freeze-thaw aging methods. After dry-wet and  
387 freeze-thaw aging, the concentrations of bioavailable (acid-soluble) Cu and Cd  
388 increased, especially in the biochar with high intrinsic metal concentration and high  
389 heavy metal content. The occurrence of this phenomenon can be explained in several  
390 ways. Initially, aging increases the specific surface area and pore volume of biochar,  
391 which in turn increases the exposure of endogenous heavy metals to the environment,  
392 resulting in the release of endogenous metals from biochar. In addition, owing to the  
393 increase in CO<sub>2</sub> adsorption and acidic functional groups during the aging process, the  
394 pH value of biochar decreases [87]. Then, endogenous heavy metals combined with  
395 organic carbon may be released due to the decomposition of unstable organic carbon

(dissolved organic carbon) and its mineralization [88]. In addition, different types of metals are activated in different ways. The activation of endogenous Cu is mainly related to the composition of organic functional groups in biochar, while the activation of Cd is mainly influenced by changes in the inorganic components and pH of biochar. Meanwhile, the increase in the leaching and bioavailability rates of endogenous heavy metals in biochar of different aging methods also differ. For example, freeze–thaw-aged biochar has higher Cu and Cd leaching rates than does dry–wet-aged biochar. Both wet–dry and freeze–thaw aging increase the available Cu content, while only increasing the available Cd in the biochar with a medium-level heavy metal content [15]. Therefore, based on the above reasons, the fate and potential pollution risks of biochar must be considered prior to the application of biochar-based environmental remediation.

## **2.2. Micro-/nano-dimensions of biochar**

The particle sizes of micro-biochar (MB) and nano-biochar (NB) are mainly smaller than 1  $\mu\text{m}$  and 100 nm, respectively. Based on the source of MB/NB in the environment, MB/NB existing in environmental media can be divided into two categories: (1) primary MB/NB, which is produced indeliberately during the preparation process or specially prepared in the laboratory through grinding, ultrasound, and other treatments; and (2) secondary MB/NB, which is produced by the interaction of bulk biochar under different environmental conditions after being applied to the environment [89]. In terms of structural characteristics, the oxygen content of MB/NB formed by ultrasonic treatment was 19.2–31.8% higher than that of the original

structure. Although MB/NB shows better dispersion in water, MB/NB with a less aromatic structure exhibits decreased carbon stability [90].

The presence of MB/NB could promote the release of heavy metal ions into the media when applied to soil. Kim et al. [91] observed that biochar particles with a particle size of less than 0.45  $\mu\text{m}$  could increase the release and mobility of arsenic in soil. Moreover, the co-migration ability of biochar with heavy metals is affected by the feedstock. Song et al. [92] reported the pollutant co-migration abilities of biochar produced by nine types of biomass and found that, compared with urban-derived MB/NB, plant-derived MB/NB contained more fused aromatic rings and functional groups. It was also found that plant-derived MB/NB showed high potential for the co-transportation of pollutants (such as  $\text{Cd}^{2+}$ ). Contrary to the positive effect of biochar in maintaining soil fertility, MB/NB promotes the loss of phosphorus in alkaline soil by mediating the retention and migration of P (Fig. 4b), which leads to a decline in soil fertility. This could be explained by the fact that P could form P-Fe/Al soil colloids through electrostatic attraction and ligand adsorption in the soil [93], which promotes the release of P-Fe/Al soil colloids and their migration to the groundwater system. More importantly, MB/NB can act as a carrier for P migration in acidic or alkaline soils, and MB/NB with its bound P has great potential for co-transportation to groundwater [90, 94]. Therefore, caution might be warranted that adding biochar to soils might result in the leaching of nutrients and pollution of the environment.

In contrast, once applied to the soil, biochar can migrate laterally via surface runoff

or vertically to groundwater systems, ultimately finding its way to the ocean through environmental media, such as rivers or the atmosphere [20]. For example, during the application of biochar, MB/NB easily separates from the biochar matrix and migrates with the soil solution [19, 21], which is caused by physical (e.g., water erosion, abrasion) or biological processes (e.g., biodegradation). Furthermore, MB/NB has significant mobility in the process of upward and downward migration in soil and aquifers [95]. Compared with bulk biochar, MB/NB has a richer mineral and O-containing composition, higher alkalinity, and higher dynamic stability (Fig. 4a) [96]. Therefore, MB/NB has a high reactivity in soil and aquatic environments [92]. When MB/NB is present in water, it has higher dispersibility because of the polar groups, along with a stronger co-migration effect on pollutants in aquatic environments, thus leading to increased water pollution and biotoxicity in aquatic organisms [21, 90]. Moreover, under the action of wind, MB/NB may enter the atmospheric environment and due to the presence of semiquinone and phenoxyl radicals, leading to ecological toxicity that may enter the organism by respiration [42].

Regarding the biotoxicity of MB/NB, it has been previously reported that particle-induced oxidative stress is a key mechanism of MB/NB cytotoxicity, which increases with a decrease in particle size. The EPFR concentration of particles with an aerodynamic diameter of less than 1  $\mu\text{m}$  is the highest [53, 97]. The toxicity of biochar is affected by its preparation method. In particular, ball-milled NB has higher biotoxicity than NB formed by other preparation methods [98]. This is because the

spherical structure of ball-milled NB makes it easier to contact and collide with cells than the original biochar or other nanomaterials such as sheets and tubes [99]. For instance, ball-milled biochar can permeate cells and induce the production of cytotoxic ROS. The produced ROS can further damage the inner structure of the cell and reduce the amount of starch granules that maintain the osmotic pressure of the cell. Ultimately, this leads to an increase in cell mortality [100]. Therefore, the potential risks of MB/NB in the environment are worthy of attention.

Recent studies have shown that the internal physical and chemical properties and the interaction with natural soil colloids may have a certain degree of influence on the aggregation and stability of MB/NB [19, 101, 102]. For example, Yang et al. [103] pointed out that the presence of more surface oxygen-containing functional groups (e.g., hydroxyl and carboxyl groups) leads to more negative surface charges of MB/NB, which in turn increases the electrostatic repulsion between colloidal particles and makes them more stable in aqueous solutions. Furthermore, certain minerals in biochar can be dissolved and release a mass of cations into the aqueous solution, in which the repulsive energy barrier between colloidal particles was screened through cationic bridging action, thus progressing the aggregation of MB/NB [104]. In contrast, in the binary system of MB/NB-soil colloids, for negatively charged soil inorganic colloids, such as kaolin, the stability of MB/NB can be increased to enhance the migration ability of MB/NB in the natural environment. In contrast, positively charged soil inorganic colloids could limit the migration of MB/NB through charge neutralization. The

behavior of MB/NB aggregation is also affected by natural organic matter, such as humic acid (HA). For example, HA can be adsorbed on the surface of MB/NB through van der Waals and hydrophobic forces, ligand exchange, and energy, which can then change the zeta potential and increase the electrostatic repulsion between MB/NB particles [105]. Such an increase in electrostatic repulsion increases the potential risk of MB/NB and further affects the adsorption performance, environmental toxicity, and migration of MB/NB and contaminants. However, one study showed that when the HA concentration was high (~5 mg/L) and divalent cations were present at high concentrations to induce cation bridging, the aggregation of biochar colloids in soil was enhanced [103]. Additionally, for pyrolysis temperature, generally, MB/NB rich in functional surface groups (i.e., low-temperature pyrolyzed MB/NB) are less likely to accumulate in the soil solution, thus having high fluidity within the soil [103, 106]. In summary, it has been shown that biochar particles can form a stable suspension in a soil solution, especially in acidic soils with low alkali saturation. Dissolved organic matter could further enhance the stability of MB/NB, enhancing the potential transport of MB/NB with moving soil water. Therefore, considering the transportation and fate of MB/NB, when biochar is applied to agriculture or environmental remediation, the raw material source of biochar, preparation temperature, and composition of soil colloids should all be considered simultaneously.

### **3. Negative impacts of biochar on the soil environment**

Biochar is widely used in soil amendment applications (Fig. 5), but its presence



may inevitably change the physical and chemical properties of the soil, thereby negatively affecting the growth conditions of microorganisms and crops in the soil [7, 107].

### **3.1. Soil physical and chemical properties**

It has been found that the pH, structure, porosity, mobility, and bioavailability of toxic elements and other properties of the soil can be changed by biochar [108, 109]. This is because as the pyrolysis temperature increases, the amount of acidic functional groups on the surface of biochar decreases with the loss of oxygen percentage, which leads to the pH of biochar gradually increasing from neutral or acidic to alkaline [109]. The increase in soil pH due to biochar may limit the supply of certain nutrients (such as  $\text{NH}_4^+$ ) to the original soil [3]. El-Naggar et al. [110] reported the failure of woody plants to establish and survive due to the large accumulation of charcoal and deficiency of micronutrients caused by increased soil pH from soil biochar application. The biochar-induced increase in soil pH may also promote the hydrolysis of N-acetyl-homoserine lactone (AHL), a signaling molecule used by gram-negative bacteria for cell–cell communication, resulting in a decrease in the bioavailability of AHL [111]. Eventually, communication between the bacterial cells is inactivated. Yang and Lu [112] evaluated the effects of five different types of biochar on the physical properties of paddy soil through field experiments and found that the addition of biochar to the soil significantly reduced the tensile strength. With an increase in the amount of biochar, the degree of soil tensile strength decreased. Compared with the control group, the

tensile strength of the five biochar (rice straw, maize straw, wheat straw, rice husk, and bamboo) treatments decreased by 63.6%, 63.3%, 50.3%, 41.7%, and 55.0%, respectively. The decrease in soil tensile strength and cohesion indicates that the ability of the soil to resist external forces is reduced, which causes the soil to rupture and move under the action of external forces [113]. Moreover, the application of biochar to soil may have a negative impact on not only the soil, but also the wider environment. For example, biochar may inhibit soil nutrient supply and crop productivity by reducing plant nutrient absorption [114]. More importantly, biochar can increase the bioavailability of toxic elements in the soil, which poses potential environmental risks to soil contaminated with toxic elements (e.g., As and Pb). For instance, El-Naggar et al. found that the application of straw biochar significantly increased the bioavailability of As in soil by 101.6% [14].

### **3.2. Crops from the soil**

The positive effects of biochar on crop growth are well known; however, through a literature review, we found that biochar still has potential risks in specific situations. This section summarizes and analyzes the internal reasons and specific situations in which biochar may cause risks. Biochar may have a direct toxic effect on plants because of the presence of hazardous organic or inorganic compounds (e.g., PAHs and heavy metals) [73]. In the process of biochar preparation, cellulose or hemicellulose in raw materials is cracked to produce gaseous hydrocarbon groups, which are then subjected to a series of reactions to form aromatic rings [115]. The content of PAHs in the soil

with biochar as an amendment was higher (Fig. 6a) than that of the soil without biochar [16]. For instance, Wang et al. [48] found that 75.0% of Chinese cabbage (*Brassica chinensis*) and 87.5% of pakchoi (*Brassica campestris*) samples had benzo[a]pyrene TEQ values higher than the maximum contaminant level. This indicates that the enrichment of crops growing in the soil absorbs the PAHs leached by biochar, which has a negative impact on the growth of crops and may even further threaten the health of animals and humans (Fig. 6b and c). To verify this, Wang et al. [48] conducted a follow-up experiment on the consumption of PAHs in vegetables by animals to assess their health risks. The total increase in lifetime cancer risk (ILCR) of adults was higher than  $10^{-6}$ , which indicated that direct contact with PAHs in vegetables grown in biochar-modified soil can harm human health. In addition, the negative environmental impact of metals contained in biochar on plants in the soil has also received close attention. Visioli et al. [28] demonstrate that electrical conductivity and Cu negatively affected both germination and root elongation at  $\geq 5$  % (application rates, w/w) rate biochar, together with Zn at  $\geq 10$  % and elevated pH at  $\geq 20$  %. Moreover, in all species, root elongation was more sensitive than germination, strongly decreasing at very high rates of chars from grape marc ( $>10$  %) and wheat straw ( $>50$  %), whereas root length was already affected at 0.5 % of conifer and poplar in cucumber and sorghum, with marked impairment in all chars at  $>5$  %. This could be explained by the fact that cell division/elongation at the root tip is relatively sensitive to metal pollutants. In the growth and development of plants, the presence of EPFRs in biochar is related to the

inhibition of plant germination and survival [24]. Liao et al. [60] prepared biochar from wheat, corn, and straw at 200, 300, 400, and 500 °C in a germination test and found that rice straw-derived biochar at 500 °C inhibited the growth of roots and stems of wheat, rice, and corn seedlings. Moreover, EPFR-induced ROS can react with macromolecules (such as glycoproteins), thereby destabilizing the cell membrane and further leading to apoptosis, which explains the inhibitory effect of free radicals on seedlings [42]. In addition, low molecular weight organic molecules (LOM) accumulate on the surface of biochar and condense in the pores during the production of biochar. The growth of animals and plants can be repressed by high concentrations of LOM compounds [116]. The germination test showed that VOCs in biochar had an inhibitory effect on the germination and growth of cress [117]. This could be explained by the fact that the re-condensation of VOCs during the pyrolysis of biochar resulted in a high content of mobile phytotoxic compounds.

In addition to PAHs, heavy metals, and EPFRs contained in biochar, NB has been widely used in agriculture and has potential risks to agricultural production [118]. For instance, Zhang et al. [89] prepared six types of biochar through pyrolysis of straw and wood chips at 300, 500, and 700 °C, followed by ultrasonic treatment (i.e., the simulation of the physical and chemical decomposition of biochar) and centrifugal separation. Furthermore, the effects of six types of NB on the seed germination and growth of rice, tomato, and reed seedlings were studied. The results showed that NB derived from lignin-rich raw biomass had an inhibitory effect on reeds, thus

significantly reducing bud length and biomass. The main reason for this phenomenon was that small-sized biochar had a cytotoxic effect on fibroblasts, since the surface of NB was an important location for hosting phenolic compounds, had a negative impact on plants, and were deposited on the biochar during biomass pyrolysis [119, 120]. In addition, the pyrolysis temperature also has a certain impact on the toxicity of MB/NB; the MB/NB obtained from low-temperature biochar contains higher levels of highly unsaturated phenolic compounds and polyphenols than the MB/NB obtained from high-temperature biochar (Fig. 7) [48]. In addition, the ability of low-temperature MB/NB to release PAHs is higher than that of high-temperature MB/NB, making low-temperature MB/NB more bio-toxic [121]. Moreover, the toxicity of biochar depends on its raw biomass. Because the pyrolysis of lignin can produce a large quantity of phenolic compounds [122], NB obtained from biomass with high lignin content has higher potential environmental risks. However, as far as current research is concerned, whether the main source of toxicity of MB/NB is the harmful substances adsorbed on it or due to its own size effect needs to be further explored.

Kim et al. [123] reported that it was difficult to obtain nitrogen from the soil because of its increased distribution on the surface of biochar, showing that as the amount of biochar applied increased, lettuce growth was further delayed. Rajkovich et al. [124] also found no growth-promoting effect of corn with more than 2% biochar added, regardless of the type of biochar. The reason for the lack of any beneficial effects at higher application rates was that the available nutrients were reduced. The fact that

biochar reduces plant nutrient elements in the soil due to adsorption has been verified in previous studies. Novak et al. [125] found that the concentration of nitrate in the soil leachate decreased after applying biochar for 25 days, and was proportional to the amount of biochar applied, which indicated that nitrogen could be adsorbed on the surface of the biochar, resulting in the inhibition of plant growth by reducing the available inorganic nitrogen. Similar conclusions have been reported in other studies [114, 126, 127]. In addition, the composition of biochar has a certain degree of influence on the nitrogen fixation ability of biochar. As the content of mineralizable components (volatile substances) in biochar increases, the nitrogen content fixed by biochar from the environment also increases, suggesting a lower available nitrogen content for plant growth [128]. In conclusion, the negative impact of biochars competing for nutrient elements required by plants in soil environments is possibly due to improper amounts of biochar being applied, as well as biochars with high contents of mineralizable components being used. Not only the adsorption of nutrients but also the adsorption of plant hormones cannot be ignored. Phytohormones, which are a type of chemical information, have a regulatory effect on plant growth and development. However, it was found that biochar had an immobilized effect on plant hormones, thereby inhibiting plant growth [73, 129-131]. Moreover, recent studies have reported that some biochar types may induce environmental risks when applied to soil under dynamic redox conditions. This is governed by the increase in mobility and phytoavailability of toxic elements (Sb, As, Cd, Zn, and Ni), as influenced by the redox-induced changes in EH

and the EH-dependent effects [132-134].

Based on the above discussion, it can be concluded that the three main reasons for the potential risks of biochar to crops in the soil are as follows: (1) the various environmental pollutants (e.g., PAHs, heavy metals, EPFR, and VOCs) contained in biochar have an inhibitory effect on the germination and rooting of crops. According to the research on the causes of various pollutants in biochars in Section 2.1.1, the selection and consideration of biomass, pyrolysis temperature, and physicochemical properties of the environmental media are the key factors affecting the negative effects of biochar in the agricultural field; (2) small-size biochar (MB/NB), especially from biomass with a high lignin content or MB/NB produced at low temperatures, may have toxic effects on crops due to the presence of phenolic compounds on its surface; (3) the types of biochar with high contents of mineralizable components may absorb nutrients (such as nitrogen, phosphorus, and inorganic salts) and plant hormones from the soil, leading to reduced plant access to important nutrients.

### **3.3. Soil organisms**

Biochar added to the soil has a direct or indirect negative impact on soil microorganisms. Indirect effects are mediated through changes in the environment [135], such as pH, or other factors related to the ecological tolerance ranges of the exposed species. For instance, the application of biochar changes the pH of the soil, and because some fungal signals (such as farnesol) are not sensitive to pH, the ratio between fungi and bacteria becomes imbalanced [111, 136]. This indicates that the influence of

biochar on the structure of the microbial community depends on the type of biochar through complex and changeable mechanisms.

Direct effects, in contrast, affect microbial activity by releasing heavy metals or organic chemicals, and can be mediated through multiple exposure pathways (ingestion or touch) [107]. For instance, PAHs unintentionally generated during the pyrolysis of biochar have mutagenic effects on salmonella/microsomes [43], and EPFRs can reduce the content of certain cellular enzymes [67]. The negative impact of PAHs is caused by chemical stress on the microbial community at a higher soil nutrient level [137]. For EPFRs, the negative impact comes from the EPFRs themselves, which causes the transfer of electrons between the biochar surface and specific cells during the remediation process, thereby changing the microbial community structure. Additionally, EPFRs may induce potential toxicity to specific soil microorganisms [42, 67].

Furthermore, the inhibitory effect of biochar on microbial activity increased as the pyrolysis temperature increased, owing to the changes in the structure and chemical composition of biochar, especially the carbon content. The reduction in C content weakens the interaction between the soil matrix and pollutants (e.g., PAHs and heavy metals), thereby increasing the bioavailability and toxicity of the pollutants [138]. The bio-toxic compounds adsorbed on biochar inhibit the growth of microorganisms [73]. Studies have found that bio-toxic compounds (e.g., catechol) are strongly adsorbed to high-temperature biochar derived from ash-rich corn stover [139, 140]. Bio-toxic compounds have been found to desorb from the biochar material used to prepare the



agar growth medium toxic to *Bordetella pertussis*, indicating that the growth-inhibiting substance was retained by biochar [73].

Arbuscular mycorrhizal (AM) fungi and exogenous mycorrhizal (EM) fungi are the most common types of mycorrhizal fungi in soil, and research has shown the positive effects of biochar on them [141]. However, there is no denying that biochar also has certain negative effects on these fungi, mostly due to nutrient effects [142]. Warnock et al. [143] found that the relative abundance of AM decreased after biochar application, while AM fungi are known to have an intergrowth relationship with more than 80% of the plants on land [130]. Studies have shown that the signal transduction process of flavonoids is disturbed by the adsorption of flavonoids on biochar [129], which poses a threat to the growth and survival of soybean plants, AM fungi plants, and AM fungi [130]. In addition to affecting the transmission of signaling molecules between microorganisms and plants, biochar also affects the exchange of information between microorganisms. Biochar can change the cell–cell communication of microorganisms by adsorbing signaling molecules and promoting their hydrolysis, thereby changing the microbial community structure (Fig. 8a) [144].

In conclusion, the mechanisms involved in the influence of biochar on microorganisms include, but may not be limited to: (1) detaining the available nutrients for microbial growth [73]; (2) promoting the adsorption and hydrolysis of signaling molecules to interrupt the interspecies communication of microorganisms (Fig. 8a) [131]; (3) the release of harmful components (e.g., PAHs, heavy metals, and organic

pollutants), which are biologically toxic to microorganisms [138]; (4) decreasing the ability of mycorrhizal fungi to colonize plant roots through the persistent adsorption of signaling compounds; [145] (5) changing the physical and chemical properties of the soil (Fig. 8c) [141]; and (6) increasing the amount of pollutants adsorbed by microorganisms.

In addition to microorganisms, biochar poses a potential threat to soil organisms. For instance, high concentrations of biochar negatively affected the survival of invertebrates in the soil (Fig. 8b). Furthermore, the presence of EPFRs in biochar may be a neurotoxin in soil organisms [53]. For instance, EPFRs in biochar can trigger the neurotoxic effects of *Caenorhabditis elegans*, thereby inhibiting its life characteristics (movement and defecation) in the soil [146]. *Caenorhabditis elegans* has also been used as food for *Bacteroides nematodes* and plays an important role in soil productivity and nutrient cycling; a decrease in the population of *Caenorhabditis elegans* would inevitably affect the hunting and growth of *Bacteroides nematodes* [147]. Additionally, since biochar has an adsorption effect on pesticides applied to agricultural production, organisms such as earthworms and mites could indirectly ingest pesticides by the casual predation of biochar particles [148]. In the worst-case scenario, pesticides may be released inside the insect gut, causing exposure to toxic concentrations. However, there is no direct evidence to prove that biochar increases the exposure of soil organisms to pesticides. This effect should be explored and studied in future studies. Moreover, small-size biochar not only increases the adsorption of contaminants, but is also easier

to be ingested by organisms, indicating that MB/NB has a stronger negative impact on organisms. The activity of applied pesticides, such as herbicides, is reduced by biochar [148, 149], which could lead to excessive use of pesticides in the agricultural production process, and further cause pesticide accumulation, leading to more serious negative environmental impacts [150]. Therefore, in view of the toxic effects of biochar on soil microorganisms and organisms, caution should be exercised when used as a soil amendment.

### **3.4. Soil organic carbon cycle**

The mineralization of soil is vital to the biological cycle of N, C, P, S, and other elements in nature. There are three main reasons for the influence of biochar on mineralization: (1) the original unstable organic matter (OM) in soil is adsorbed on the surface of biochar to form adsorbent protection [151]; (2) Biochar can prevent OM adsorbed in the mesopores of biochar from mineralization by isolating microorganisms and enzymes outside the mesopores. It can also greatly reduce the activity of laccase (a type of enzyme phenol oxidase that can use molecular oxygen to catalyze the oxidation of aromatic compounds), and even inactivate laccase through adsorption, thus having a mesoporous protection mechanism for OM [152]; (3) Biochar also promotes the formation of soil mineral aggregates and reduces the degradation of biochar and soil organic carbon (SOC) to a certain extent [153]. Therefore, when biochar is applied to soil, it may have an inhibitory effect on the SOC cycle.

## **4. Negative impacts of biochar on aquatic environments**

Some studies have shown that biochar also poses potential environmental risks to aquatic environments, including the enhancement of eutrophication, acceleration of pollutant migration, and inhibition of aquatic organism growth (Fig. 9).

#### **4.1. Eutrophication**

Biochar may contain endogenous N and P because of the composition of their biomass feedstocks (such as cow dung) [154]. As such, inorganic N and P can be released from biochar and become a source of nutrients. Chen et al. [155] reported that the leaching of  $\text{NH}_4^+$  from biochar into an aquatic environment accounted for 0.3–4.92% of the total  $\text{NH}_4^+$  concentration. Similarly, Park et al. [156] observed that the level of phosphate released by sesame-straw-derived biochar was higher. The content of released phosphate changed from 62.6 to 168.2 mg/g with an increase in pyrolysis temperature. The low binding affinity of phosphate to biochar with low Ca and/or Mg content may be responsible for the high levels of  $\text{PO}_4^{3-}$  released in the water phase [157]. Additionally, the abundant ions in water not only weaken the adsorption ability of biochar to target pollutants, but also promote the release of inorganic N/P adsorbed to biochar. For instance, Novais et al. [158] reported that a pure water solution extracted more than 20% of P from used poultry manure and sugarcane straw biochar after four extraction rounds, while  $\text{HCO}_3^-$  solution could extract more than 90% of P. Therefore, when biochar is used on a large scale, its existence and accumulation in aquatic environments may accelerate the eutrophication of water. In conclusion, when applying biochar in aquatic environments rich in ions, it is recommended to use a biochar with a

lower content of endogenous N/P (i.e., pay attention to the choice of biomass). In addition, the application of modified biochar materials requires special attention. Studies have shown that the use of chloro-phosphate-impregnated biochar (CPBC) can remove  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  from sewage. However, in the first 20 min after the addition of CPBC, the content of available phosphorus in the solution increased because of the dissolution of  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  [159].

#### **4.2. Migration of pollutants**

There are also potential environmental risks of co-transportation in the use of carbonaceous nanocomposites because the biochar nanocomposite could act as an active carrier [92]. Biochar with its adsorbed pollutants can infiltrate the surface and groundwater through surface runoff, ditches, or irrigation [160], thereby posing potential environmental risks to aquatic environments such as groundwater and rivers [21]. The co-migration ability of the nanocomposites was also affected by the biochar source. Under the same experimental conditions, the enhancement of  $\text{Cd}^{2+}$  migration ability by biochar- $\text{Fe}_3\text{O}_4$  nanocomposites derived from wheat straw was significantly higher than that derived from sawdust [160]. This could be explained by the fact that biochar with a high content of mineral components (such as calcium carbonate) is beneficial for  $\text{Cd}^{2+}$  adsorption [161], thereby increasing the diffusion and transfer of  $\text{Cd}^{2+}$  in the environmental media.

MB/NB is known to exhibit higher mobility and accessibility owing to surface reactivity and polarity, accelerating the transfer and diffusion of environmental

pollutants [21]. Since more polar groups are present in MB/NB, they have higher dispersibility in natural water [90], along with a stronger co-migration effect on pollutants in the aquatic environment. In addition, biochar-based metal oxide/hydroxide composite materials are mainly used in aquatic environments to remove heavy metals and organic and inorganic pollutants. Therefore, when applying biochar materials, such as MB/NB or biochar nanocomposites, to environmental media, especially aquatic environments, special attention should be paid to the potential risk of promoting the transfer and diffusion of pollutants. Moreover, the selection of appropriate biomass types and preparation methods for amendment materials, as well as methods for controlling the potential of co-migration of pollutants and carbonaceous nanocomposites in the underground environment should be the focus of future research.

#### **4.3. Aquatic organisms**

In one study, by exploring the degree of toxicity of biochar on a series of organisms, Oleszczuk et al. [33] found that biochar had the highest impact on crustaceans, and the level of PAH content in biochar was directly proportional to the mortality of crustaceans (Fig. 8d). Because biochar absorbs the substances necessary for chemical communication in symbiotic organisms, nutrient bioavailability is reduced, and the symbiosis of microorganisms and plants is disturbed. For instance, Chi and Liu [162] added biochar produced from wheat straw at 400 or 700 °C to bed sediments at a rate of 3% (w/w), and its effects on the growth of *Vallisneria spiralis* and the root and stem biomass were studied. After 54 days, compared with the control experiment, the

795 presence of 700 °C biochar not only showed a lower *Vallisneria spiralis* biomass, but  
796 also a lower root length. Additionally, EPFRs in biochar were found to generate  
797 hydroxyl free radicals in aquatic environment media, which could also induce the  
798 generation of ROS (i.e., hydroxyl free radicals) in aquatic plant cells and cause damage  
799 to cells and organs [42]. For instance, Zhang et al. [31] found that three prepared  
800 biochars significantly promoted the generation of cellular ROS in *Streptococcus*  
801 *obliquus*. The ROS levels induced by the biochar obtained at 300, 400, 500, and 600 °C  
802 at a certain concentration (800 mg/L) were 120%, 134%, 125%, and 113% higher than  
803 the control, respectively. Except for ROS, when the concentration of biochar was  
804 greater than 200 mg/L, the SOD activity of all exposed groups was also significantly  
805 higher than that of the control group. This indicates that the redox balance of  
806 *Streptococcus obliquus* is disrupted by biochar. Meanwhile, it was found that the  
807 chlorophyll-*a* (Chl-*a*) concentration in *Streptococcus obliquus* was decreased by  
808 biochar. Biochar prepared at 500 °C had a high inhibition rate (89%) for Chl-*a* at a  
809 concentration of 500 mg/L. Steinberg et al. [163] reported that the photosynthetic  
810 oxygen content of *Ceralophyllum demersum* was reduced by EPFRs. This could be  
811 explained by the fact that the formation of semiquinone free radicals in biochar hinders  
812 the influence on the electron transfer chain by acting as an electron scavenger in the  
813 humus and the plants growing in the applied media, thereby hindering oxygen  
814 production from plant photosynthesis [42]. Liu et al. [90] produced NB through the  
815 collapse of pores and fracture of the skeleton, and found that MB/NB with its associated

pollutants may trigger exposure risk to aquatic organisms due to the high dispersion of MB/NB in natural waters. Among the negatively affected aquatic organisms, algae are one of the most sensitive to MB/NB. The toxicity of MB/NB to algal cells can be directly related to their exposure as well as to indirect effects, such as shading effects on MB/NB produced on the cells (with negative consequences in light adsorption and photosynthesis) and the adsorption of nutrients on MB/NB [164]. Different species of algae have different toxic sensitivities to MB/NB exposure. For instance, MB/NB can be directly ingested and accumulated in aquatic organisms, thus posing a potential environmental risk [165]. In addition, MB/NB is widely present in aquatic media by flowing into surface water or groundwater systems owing to its high migration capacity. Moreover, the various pollutants carried by MB/NB continued to accumulate after entering the aquatic environment. Because of the various interactions between MB/NB and environmental media, the adsorbed pollutants may be released, which could cause serious environmental risks. The interaction between MB/NB and many pollutants, such as pesticides, metals, drugs, and surfactants, can result in increased toxicity to aquatic organisms [164].

## **5. Negative impacts of biochar on the atmospheric environment**

During the application of biochar to environmental media, its potential negative impacts on the atmospheric environment are mainly reflected in the change in the atmospheric greenhouse effect and the increase in air particulate concentration (Fig. 10).



## **5.1. Atmospheric greenhouse effect**

Biochar also plays an important role in the atmosphere by affecting CH<sub>4</sub>, N<sub>2</sub>O, and other GHG emissions [166]. However, some studies have shown that the application of biochar also has a negative impact on GHG emissions, which in turn brings potential environmental risks [73, 167, 168]. The N dynamics are affected by soil pH, aeration, and type of biochar [169, 170]. When biochar is applied to the soil, it may affect soil N<sub>2</sub>O emissions by influencing the demeanor and activity of microorganisms [171]. For example, the addition of straw-derived biochar to soil regulates the surrounding pH, which could enhance the growth of ammonia-oxidizing bacteria and promote the increase in nitrification rate, thereby causing an increase in soil N<sub>2</sub>O emissions [169]. This phenomenon is mainly due to the porous structure of biochar, which leads to the adjustment of diverse microbial habitats. At higher temperatures in summer, biologically induced anoxic conditions in biochar pores acting as microsites may be promoted, under which complete denitrification to N<sub>2</sub> occurs, leading to N<sub>2</sub>O uptake and promoted CH<sub>4</sub> production [167]. The ash concentration of biochar also has an impact on N<sub>2</sub>O emissions. This is mainly because high-salt biochar will cause a “salting-out effect,” which leads to high N<sub>2</sub>O emissions [172]. Meanwhile, Cayuela et al. [173] found a positive correlation between N<sub>2</sub>O emissions and ash concentration in a study on nine biochars under denitrification conditions. Therefore, the importance of the concentration of mineral components in biochar in the field of GHGs needs further research. Additionally, biochar derived from different raw materials may have

different effects on N<sub>2</sub>O concentration in the atmosphere [174], considering the different interactions between microbes and biochar with various properties. For instance, Xu et al. [168] found that straw-derived biochar significantly reduced soil N<sub>2</sub>O emissions by 51.4–93.5%, while the use of biochar derived from camellia husk increased soil N<sub>2</sub>O emissions. Meanwhile, different contents of NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N in biochar led to different levels of N<sub>2</sub>O emissions in the soil [175]. Moreover, regarding the impact of soil texture on N<sub>2</sub>O emissions, biochar could significantly reduce N<sub>2</sub>O emissions in finer soils, while the average use of biochar in coarse soils increases N<sub>2</sub>O emissions by 53% (under high moisture conditions) [166]. The impact of soil pH has a significant impact on the N<sub>2</sub>O/N<sub>2</sub> emission ratio; N<sub>2</sub>O/N<sub>2</sub> is negatively correlated with saturated soil pH [176]. Based on the above discussion, it is not possible to accurately determine the N<sub>2</sub>O concentration in the atmosphere around biochar-modified soils. More research on biochar in different types of agricultural systems with various climatic conditions on the impact of N<sub>2</sub>O emissions is necessary.

Biochar mainly affects the decomposition ability of microbial communities in the soil by influencing its species and activity. Therefore, terrestrial organic carbon emitted into the atmosphere in the form of CO<sub>2</sub> is reduced, thereby reducing the greenhouse effect [141]. However, Zimmerman et al. [177] found in a 1-year field experiment that all other types of biochar-soil mixtures released more CO<sub>2</sub> than related soils without biochar and had higher initial CO<sub>2</sub> release rates. This is probably because biochar itself, especially freshly prepared biochar produced at lower temperatures, is inherently

878 unstable, thus contributing to the loss of degradable C in the mixture. The mechanism  
879 most often proposed involves the growth of r-strategist microbes that are adapted to  
880 respond quickly to newly available C sources, re-mineralize soil nutrients, and co-  
881 metabolize more refractory OM such as soil humic materials in the process [178].  
882 Regarding the effect of soil texture and biomass sources on soil CO<sub>2</sub> emissions, three  
883 types of biochar (straw, umbrella wood, and grass) were applied to sandy loam and  
884 sandy soil in a short-term incubation experiment by El-Naggar et al. [114]. The results  
885 showed that the CO<sub>2</sub> emission of sandy loam was 2–3 times higher than that of sandy  
886 loam because of the higher abundance of microbial communities in sandy loam. Rice  
887 straw biochar treatment induced the highest CO<sub>2</sub> emission rate in sandy soil, which was  
888 attributed to the high content of dissolved organic carbon in the aliphatic group of rice  
889 straw biochar. Meanwhile, Wang et al. [179] conducted a meta-analysis based on 116  
890 observations, and the results showed that after the addition of biochar, sandy soils  
891 usually showed increased CO<sub>2</sub> emissions due to the stimulation of microbial activity in  
892 soils with poor soil fertility. Furthermore, a study reported that biochar could change  
893 the utilization of carbon by microorganisms in the soil. Coupled with the catalytic  
894 reduction of minerals or free radicals and the adsorption of NH<sub>3</sub>, the main role of fungi  
895 or bacteria in the soil GHG emissions process may change [177]. Meanwhile,  
896 considering the contribution rate of methane and nitrous oxide to the greenhouse effect,  
897 the impact of biochar requires more comprehensive analysis methods such as LCA.

## **5.2. Particulate concentrations in the atmospheric environment**

The application of biochar may increase particulate matter (PM<sub>10</sub>) emissions [180, 181]. The typical characteristics of biochar are a low bulk density, large surface area, and variable particle size distribution, which makes it easy for biochar to be released into the atmosphere by natural or mechanical interference and contribute to the measured PM<sub>10</sub> [110, 115]. Aged biochar is more likely to be broken into small particles because of its reduced mechanical strength [182]. Compared with bulk biochar, biochar in small and light particles can easily enter the atmosphere under natural wind conditions, resulting in an increased PM<sub>10</sub> concentration [115]. Ravi et al. [183] reported that PM<sub>10</sub> emissions were generally higher in all soils at all biochar application rates and wind velocities. Meanwhile, monovalent cations have a dispersive effect on soil particles, which leads to aggregate instability and colloid mobilization, resulting in the amended soil being more susceptible to dust emission [115, 180]. It is well known that PM<sub>10</sub> is hazardous to human health, can be deposited in the lungs, and even enter the alveoli and blood. The deposition of particulates on the alveoli damages the alveoli and mucous membranes, causing a series of pathologies such as chronic rhinitis and bronchitis [184]. Because of the high adsorption of biochar to pollutants, the adsorbed pollutants may be discharged into the air along with the biochar and may be released from the biochar to the atmosphere. From the perspective of dust emissions, biochar-bound pollutants (such as neurotoxins, carcinogens, mutagens, and reproductive toxins) pose a threat to human health when the biochar dust is inhaled by humans [115]. Using

the LCA method for evaluation, the results of some studies have shown that biochar-related air pollution may contribute to a larger negative effect over its entire life cycle due to potential adverse human health impacts [185, 186]. However, there is currently a lack of relevant research on several associated topics: the possibility of biochar as dust emissions, the possibility that the pollutants in biochar are adsorbed by humans after being released, and the bioavailability of biochar after being adsorbed. In agricultural settings, this airborne release may occur during the application of biochar to the soil, or after it has been incorporated through natural wind-driven erosion or mechanical farming events [115]. Therefore, it is necessary to pay special attention to the problem caused by dust emissions when applying biochar to actual agricultural production.

Micro-/NB formed from larger biochar or originally existing in biochar is usually dispersed in the atmosphere in the form of dust during the production and use of biochar, thereby posing potential risks to human health due to the nature and characteristics of MB/NB [120]. Sgro et al. [187] observed the cytotoxic cell internalization of fine biochar particles. However, Sigmund et al. [120] did not observe the internalization of biochar in NIH 3T3 mouse fibroblast cells. This indicates that the dust formed by the biochar particles had a cytotoxic effect on the fibroblast cells. This cytotoxic effect was related to the size distribution of the biochar, which increased with a decrease in particle size [188]. Therefore, compared with bulk biochar, MB/NB has a higher biological risk through biological inhalation. The presence of semiquinone and phenoxy radicals may

lead to activated species in combustion-generated particles and ambient fine particulate matter (PM) [42, 189]. The generated active substances accumulate in the human respiratory tract and induce the production of ROS, thus causing oxidative stress and threatening human health [189].

## **6. Detection, assessment, and avoidance of biochar environmental risk**

### **6.1. Risk detection and assessment of the soil environment**

#### **6.1.1. Phytotoxicity**

According to the summary of this review, biochar has toxic effects on plants in soil. When biochar is applied to real soil, it is necessary to evaluate its phytotoxicity. At present, the phytotoxicity research of biochar is mainly based on germination experiments, which have many shortcomings, such as requiring relatively long experiment times, having an unclear internal mechanism, and other uncontrollable factors [190-192]. More importantly, it is difficult to compare and summarize different studies because of the varying dependence on seed species [190]. Therefore, phytotoxicity analysis with a certain quantitative index is of practical significance for the application of biochar. Ruzickova et al. [193] proposed that in the presence of organic compounds in biochar, the ratio of organic carbon to elemental carbon (OC/EC) can be evaluated to determine whether biochar is phytotoxic (based on the recognition that biochar is phytotoxic because of the presence of organic compounds [194]). The phytotoxicity of biochar in soil can also be predicted by the ratio of aromatic organic compounds to aliphatic organic compounds (AL/AR) (e.g., AL/AR value < 0.5,

indicating the domination of aliphatic compounds, which are involved in biochar toxicity). Additionally, Kong et al. [195] proposed the detection and evaluation of the phytotoxicity of biochar from the perspective of metabolism. In their experiment, the authors investigated the toxicology of sewage-sludge-derived biochar to wheat by integrating metabolomics and physiological analysis. A total of 514 peaks were detected in the wheat root extract, of which 211 were identified. The metabolites analyzed were roughly classified into amino acids, organic acids, and sugars. It was found that the sewage-sludge-derived biochar obtained from different pyrolysis temperatures led to significantly different wheat metabolism profiles, particularly amino acid metabolites (e.g., proline). The significant reduction in wheat amino acid metabolism indicated that biochar was phytotoxic, and that many amino acids, including valine, alanine, isoleucine, proline, oxyproline, orthoaline, ornithine, puthumine, and aminomalonic acid, were downregulated by less than four times under biochar exposure, compared with the control group. This is mainly because the enhancement of oxidative stress caused by biochar in the organism is manifested in the downregulation of amino acid metabolism [196]. At present, the toxicity detection and evaluation of biochar is not only lacking in depth, but also requires a certain degree of universality. Therefore, the establishment of standardized and universal evaluative mechanisms or indicators should be the focus of future biochar toxicity research.

#### **6.1.2. Microbial community**

In Section 3.3, the negative effects of biochar on soil microbial communities are

982 explained. Currently, the phosphorus lipid fatty acid (PLFA) method is mainly used to  
983 detect the impact of biochar on microorganisms [137, 197]. The PLFA method is a  
984 technology based on modern biochemical theory, which provides an effective method  
985 for analyzing soil microbial communities without the need for separation or culturing  
986 [198]. Additionally, due to the mutagenic substances (e.g., PAHs and dissolved organic  
987 carbon) present in biochar, it is necessary to conduct in-depth research on the genetic  
988 changes in microorganisms. Qiu et al. [199] used 16S ribosomal ribonucleic acid (16S  
989 rRNA) sequencing to analyze the dynamic changes in bacterial community composition  
990 in compost with the addition of biochar, and found that the relative abundance of  
991 actinomycetes increased in the late composting period, but the relative abundance of  
992 red caterpillars decreased sharply. A differential operational taxonomic unit abundance  
993 analysis was conducted to determine the effect of biochar addition on microbial  
994 community separation. It was found that the addition of biochar increased the  
995 abundance of specific microbial populations in the compost. Moreover, to gain a more  
996 comprehensive understanding of microbial community changes, high-throughput  
997 sequencing, network technology, denaturing gradient gel electrophoresis, and other  
998 methods can be combined and applied to investigate the impacts of biochar. For  
999 example, Qiu et al. [199] found that biochar has a negative impact on the number and  
1000 activity of *Microbacteriaceae* and *Aeromicrobium* through high-throughput sequencing  
1001 and network technology. However, most quantitative analysis methods have certain  
1002 deviations when analyzing the influence of biochar on microbial community structure.



Therefore, a reasonable combination of two or more methods should enable a more comprehensive understanding of the effects of biochar on microbial communities. Future research should therefore focus on the use of standard and universal microbial community measurements, as well as analysis methods for long-term experiments and field research on different soil types.

## **6.2. Risk detection and assessment of aquatic environments**

Toxicity tests of biochar to aquatic organisms are mostly carried out through laboratory-level toxicity simulation experiments. Toxic detection and evaluation of fish are particularly important in aquatic environments of economic significance. Abakari et al. [200] reared tilapia (*Oreochromis niloticus*) in the presence of biochar, and evaluated the toxicity of biochar to tilapia through its performance parameters (e.g., fish growth parameters, analysis of fish welfare indicators, proximal analysis of fish back muscle, and determination of antioxidant and immune enzyme activities). Additionally, the risk substances (i.e., biochars) that enter the aquatic environment through various channels may also act on and damage algae [201]. Therefore, algae are also one of the main links for evaluating the toxicity of biochar to aquatic organisms. Zhang et al. [31] proposed four quantitative indicators in the acute toxicity test of *S. obliquus* (model aquatic algae): cell growth (inhibition), Chl-*a* (decrease in concentration), ROS content (upregulation), and SOD content (upregulation). Finally, through a comprehensive evaluation of these indicators, the biotoxicity of biochar to the aquatic algae model was determined. Mondal et al. [202] measured the cell density

of the microalgae *Scenedesmus* sp. (a model organism representing the phytoplankton and eukaryotic system) through a growth-inhibited toxic test to evaluate the aquatic toxicity of biochar. Furthermore, the microbial toxicity test has been shown to be an important method for detecting the toxicity of biochar to aquatic organisms. For example, the luminescence intensity of luminescent bacteria (*P. phosphoreum* T3 spp.) after treatment with biochar was detected by Zhang et al. [31], and it was found that the luminescence inhibition rate increased with an increase in biochar concentration. Polymerase chain reaction (PCR) involves in vitro amplification of specific deoxyribonucleic acid fragments [203]. In the toxicology study of protozoa, phytoplankton, zooplankton, and fish, the results obtained using PCR provide a scientific basis for the ecological risk assessment of pollutants [204, 205]. At present, there are few studies on the application of PCR in the field of biochar-aquatic toxicity detection. Therefore, this point should attract more attention in future research.

### **6.3. Risk detection and assessment of the atmospheric environment**

The PM produced during the pyrolysis of biochar not only increases the concentration of atmospheric PM, but may also have a certain toxic effect on organisms [115]. Therefore, the capture and toxicity detection of PM emitted from the pyrolysis of biochar is essential [206]. Dunnigan et al. [207] used a cascade impactor made of stainless steel with a size range of 0.1–10  $\mu\text{m}$  to collect PM produced by the combustion of raw pyrolysis volatiles. Then, a gas chromatography-mass spectrometer was used to analyze the PAHs in the PM samples. The results showed that as the pyrolysis

temperature increased, the PAH concentration of PM increased by 119% between 400 °C (403 µgPAH/gPM) and 800 °C (882 µgPAH/gPM). In addition, between raw pyrolysis volatile production temperatures of 400–800 °C the benzo(a)pyrene (BaP) – TEQ of the PM increased from 19.1 to 149.1 µgPAH/gPM. Therefore, running the pyrolysis-combustion process at a lower pyrolysis temperature will lead to the potential for PM Low toxicity. Notably, in intensive aquaculture areas, agricultural dust is the largest contributor to PM in the air [115]. Therefore, a separate study on the contribution of biochar to agricultural dust emissions is of great significance for its application as a soil amendment. Li et al. [180] used dust generators to simulate possible dust conditions under farming conditions (a huge dust cloud formed in a continuous plume) and collected dust samples. The relative biochar content in dust was determined by a special molecular labeling method, which was evaluated by measuring the benzene polycarboxylic acid (BPCA) produced by the digestion of nitric acid samples. The separation, analysis, and capture of biochar in mixed cases are difficult because biochar does not have its own separation, characterization, or quantitative techniques. Poot et al. [208] indicated that biochar can be used to quantify pyrolyzed carbonaceous substances on different substrates. Therefore, the separation technology of various carbonaceous substances such as Method CTO-375 (a technique for determining black carbon with chemothermal oxidation at 375 °C in active air flow) [209], BPCA [180], Cr<sub>2</sub>O<sub>7</sub> [210], and TOT/R (thermal–optical transmittance/reflectance) [211], can be selectively applied to the separation of biochar, which will help promote the

development of biochar atmospheric environmental risk assessment.

#### **6.4. Life cycle assessment**

As discussed in this review, while biochar brings benefits, potential risks are also difficult to ignore. Therefore, in practical applications, it is necessary to systematically evaluate the risks and benefits of biochar in complex ecosystems. In recent years, LCA is a widely recognized standardized method that has been widely used to evaluate the efficiency of biochar systems [26, 212]. LCA consists of four parts: target definition and scope, life cycle inventory analysis, life cycle impact assessment, and interpretation [213]. Using LCA, the environmental effects of biochar have been determined by calculating various indicators, such as net GHG emissions (i.e., GHG emissions reduction of biochar minus GHG emissions of biochar preparation, transportation, and other processes) [214], and the global warming potential, which is used to measure the impact of GHG emissions from biochar systems on global warming [215]. As another indicator, the sensitivity index (i.e., sensitivity coefficient, critical point) was used to draw the sensitivity analysis chart (table), such that the degree of influence of each factor in the biochar system on the overall environmental effect can be understood [9]. The N and P efficiency coefficients of the main fertilizers required for the growth of crops (biochar feedstock) have also been used to evaluate the eutrophication impact of biochar systems [216]. For instance, the net negative impact of biochar systems on acidification and eutrophication was assessed by Peters et al. [217] through LCA. The effects of acidification and eutrophication increased with an increase in biochar

production, mainly due to an increase in the amount of biomass that needed to be transported and treated per hectare. Additionally, compared with direct biomass combustion, biochar systems achieve GHG reductions at the expense of reduced energy efficiency and increased negative impacts. Esteves et al. [218] also pointed out that the emissions released during upstream operations would have an adverse impact on environmental benefits owing to the use of fossil energy. Moreover, from the overall perspective of bio-LCA (introducing biodiversity in LCA), the best use of biochar is as an alternative for stone coal in power plants under the premise of producing biochar in modern ultra-low emission pyrolysis equipment [219]. However, in rural areas of Africa or Southeast Asia, it is usually not possible to use more technologically advanced pyrolytic devices owing to economic and social limitations. Without the benefits of energy production offset, the LCA results of the biochar systems will most likely result in negative outputs [220]. Similarly, biochar production systems in tropical rural areas have potentially significant negative impacts on the environment because of the massive emissions of gases and aerosols during the production process, which cannot be compensated for by carbon sequestration [186, 221]. Although a large number of studies have evaluated the benefits of biochar production through LCA, the results of the biochar life cycle depend on the choice of method and assumptions [222]. Therefore, these differences between studies make it difficult to directly compare the corresponding research results or obtain causality that is applicable to most or even all biochar systems.

## **6.5. Risk avoidance measures**

Based on the above detection and tracking technologies, supplemented by modern biochar improvement and optimization technologies, there is an urgent need to reduce or even avoid toxicity risks in the field of biochar research. This is not only beneficial for expanding the application range, but also for increasing the potential value of biochar. The toxicity of biochar is mainly due to the feedstock and production conditions; therefore, feedstock with low harmful substances should be selected. Feedstock containing plant biomass is recommended because it contains fewer PAH precursors [32]. In terms of the pyrolysis rate, slow pyrolysis is recommended. Biochar produced at slow speed has lower ecological risks compared with the biochar produced at fast speed, which is mainly reflected in the lower harmful substance content of the biochar produced at low temperature and slow speed, as well as the process's limited ability to immobilize nutrient elements in the soil and stronger mineralization ability [114, 126]. Moreover, biochar prepared at low temperatures has a lower content of harmful substances (e.g., PAHs) and lower ecotoxicity than biochar prepared at high temperatures. Moreover, the concentration of PAHs usually decreases with increasing pyrolysis time and temperature [29].

The application of biochar to soil should first determine the physical and chemical properties of the medium (e.g., soil moisture and aeration). For instance, owing to the low soil water content, soil dust emissions have been found to increase after the application of biochar. Li et al. [180] suggested that tilling after wetting biochar-

amended plots effectively reduced the exposure to both soil and biochar particles. However, unlike fine-grained soils, maintaining high water levels near saturation is necessary for coarse-grained soils to achieve maximum dust reduction. Moreover, regarding the particle size of the applied biochar, we suggest that biochar should be added to soil as large particles where the amount of sorption is lower (due to the reduced surface area-to-volume ratio), thereby reducing the capacity for ingestion or transfer to crops or animals. Finally, the amount of biochar had an overall potentially negative impact on the growth of plants in the soil. Therefore, it is necessary to determine the appropriate amount of biochar for practical applications. For example, Baronti et al. [223] found that more than 1.7% (more than 60 t/ha) biochar applied to soil resulted in a decrease in the dry matter yield of perennial ryegrass. Li et al. [224] found that adding 1% (w/w) or 3% (w/w) of biochar can reduce the soil loss rate by simulating rainfall events, while adding 7% (w/w) of biochar can increase it.

When using biochar in an aquatic environment, in addition to the requirements mentioned above for the selection of feedstock, biochar with lower N and P content and lower mineral content is more suitable [154, 161]. The use of large biochar particles is recommended to prevent smaller biochar particles from increasing both the migration rate of pollutants and the possibility of uptake by aquatic organisms [90]. Meanwhile, biochar fixation technology can be used to avoid the environmental risks caused by smaller particles. For example, biochar can be prepared into macroscopic materials such as sheets with large volumes, such as biochar foam, thus effectively inhibiting its long-

distance migration and achieving effective recovery [225]. In addition, considering that the biotoxicity of EPFRs in aquatic environments is higher than that of EPFRs in the soils (i.e., soil exhibits high complexation, and EPFRs can induce the generation of hydroxyl free radicals), combined with the reasoning put forth in Section 2.1.1, we recommend the use of hardwood lignin, which contains fewer precursor substances than softwood lignin. Regarding modified biochar, current studies tend to use magnetic biochar to facilitate recovery from the aquatic environment [22].

In addition to the studies on the corresponding avoidance measures given above, multiple issues remain that have not been resolved. For example, Zhang et al. [31] confirmed that biochar had a significant toxic effect on aquatic animals and plants because of the induced production of ROS. Therefore, it is urgent to determine the ability of biochar to induce ROS in aquatic environments. Meanwhile, the modified biochar currently used at large scales also has correspondingly larger environmental risks due to the presence of oxygen-containing functional groups and heavy metals, as mentioned in this article [123, 226]. Therefore, with regard to biochar risk avoidance measures, substantial improvements could still be made in the application technologies represented by these examples, which is worthy of further investigative research.

## **7. Conclusion and outlook**

In summary, biochar poses potential environmental risks to the soil, water, and atmosphere due to its harmful components, adverse surface properties or structure, and chemical characteristics at micro-/nano-dimensions. Moreover, the wider application



1171 of biochar still has potential environmental uncertainties. As stated in this article,  
1172 complicated connections between physical properties and unpredictable chemical  
1173 interactions exist between biochar and various aspects of the environment to which it  
1174 is applied, resulting in a wide variety of possible negative impacts. Therefore, the  
1175 following points should be considered in future research:

1176 (1) To achieve optimal environmental remediation performance of biochar, it is  
1177 necessary to further investigate the relationship between certain production factors (e.g.,  
1178 biomass sources and preparation conditions) and the environmental risks of biochar in  
1179 subsequent studies. It is feasible to use LCA to assess the potential environmental risks  
1180 of biochar.

1181 (2) It is necessary to further investigate the comprehensive mechanism of the negative  
1182 impact of biochar on the environment at the microcellular and molecular levels.  
1183 Moreover, the interaction between biochar and various environmental media in the  
1184 biosphere (i.e., atmosphere, water, and soil), as well as the overall macroscopic effect  
1185 of biochar's negative environmental impact on the entire ecosystem also needs further  
1186 exploration.

1187 (3) Whether the main source of MB/NB toxicity originates from the harmful substances  
1188 adsorbed on the product or is due to its own size effect, the internal mechanism of  
1189 MB/NB's negative impact on the environment also needs to be explained in future  
1190 studies.

1191 (4) In terms of the effects of biochar being discharged as dust during application, some

knowledge gaps exist, including whether the desorption of attached pollutants is possible, or whether desorbed contaminants may be inhaled by humans after entering the atmosphere, as well as whether such materials are bioavailable after entering the human body. These issues require more comprehensive and systematic evaluation and research based on quantitative measurement indicators in the future, including LCA, systematic toxicological assessment, and epidemiological investigation. In addition, considering the negative effects of biochar particles, membrane and biochar fixation technology should be further studied to understand their potential ability to change the application form of biochar.

(5) Owing to the complexity of the ecosystem, as well as the changeability of biochar, there is a need for more research to understand the basis of simple evaluation mechanisms for describing the behavior of biochar in the ecological environment. Meanwhile, considering that certain environmental differences and related systematic errors are difficult to eliminate (such as those related to climate, soil type, or detailed information about raw materials or pyrolysis devices), various testing and evaluation methods should be unified within certain topics to make accurate comparisons; for example, the feedstock and environmental characteristics of biochar in the same region are generally similar. Additionally, economic sustainability assessments combined with environmental assessments would be useful for understanding the future priorities of biochar application.

(6) Finally, to achieve the industrial control and formulation of corresponding standards,

1213 professional knowledge and capabilities are required for the practical application and  
1214 management of biochar. The International Biochar Initiative has formulated standards  
1215 for the safe use of biochar in soil and issued a white paper on the pollutant-biochar-  
1216 component dioxin (i.e., the production, hazard analysis, and detection report  
1217 requirements of dioxin). Similarly, other environmental media and environmentally  
1218 harmful substances in biochar require corresponding standards and summaries, which  
1219 is of great significance to the sustainable development and safe application of biochar.  
1220 Meanwhile, existing avoidance measures should be standardized and unified. In  
1221 addition, further investigation is needed into methods that have not yet been proposed  
1222 to avoid the potential environmental risks of biochar.

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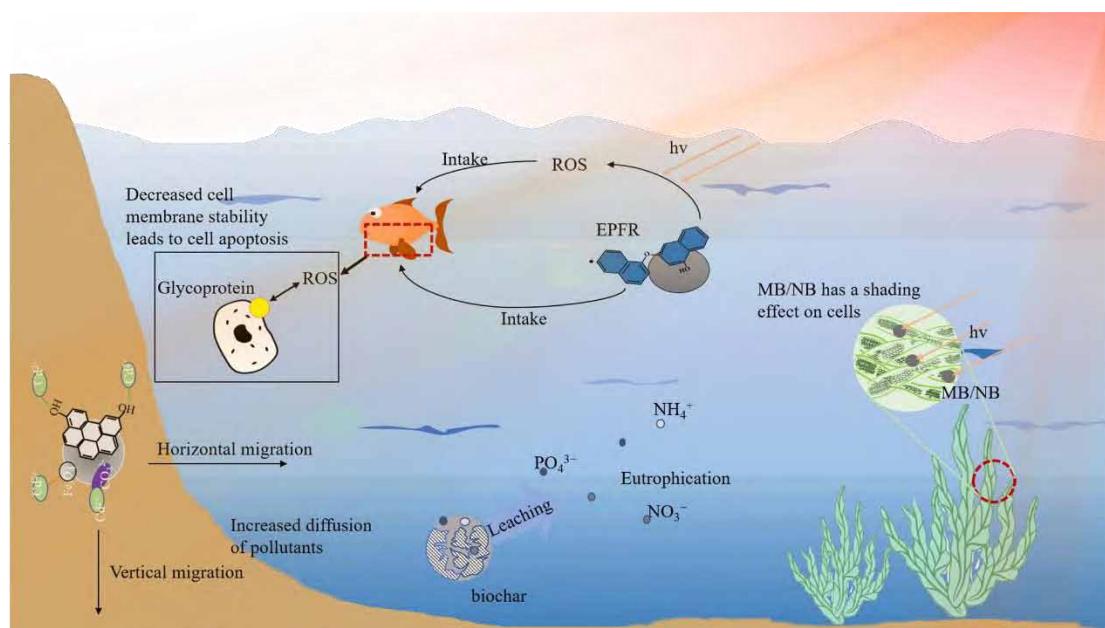
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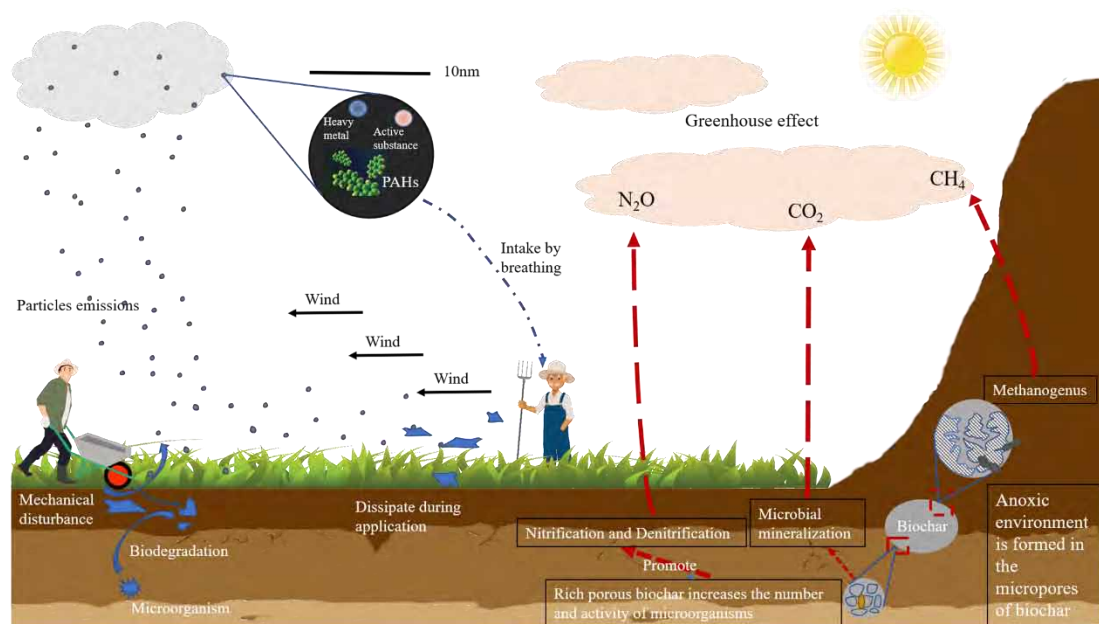
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**Fig. 9.** Schematic diagram of potential negative environmental impact of biochar in aquatic environment.



**Fig. 10.** Schematic diagram of the potential negative environmental impact of biochar in the atmospheric environment.

**Table 1** Main pollutants and avoidance measures of biochar obtained under different biomass and preparation conditions.

Biomass/Conditions		Dominant pollutants	Total concentrations	Bioavailability	Risk avoidance measures	Reference
Wood biochar	Pin wood					
	Chips	Heavy metals		Sometimes more than 50%	Biomass with low heavy metal	[34]
	Bamboo	(Zn, Mn)	--	of the total	content is recommend	
	Oak					
		Heavy metals (Zn, Cu, Pb,)	41.4-54.6, 2.7-11.6, 6.6-7.6 mg/kg	7-10%, 12-32%, 14-18%		[230]
	Sewage sludge	PFCs (PFOA, PFOS)	10.6-11.5 ng/g, 4.8-6.3 ng/g	--	--	[231]
		PAHs	13.88-15.49 mg/kg	11.75 µg/L		[44]
	Food waste (with high content of salt)	Dioxins	--	1.2 pg/g TEQ	Choose biomass with low chlorine content	[29, 50]
	Softwood (Douglas fir)	EPFR	--	--	Hardwood is recommended	[56]
	Plant (herbaceous plant)	MB/NB	--	The toxicity increased with the decrease of particle size	Woody plant biochar is less prone to physical aging	[76, 97]
High temperature		Heavy metals	Increases with increasing temperature (200-700 °C)	--	Reasonable selection of pyrolysis temperature	[36]
		EPFR	Increases with increasing temperature	Increases with increasing temperature		[31]
		PAHs			Reasonable selection of pyrolysis temperature	[36]
	Low temperature	MB/NB	--	--	Consider the pH of biochar and medium	[103]
	pH	Heavy metals	--	pH 3-7: decline pH 7-13: rise	Slow pyrolysis is recommended	[36]
Pyrolysis rate		PAHs (fast, flash evaporation)	--	--		[29]



**Table 2** The types and concentrations of heavy metals in some of biomass and corresponding biochar.

Biomass category	Biomass	Types of main heavy metals	Concentrations of heavy metals (mg/kg)	Leachability of heavy metals (mg/kg)	Bioavailability of heavy metals (mg/kg)	Reference
Animal excrements	Pig manure	Zn, Cu	129.24, 122.89	1.21, 2.38	31.05, 129.24	[232]
Sewage sludge	Municipal sewage sludge	Zn, Cu, Pb, Fe	2103.6 ± 61.1, 690.8 ± 4.3, 438.3 ± 6.3, 192.8 ± 407.6	--	47.50, 11.30, 10.38, 196.60	[233]
Sewage sludge	paper mill sludge	Zn, Cu, Pb, Ni	332.79, 146.97, 52.99, 20.81	7.98, 3.72, 0.72, 1.81	1.12, 4.03, 0.83, 0.49	[36]
Plant	Miscanthus	Zn, Cu, Pb, Ni, Cr	102.00, 2.22, 22.30, 9.95, 18.00	--	--	[33]
Plant	Wicker	Zn, Pb	21.60, 32.90	--	--	[33]
Plant	Pennisetum sinese	Cu, Cd	MB: 21.40, 6.31	2.31, 1.64	3.93 ± 0.20a, 1.47 ± 0.12a	[15]
			HB: 40.20, 5.29	1.22, 0.80	3.26 ± 0.15bc, 0.53 ± 0.05cd	
Food waste	Restaurant food waste	Zn, Pb, Fe, Mn	0.03, 0.03, 4.21, 0.03	--	--	[33]
Food waste	Coconut shell	Zn, Cu, Mn	41.46, 33.84, 41.47	--	--	[234]

HB, MB: biochars with different concentrations of Cu and Cd were produced from the straws of *Pennisetum sinese* grown in moderately-polluted (MB) and highly-polluted (HB) soils.

**Table 3** Total and bioavailable PAHs content in biochar derived from different biomass and operating conditions.

Biomass	Temperature (°C)	Production conditions	PAHs	Total PAHs concentration (µg/kg)	Dominant PAHs	Bioavailable PAHs	Reference
Hemp	500	Atmosphere: N2 Residence time: 30min	16 US EPA	34900 (dry mass)	2- ring (NAP), 3- ring (PHE)	N/D	[43]
Wood pellets	500	Atmosphere: N2 Residence time: 30min	16 US EPA	33700 (dry mass)	3- ring (PHE)	N/D	[43]
Corn stover	350	--	16 US EPA	1609	3- ring (PHE)	1.62 ng/L	[29]
	450			1959	2- ring (NAP)	1.41 ng/L	
	550			1770	2- ring (NAP)	1.303 ng/L	
Pine wood (PW Pinus ponderosa)	500	--	16 US EPA	106	3- ring (PHE)	1.297 ng/L	[29]
	700			111	2- ring (NAP)	1.103 ng/L	
	900			73	2- ring (NAP)	1.304 ng/L	
Hardwood	--	--	16 US EPA	338	2- ring (NAP)	1.904 ng/L	[29]
Sewage sludge	500	Atmosphere: N2 Residence time: 3h	16 US EPA	2263	3- ring (PHE)	44 ng/L	[235]
	600			1730		51 ng/L	
	700			1449		46 ng/L	
Wood	450	Residence time: 48h	16 US EPA	9556	2- ring	N/D	[32]
Rice husk				64650	2- ring		
Softwood				8701	2- ring		
Rice	500	gasification	16 US	2267	4- ring (PYR)	N/D	[28]
Poplar wood	1200			15660	4- ring (PYR)		

Grape marc			EPA	3810	3- ring (ACY)		
Wheat straw				15840	4- ring (PYR, FLT)		
Softwood pellets	550	Residence time: 20min Some biochars went through re-condensation	16 US EPA	6090-53420	2- ring, 3- ring (PHE)	<0.001- 2.040 µg/g	[72]

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