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Review

# Potential hazards of biochar: The negative environmental impacts of biochar 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 a large surface area, porous structure, and abundant surface O-containing functional groups. However, some surface properties (i.e., (i) some surface properties (i.e., organic functional groups and inorganic components), (ii) changes in pH), and (iii) chemical reactions (e.g., aromatic C ring oxidation) that occur between biochar and the application environment may result in the release of harmful components. In this study, biochars with a potential risk to the environment were classified according to their harmful components, surface properties, 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 negative environmental impacts of biochar on soil, water, and atmospheric environments. It also 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.

## 1. Introduction

With the 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 (Chen et al., 2020; Wang et al., 2020b; Zhang et al., 2019a). In recent years, biochar has been widely applied for soil improvement (Teixidó et al., 2013; Ye et al., 2019), agricultural production (Oladele and Adetunji, 2020; Xia et al., 2020), greenhouse gas (GHG) emission reduction (Paustian et al., 2016; Roberts et al., 2010), water pollution treatment (Qin et al., 2020; Xing et al., 2020), waste management (Sparrevik et al., 2014; Yang et al., 2020), and other purposes (Fig. 1) because of its large surface area, rich porous structure, and 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 radicals (EPFRs), dioxins, and perfluorochemicals (PFCs)] may be produced 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 of biochar owing to its potentially harmful components and various interactions with the environment (El-Naggar et al., 2020; Cui et al., 2021).

Meanwhile, the evolution (aging) of biochar upon being subjected to environmental processes may produce negative effects in the environment (media) owing to changes in its properties, which not only affect the medium itself but also the interface of the medium (Rombola et al., 2019; Joseph et al., 2010). A soil–water–gas cycle is possibly induced during biochar transportation (Chen et al., 2018b). Biochar may be transported from soil to water due to migration and leaching, from water to soil due to runoff, from soil to the atmosphere due to wind erosion and weathering, and finally from the atmosphere to soil or water due to free settlement and precipitation (Wang et al., 2013a, 2013b; Novak et al., 2009). Therefore, it is imperative to systematically discuss the negative

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environmental effects of biochar from the perspective of various media to avoid possible risks.

Previous reviews and studies on biochar have mainly focused on the modification of biochar (Ye et al., 2020), reaction mechanisms (Yang et al., 2020), and the active role of biochar in environmental remediation (Deng et al., 2021). However, the negative effects and potential risks of biochar have only recently been highlighted. For example, Zhang et al. (2019a) and Lian and Xing (2017) briefly mentioned the environmental risks of biochar in their commentaries; however, the comprehensive phenomena and mechanisms involved require elucidation. Similarly, Godlewska et al. (2021) reviewed the potential environmental risks of biochar in a single environmental medium (soil); however, the potential hazards of biochar to water and the atmosphere, as well as the comprehensive effects on different media, must be investigated. The utilization of life cycle assessment (LCA) to assess the negative impacts of biochar has recently been focused on (Owsianiak et al., 2018; Wowra et al., 2021), which should be summarized and reviewed for research guidance. Therefore, the overall potential risks of biochar application in soil, water, and the atmosphere must 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 on 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 previous studies (Visioli et al., 2016; Hale et al., 2012; Lyu et al., 2016; Zhang et al., 2019c), 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. 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 amount of biochar may have negative environmental impacts over a short period and can be reduced or degraded in the long term (Quilliam et al., 2013b), these phenomena are correlated with actual field remediation conditions. Therefore, these laboratory-scale studies have high relevance in the field.

*2.1.1.1. Heavy metals.* The content and bioavailability of heavy metals in biochar varies with biomass type. When biomass with a 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, often grows in soils fertilized with sewage sludge or wastewater and shows high accumulation of trace metals (Galbally et al., 2014). Oleszczuk et al. (2013) also reported that *Miscanthus*-derived biochar showed a higher hazardous metal content than other biochars and might leach heavy metals to the environment. von Gunten et al. (2017) found that in wood biochar (derived from pin wood chips, bamboo, or oak), heavy metals such as Zn and Mn (present in large amounts) may mainly exist in the form of monovalent and divalent cations. Therefore, these heavy metals are weakly adsorbed onto the biochar matrix and are easily released, even under mild conditions (such as irrigation) (Forghani et al., 2012). Wood-derived biochar has a large surface area (180–270 $m^2/g$), and thus a higher heavy metal concentration in the exchangeable/acid-soluble fraction (sometimes greater than 50% of the total) may lead to higher heavy metal bioavailability (von Gunten et al., 2017). Controlling the pyrolysis temperature is also important for controlling the heavy metal content in biochar. For example, Devi and Saroha (2014) found that the Cu, Pb, and Zn contents in biochar increased significantly as the temperature increased, and when the pyrolysis temperature increased from 200 °C to 700 °C, the contents of the three metals increased by 61%, 73%, and 65%, respectively. This occurred mainly because as the temperature increased, the organic matter (OM) present in the biomass decomposed, which in turn led to the release of heavy metals bound to the OM. It has been found that the heavy metal bioavailability in biochar may decrease as the pyrolysis temperature increases (Devi and Saroha, 2014). The

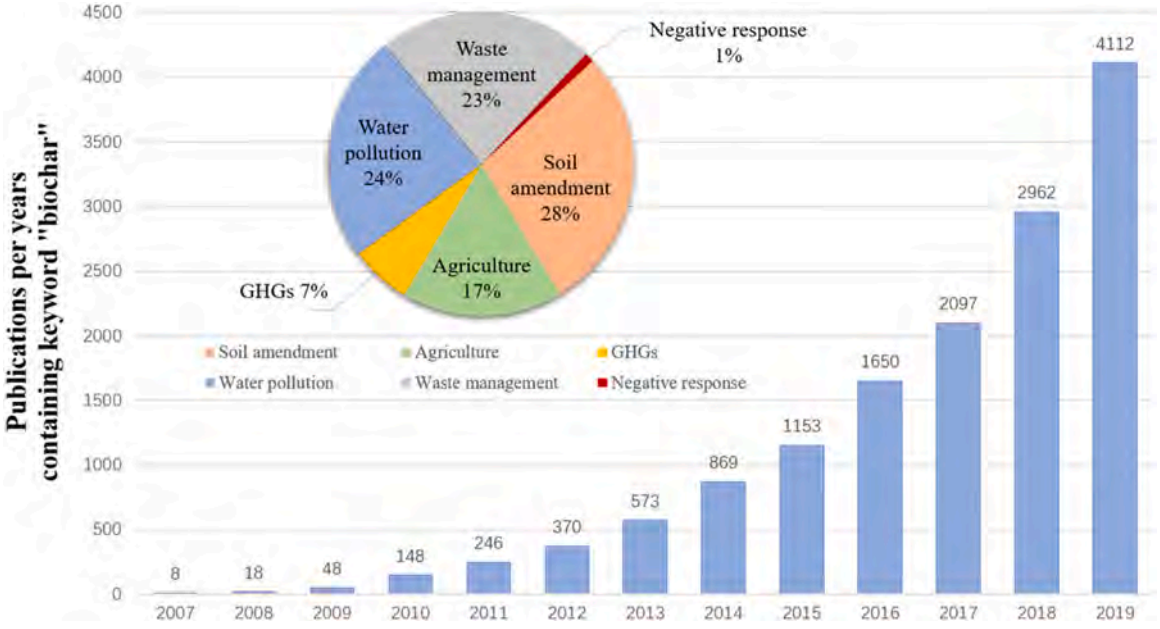


**Fig. 1.** Publications per year containing the keyword "biochar" on indexed journals between 2007 and 2019. The percentage of motivation in biochar application. The data is based on the search results from Web of Science (Nov. 2020).

environmental risk of heavy metals in biochar not only depends on the heavy metal content and pyrolysis temperature, but also on the pH, existing forms of heavy metals, mineral structures, and application environment. Devi and Saroha (2014) reported a contrasting effect of pH on the leaching capacity of heavy metals in sludge biochar. The heavy metals in the biochar showed the maximum leaching ability at a pH of 3 because low pH conditions generally enhance metal dissolution. As the pH of the solution increased from 3 to 7, the leaching amount decreased. A further increase in the solution pH from 7 to 13 led to an increase in the leaching of heavy metals, especially Cr. This might have occurred because the leached Cr reacted with CaO to form $CaCrO_4$ after carbonate decomposition (Zheng et al., 2010). Meanwhile, the environmental medium may change the forms of heavy metals in biochar, which may change the potential risk degree of the latter. Studies have shown that the environmental risks in different forms of heavy metals are in the order (from high to low) of carbonate-bound state, Fe-Mn oxide-bound state, OM, sulfide-bound state, and residual state. When alkaline biochar with a high heavy metal content (higher content of acid-soluble or exchangeable fractions) is used in acidic soil media, Cd, Zn, Pb, and Cu in the biochar may be activated and converted from a low-risk state (e.g., residual state) to a high-risk state (e.g., carbonate-bound state) (Bandara et al., 2017). This is mainly because with the decrease in soil pH, the free metal components of heavy metals in the soil, the reciprocal action, and the heavy metal contact and absorption of the plant may increase (Wu et al., 2021b). Therefore, the type of biomass feedstock and pyrolysis temperature should be correctly selected when producing biochar to reduce its heavy metal content as much as possible (Table 1). If the application of biochar with a high heavy metal content cannot be avoided (Table 2), then it is necessary to systematically consider the relationship between the biochar and the environmental medium, such as the soil pH, to minimize the environmental risks of biochar due to the presence of heavy metals. The literature provides contradictory results. Chagas et al. (2021) reported that when using sludge biochar with a high heavy metal content, heavy metal leaching in the environmental medium was measured using diethylenetriamine pentaacetate, and it was found that the amount of heavy metal leaching was lower than the highest limit of the international standard. This might have occurred because the biomass component bonded with the high-concentration metal component during the char formation process, thereby resulting in the formation of a metal–C/metal–O–C bond structure (Alipour et al., 2021), which stabilized the heavy metal morphology and made leaching more difficult. However, to review the potential risks of biochar as thoroughly as possible, this relatively stable combination should also be treated as a potentially risky environmental pollutant (Odinga et al., 2020).

*2.1.1.2. PAHs.* PAHs, which have high biotoxicity, 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) (Hale et al., 2012) (Table 3). The PAH content in biochar from different feedstocks is naturally different; biochar obtained from hemp has a higher mutagen content than that obtained from wood (Anjum et al., 2014). Because there are few PAH precursors in plant biomass, the main PAH in biochar produced from plant biomass-dominated feedstocks is light naphthalene. Hale et al. (2012) conducted a quantitative analysis of PAHs in more than 50 biochars by slow pyrolysis (characterized by slow heating of organic material to approximately 400 °C in the absence of O with long solid and gas residence times, typically for several minutes to hours) between 250 °C and 900 °C. It was found that the total concentration of PAHs in the slow pyrolysis biochar was lower than that in the fast pyrolysis and gasification biochar. Flash evaporation also increased the PAH content of biochar. The PAH content in biochar generally decreases as the pyrolysis time and temperature increase. Hale et al. (2012) reported that the PAH concentration of pine wood at 900 °C was significantly lower than that at all other production temperatures (except for at 600 °C) because the π–π interactions between PAHs and biochar would be disrupted by an increase in pyrolysis time and temperature. Additionally, as the pyrolysis temperature increased, 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

**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 Bamboo Oak) | Heavy metals (Zn, Mn) | – | Sometimes more than 50% of the total | Biomass with low heavy metal content is recommend | (von Gunten et al., 2017) |
| Sewage sludge | 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% | – | (Chen et al., 2018a) |
| | PFCs (PFOA, PFOS) | 10.6-11.5 ng/g, 4.8-6.3 ng/g | – | | (Sun et al., 2011) |
| | PAHs | 13.88-15.49 mg/kg | 11.75 μg/L | | (Chen et al., 2019b) |
| Food waste (with high content of salt) | Dioxins | – | 1.2 pg/g TEQ | Choose biomass with low chlorine content | (Hale et al., 2012; Sørmo et al., 2020) |
| Softwood (Douglas firs) | EPFR | – | – | Hardwood is recommended | (Lei et al., 2019) |
| Plant (herbaceous plant) Ball milling technology | MB/NB | – | The toxicity increased with the decrease of particle size | Woody plant biochar is less prone to physical aging | (Luo et al., 2017; Jia et al., 2021) |
| High temperature | Heavy metals | Increases with increasing temperature (200-700 °C) | – | Reasonable selection of pyrolysis temperature | (Devi and Saroha, 2014) |
| | EPFR | Increases with increasing temperature | Increases with increasing temperature | | (Zhang et al., 2019c) |
| Low temperature | PAHs | – | – | Reasonable selection of pyrolysis temperature | (Devi and Saroha, 2014) |
| | MB/NB | | | | (Yang et al., 2019) |
| pH | Heavy metals | – | pH 3-7: decline<br>pH 7-13: rise | Consider the pH of biochar and medium | (Devi and Saroha, 2014) |
| Pyrolysis rate | PAHs (fast, flash evaporation) | – | – | Slow pyrolysis is recommended | (Hale et al., 2012) |

**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 | (Meng et al., 2017) |
| 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 | (Lu et al., 2013) |
| 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 | (Devi and Saroha, 2014) |
| Plant | Miscanthus | Zn, Cu, Pb, Ni, Cr | 102.00, 2.22, 22.30, 9.95, 18.00 | – | – | (Oleszczuk et al., 2013) |
| Plant | Wicker | Zn, Pb | 21.60, 32.90 | – | – | (Oleszczuk et al., 2013) |
| Plant | Pennisetum sinese | Cu, Cd | MB: 21.40, 6.31 | 2.31, 1.64 | 3.93 ± 0.20a, 1.47 ± 0.12a | (Cui et al., 2021) |
| | | | 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 | – | – | (Oleszczuk et al., 2013) |
| Food waste | Coconut shell | Zn, Cu, Mn | 41.46, 33.84, 41.47 | – | – | (Castilla-Caballero et al., 2020) |

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 | (Anjum et al., 2014) |
| Wood pellets | 500 | Atmosphere: N2 Residence time: 30min | 16 US EPA | 33700 (dry mass) | 3- ring (PHE) | N/D | (Anjum et al., 2014) |
| Corn stover | 350 | – | 16 US EPA | 1609 | 3- ring (PHE) | 1.62 ng/L | (Hale et al., 2012) |
| | 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 | (Hale et al., 2012) |
| | 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 | (Hale et al., 2012) |
| Sewage sludge | 500 | Atmosphere: N2 | 16 US | 2263 | 3- ring (PHE) | 44 ng/L | (Kończak et al., 2019) |
| | 600 | Residence time: 3h | EPA | 1730 | | 51 ng/L | |
| | 700 | | | 1449 | | 46 ng/L | |
| Wood | 450 | Residence time: 48h | 16 US EPA | 9556 | 2- ring | N/D | (Quilliam et al., 2013b) |
| Rice husk | | | | 64650 | 2- ring | | |
| Softwood | 500 | | | 8701 | 2- ring | | |
| Rice | | | | 2267 | 4- ring (PYR) | | |
| Poplar wood | 1200 | gasification | 16 US EPA | 15660 | 4- ring (PYR) | N/D | (Visioli et al., 2016) |
| Grape marc | | | | 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 | (Buss et al., 2015) |

biochar is reduced during the leaching process, resulting in the diffusion of PAHs through the internal matrix and accelerating the desorption of PAHs (Chen et al., 2019b; Van de Wiele et al., 2004). Chen et al. (2019b) evaluated the leaching behavior of PAHs in biochar derived from sewage sludge pyrolyzed at different temperatures (300–700 °C). The total PAH concentration in the leachate reached its peak of 11.75 μg/L at 700 °C, which was equivalent to 15.9% of the total PAHs in the biochar. Rombolà et al., (2015) proposed that almost 1 year after the last biochar application, the total PAH concentration in the amended soils (153 ± 38 ng/g) was significantly higher than that in the control soil (24 ± 3 ng/g). Similarly, Quilliam et al. (2013a, 2013b) found that the concentration of 16 United States Environmental Protection Agency priority PAHs in a soil amended with wood-based biochar (50 t/ha) for 3 years was 1953 μg/kg, which was observably higher than that of the control soil (1131 μg/kg). This phenomenon occurred 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 OM combined with PAHs (Wang et al., 2018). Regarding the environmental risk of PAHs, their bioavailability is more important and is mainly affected by the pyrolysis temperature and biomass of the raw materials. Some studies reported that biochar produced at low pyrolysis temperatures may contain a high content and bioavailability of PAHs (Hale et al., 2012) (Table 3). 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 (Hale et al., 2012).

*2.1.1.3. Dioxins.* Harmful components, such as dioxins, may also be produced during biochar preparation (Tsouloufa et al., 2020). The preparation conditions are the key factors affecting the amount of dioxins in biochar. Hale et al. (2012) quantitatively studied the dioxins (130 toxic and non-toxic dioxins) in more than 50 types of biochars (derived from food waste, digested milk fertilizer, pine wood, and pine) produced by slow pyrolysis between 250 °C and 900 °C with concentrations ranging from 84 ng/kg to 92 ng/kg. Food waste, which often

has a high salt content, has been shown to contain a significant amount of dioxins (Sørmo et al., 2020). The selection of the biochar pyrolysis temperature also has an effect on the formation of dioxins. Although dioxins are destroyed at production temperatures of > 1000 °C, the energy consumption increases significantly. Therefore, the initial biomass feedstocks should have sufficiently low Cl contents to prevent the formation of detectable levels of dioxins (Wiedner et al., 2013). However, the dioxin concentration alone is not a direct indication of the environmental risk of dioxins because 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 are 17 ng/kg and 20 ng/kg TEQ, respectively. Lyu et al. (2016) discovered that the dioxin concentration was 50–610 pg/g in wood chip-derived biochar produced at 250–700 °C, and the TEQ was significantly lower (1.7-9.6 pg/g). Hale et al. also observed the highest TEQ concentration (1.2 pg/g TEQ) in biochar derived from food residues at 300 °C (Hale et al., 2012). The bioavailable dioxin content was below the detection limit. Therefore, the dioxin content in biochar is generally low. However, environmental contamination can still occur under circumstances with repeated application of biochar containing these compounds.

*2.1.1.4. EPFRs.* A very strong EPFR signal can be detected in biochar, which is generally $10^{18}$ unpaired spins per gram (Fang et al., 2014). These EPFRs are widely involved in environmental processes during the production and large-scale application of biochar (Pan et al., 2019). 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) (Odinga et al., 2020). Because there are two possible cleavage positions in the cellulose chain, free radicals may be formed via the uniform cleavage reaction of the chain (Zhang et al., 2013). Compared with cellulose and hemicellulose, lignin has a tighter structure. Thus, cellulose undergoes a strong decomposition reaction, which includes the gradual reaction of EPFRs (Kibet et al., 2012). Compared with non-wood and hardwood lignin, softwood lignin contains more G-type subunits and a phenylcoumaran structure, which contains a weak α-aryl ether bond, thereby leading to the production of more free radicals under the same conditions (Lei et al., 2019). Therefore, more attention should be paid to the potential environmental risks of EPFRs in the application of biochar, especially softwood-derived (e.g., Douglas fir) biochar. In addition, EPFRs can be produced from biochar residues in the environment. This process occurs mainly because of the presence of transition metals, such as $Fe^{2+}$ (Assaf et al., 2016). Transition metals are usually transferred onto biomass via chemical adsorption during pyrolysis and then continue to transfer electrons from the polymer to the metal center, thereby leading to the formation of EPFRs (Ruan et al., 2019). Lignin and cellulose in biomass may be decomposed to form aromatic molecular precursors during pyrolysis and converted into EPFRs after exposure to air. In addition, a stable EPFR can be generated directly without precursors at high pyrolysis temperatures (Fig. 2a) (Maskos et al., 2005). In addition to the influence of the type of biomass

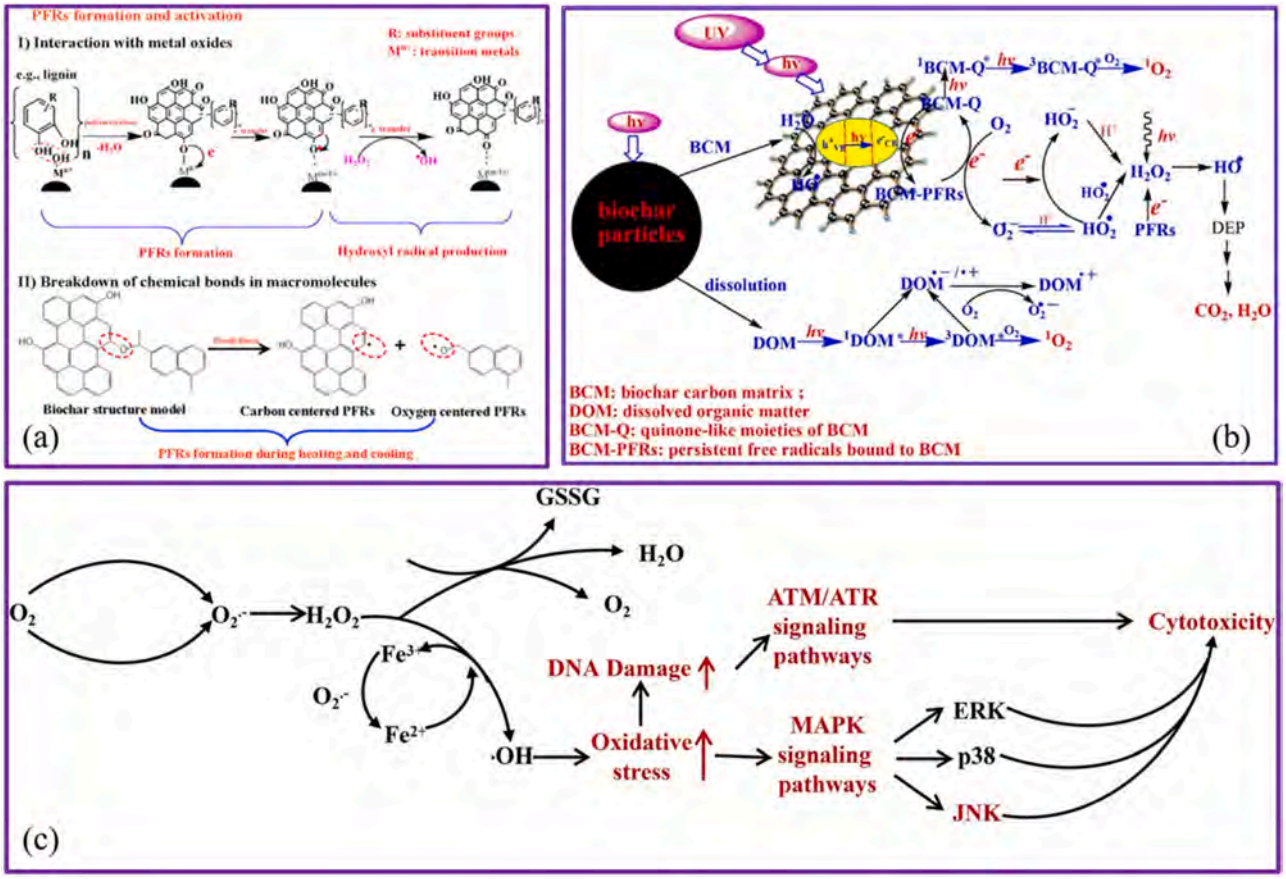


**Fig. 2.** EPFR induces the formation of ROS and the biological toxicity mechanism of ROS production (a) Schematic of the mechanisms of PFR formation and free radical generation on biochar, including: I) the interaction between organic compounds containing oxygenous functional groups and metal oxidation, and II) the breaking of chemical bonds in macromolecules during heating and cooling. (b) Proposed framework for ROS formation from biochar suspension under light. (c) The mechanism of ROS biological toxicity, the figure is modified from reference materials.
(a) Reproduced with permission from ref (Zhu et al., 2017). Copyright 2017 Elsevier. (b) Reproduced with permission from ref (Ruan et al., 2019). Copyright 2019 Elsevier. (c) Reproduced with permission from ref (Liang et al., 2019). Copyright 2019 Elsevier.

on the EPFR content in biochar, in one study, the EPFR signal intensities increased as the pyrolysis temperature increased (Liao et al., 2014). This indicated that the increase in pyrolysis temperature (200–500 °C) caused the formation of EPFRs in the biochar. When the pyrolysis temperature was further increased to 600 °C, the organic compounds in the biomass, which are the main components required for EPFR formation, decomposed (Zhang et al., 2019c; Fang et al., 2015). Moreover, the concentration of EPFRs in the biochar increased at higher temperatures. Considering the binding ability of environmental media (especially soils with a high complexing/binding capacity), the total EPFR concentration cannot directly represent the toxicity index; however, the bioavailability of EPFRs should be used as an index for toxicity assessment. Maskos et al. (2005) found that the free radicals produced by biochar obtained at a high temperature of 450 °C had greater environmental sustainability than those produced by biochar obtained at 320 °C. This suggests that the pyrolysis temperature affects not only the free radical content in biochar, but also the environmental sustainability of free radicals. Accordingly, the importance of the pyrolysis temperature in biochar production should be determined.

A study of persistent free radicals similar to EPFRs 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 (PM) in the atmosphere (Stephenson et al., 2016), which is the result of redox reactions under atmospheric conditions (Nwosu et al., 2016). Thus, EPFRs in biochar are stable on the surface of transition metals and can persist in the atmosphere (Odinga et al., 2020). EPFRs 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 environmental media (Fig. 2c) (Dellinger et al., 2000). The internal mechanism of ROS production induced by EPFRs can be explained by the semiquinone-phenoxyl hypothesis, which states that semiquinone radical anions react with molecular O to form superoxide, which then reacts with biological reduction equivalents (such as nicotinamide adenine dinucleotide phosphate and ascorbate) to disproportionate to hydroxyl peroxide (Lomnicki et al., 2008). Moreover, the biotoxicity and cytotoxicity of EPFRs may be related to induced oxidative stress, which can lead to cell cancer and death (Liao et al., 2014; Xue et al., 2020). Balakrishna et al. (2009) found that EPFRs significantly increased ROS production in BEAS-2B cells and reduced cellular antioxidants, which ultimately led to cell death. Therefore, the ratio of oxidants and antioxidants may become imbalanced owing to the ROS induced by EPFRs, thereby leading to cell death (Xue et al., 2020; Kisin et al., 2011). Meanwhile, the ROS induced by EPFRs may also react with macromolecules (e.g., glycoproteins), thereby leading to membrane instability, which further results in cell apoptosis (Odinga et al., 2020). Zhang et al. (2019c) used pine needle-derived biochar to explore its biotoxicity to aquatic algae. The results showed that EPFRs in the biochar induced the production of not only acellular ROS (e.g., ·OH) in water (Fig. 2b), but also intracellular ROS in aquatic organisms. Therefore, the ROS and superoxide dismutase (SOD) activities in algae cells were both upregulated, thereby leading to oxidative damage.

*2.1.1.5. Other contaminants.* In addition to the typical pollutants mentioned above, which are often discussed, there may be other environmentally harmful substances in biochar owing to the different types of raw materials used for biochar production. For example, PFCs are persistent pollutants with high resistance to both chemical and thermal degradation (Yu et al., 2009). Kim et al. (2015b) studied the pollution caused by perfluorooctane sulfonic acid (PFOS) and perfluorooctane acid (PFOA) present in plant residues and sewage sludge after biochar formation. It was found that the total residual concentration of PFOA and PFOS in the sludge biochar was 15.8–16.9 ng/g, which did not decrease significantly after pyrolysis. However, these perfluorocarbons were not found in plant-derived biochar. Additionally, biotoxic VOCs are potential environmental pollutants in biochar. For instance, Spokas et al. (2011) tested the VOC content in biochar produced from more than 30 material types under different conditions and found that acetone, benzene, methyl ethyl ketone, toluene, and methyl acetate were identified in more than half of the biochars. Buss et al. (2015) also observed that the re-condensation of VOCs occurred during the preparation of biochar from pyrolyzed cork, which in turn resulted in a higher VOC content.

### 2.1.2. External pollutants adsorbed onto biochar

After biochar is applied to an environmental medium, it undergoes physical, chemical, and biological actions during its contact with various parts of the medium, which promotes its aging and significantly changes its characteristics (Lehmann et al., 2011) (Fig. 3). Physical aging mainly refers to the effect of various physical factors on biochar after entering the environment. For example, owing to wear, impact, or wind effects, biochar may shrink in size after entering the environment. Compared to woody plant biochar, herbaceous plant biochar is more susceptible to such physical forces (Skjemstad and Graetz, 2003). Under the action of these physical conditions, large pieces of biochar may be broken up, thereby exposing more surface area, which is beneficial to chemical and biological aging processes (Prendergast-Miller et al., 2014). Chemical aging mainly refers to changes in the chemical structure (property) of biochar due to chemical oxidation after application in the environment (Luo et al., 2017). Through the analysis and summary of the literature, it was found that oxidants can violently oxidize biochar, altering its surface structure and resulting in the generation of oxygen-containing functional groups (hydroxyl, nitro, and carboxyl groups) (Wang et al., 2017). Biological aging mainly refers to the process by which microorganisms use biochar as a substrate for oxidative respiration and other life activities (Zimmerman, 2010). 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, thereby resulting in biochar degradation (Czimczik and Masiello, 2007).

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

(1) Theoretically, the increase in O-containing functional groups on the surface of the aged biochar strengthens the ion exchange with heavy metals (Luo et al., 2017; Wu et al., 2021a). However, Guo et al. (2014) proposed that over a range of pH (5.0-6.8), the cation exchange capacity and adsorption capacity of Cu(II) on the aged biochar were smaller than those of new biochar. The dissociation properties of oxygen-containing functional groups change during aging, which may be the mechanism of inhibiting Cu(II) adsorption during aging of biochar. Compared to low pH range (3.3–5.0), within a relatively high pH range (5.0–6.8), functional groups (phenolic hydroxyl) that are more difficult to dissociate played a major role. Furthermore, the aging process could make it more difficult for functional groups on the biochar surface to dissociate, thus inhibiting the adsorption of Cu(II). Therefore, it is necessary to comprehensively consider the pH of the medium and the internal mechanism of the heavy metal adsorption by biochar when determining the changes in the heavy metal adsorption capacity of the aged biochar. 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 (Choppala et al., 2016), thereby reducing the amount of heavy metals adsorbed by biochar.
(2) PAHs are adsorbed onto biochar via the π–π interaction between the benzene ring of PAHs and the aromatic C structure of biochar. However, during the biochar aging process, aromatic C rings rich in π–π electrons become oxidized (Joseph et al., 2010). Therefore, aged biochar may also cause the release of organic pollutants

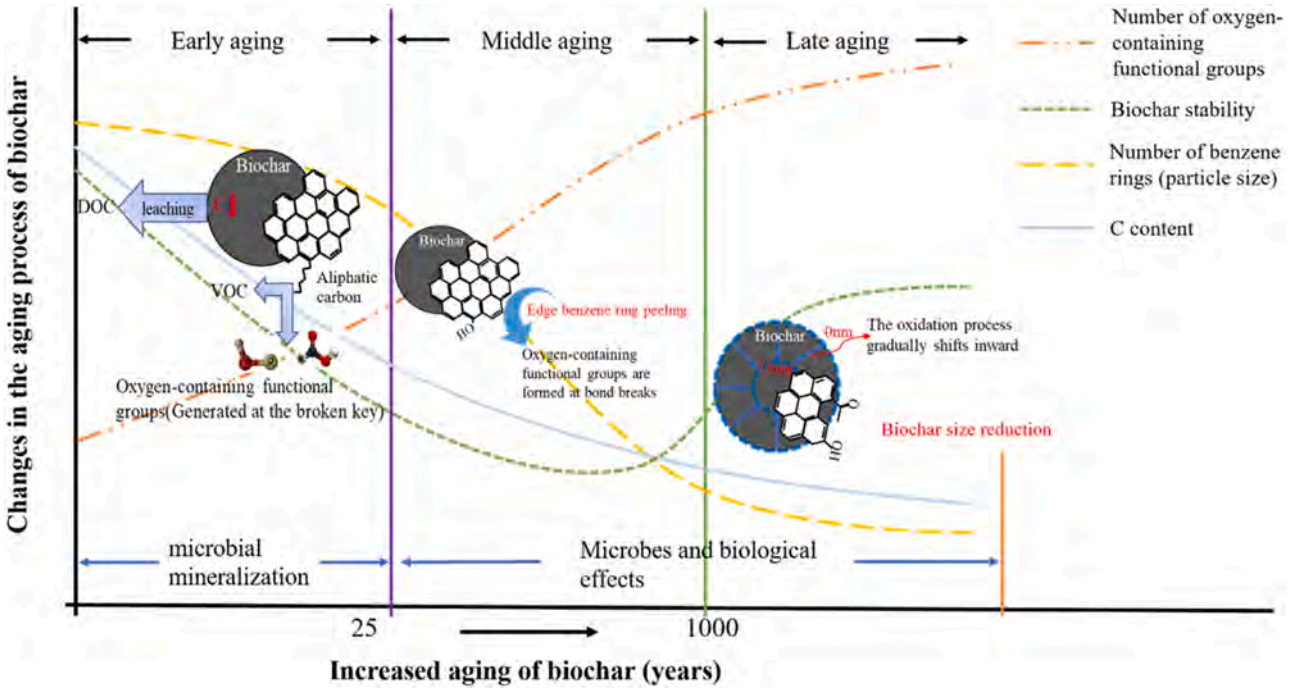


**Fig. 3.** Schematic diagram of structural changes during oxidation and aging of biochar.

originally adsorbed onto the biochar, thereby causing secondary environmental pollution.

(3) Aged biochar is more prone to biodegradation or physical decomposition, thereby resulting in the release of a series of biochar components (e.g., dissolved OM and soluble black C) and endogenous pollutants (e.g., heavy metals) (Mia et al., 2017; Liu et al., 2017; Khan et al., 2013; Li et al., 2019a). For example, Cui et al. (2021) found that aging can activate heavy metals in biochar, which can improve the leaching rate and bioavailability of heavy metals, thereby posing potential environmental risks. In their study, biochars with high, medium, and low heavy metal contents were aged using dry–wet and freeze–thaw aging methods. After dry–wet and freeze–thaw aging, the concentrations of bioavailable (acid-soluble) Cu and Cd increased, especially in the biochar with a high intrinsic metal concentration and high heavy metal content. This phenomenon can be explained by several factors. Initially, aging increases the specific surface area and pore volume of the biochar, which in turn increases the exposure of endogenous heavy metals to the environment, thereby resulting in the release of endogenous metals from the biochar. In addition, owing to the increase in $CO_2$ adsorption and acidic functional groups during the aging process, the pH of the biochar decreases (Xu et al., 2018). Endogenous heavy metals combined with organic C (OC) may then be released owing to the decomposition and mineralization of unstable OC (dissolved OC) (Huang et al., 2019). 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 the biochar, whereas the activation of Cd is mainly influenced by the changes in the inorganic components and pH of the biochar. Meanwhile, the increase in the leaching and bioavailability rates of endogenous heavy metals in biochar with different aging methods also differ. For example, freeze–thaw-aged biochar has higher Cu and Cd leaching rates than dry–wet-aged biochar. Both wet–dry and freeze–thaw aging increase the available Cu content, while only increasing the available Cd in biochar with a medium heavy metal content (Cui et al., 2021). Therefore, the fate and potential pollution risks of biochar must be considered prior to biochar-based environmental remediation.

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

Micro-biochar (MB) and nano-biochar (NB) particles are mainly smaller than 1 μm 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, namely (1) primary MB/NB, which is produced non-deliberately during the preparation process or specially prepared in the laboratory via grinding, ultrasound, and other treatments; and (2) secondary MB/NB, which is produced by the interaction of bulk biochar with the environment after application (Zhang et al., 2020a). In terms of structural characteristics, the O 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 C stability (Liu et al., 2018b).

The presence of MB/NB can promote the release of heavy metal ions into the medium when applied to soil. Kim et al. (2018) observed that biochar particles with a particle size of less than 0.45 μm could increase the release and mobility of As in soil. Moreover, the co-migration ability of biochar with heavy metals is affected by the feedstock. Song et al. (2019) 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. Plant-derived MB/NB also showed high potential for the co-transportation of pollutants (such as $Cd^{2+}$). Contrary to the positive effect of biochar in maintaining soil fertility, MB/NB promotes the loss of P 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 can form P-Fe/Al soil colloids via electrostatic attraction and ligand adsorption in the soil (Arai and Livi, 2013), 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 bound P has great potential for co-transportation to groundwater (Liu et al.,

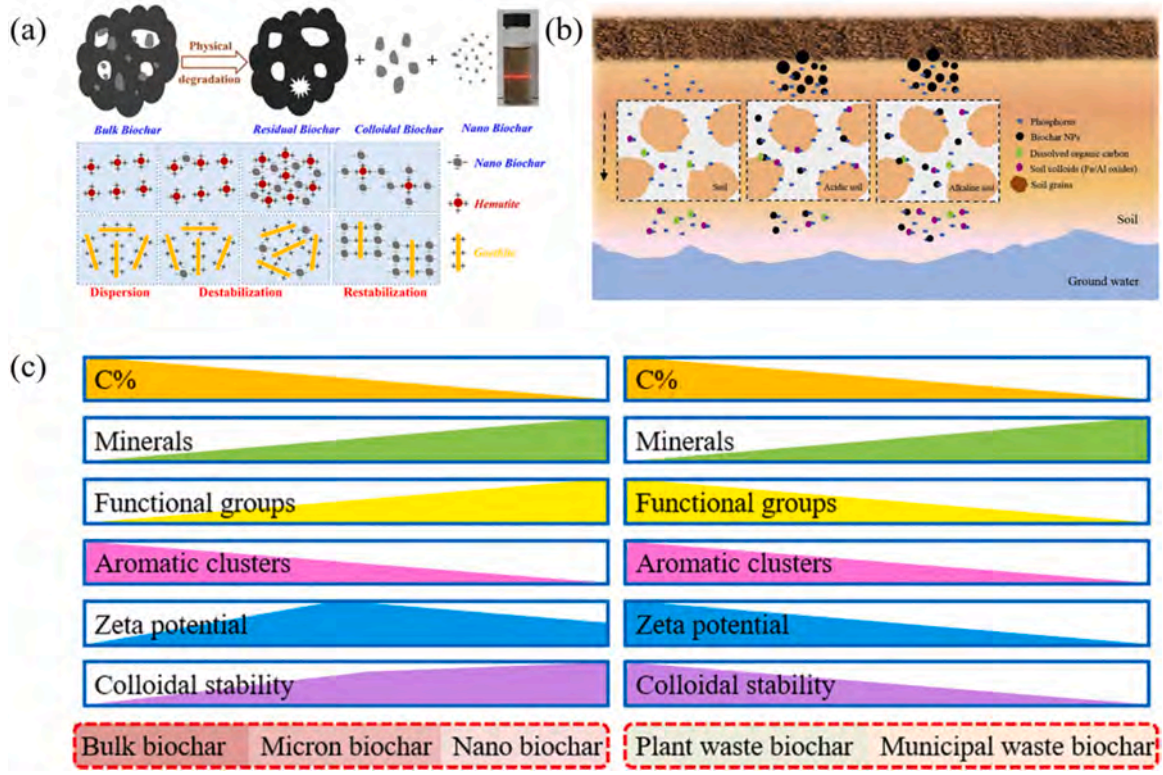


**Fig. 4.** MB/NB's main negative environmental impact and internal mechanism; (a) Biochar could be weathered in the environment to form MB/NB with high activity. (b) MB/NB promoted the loss of P in alkaline soil by increasing the release of Fe / Al soil colloids, and soil fertility decreased. (c) Schematic diagram of the composition and structure changes of urban-origin biochar and plant-origin biochar from bulk to micron- and nano-level particles.
(a) Reproduced with permission from ref (Liu et al., 2018b). Copyright 2018 ACS publications. (b) Reproduced with permission from ref (Jiang et al., 2015). Copyright 2019 Elsevier. (c) Reproduced with permission from ref (Song et al., 2019). Copyright 2019 Elsevier.

2018b; Chen et al., 2018c). Therefore, adding biochar to soils might result in nutrient leaching 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 reaching the ocean via environmental media, such as rivers or the atmosphere (Novak et al., 2009). For example, during biochar application, MB/NB easily separates from the biochar matrix and migrates with the soil solution (Wang et al., 2013a; Wang et al., 2013b), which is caused by physical (e.g., water erosion and 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 (Qu et al., 2016). Compared with bulk biochar, MB/NB has a richer mineral and O content, higher alkalinity, and higher dynamic stability (Fig. 4a) (Xu et al., 2017). Therefore, MB/NB has a high reactivity in soil and aquatic environments (Song et al., 2019). 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, thereby leading to increased water pollution and biotoxicity in aquatic organisms (Wang et al., 2013b; Liu et al., 2018b). Moreover, under the action of wind, MB/NB may enter the atmospheric environment and cause ecological toxicity in organisms via respiration owing to the presence of semiquinone and phenoxyl radicals (Odinga et al., 2020).

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 as the particle size decreases. The EPFR concentration of particles with an aerodynamic diameter of less than 1 μm is the highest (Pan et al., 2019; Jia et al., 2021). 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 (Lyu et al., 2018a). 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 (Liu et al., 2019b). 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. This ultimately leads to an increase in cell mortality (Lin et al., 2012). 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 influence the aggregation and stability of MB/NB (Wang et al., 2013a; Chen et al., 2017b; Saleh et al., 2008). For example, Yang et al. (2019) pointed out that the presence of more surface O-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. Some minerals in biochar can be dissolved and release cations into aqueous solutions, in which the repulsive energy barrier between colloidal particles is screened via cationic bridging action, thereby progressing the aggregation of MB/NB (Liu et al., 2018a). 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 their migration ability in the natural environment. In contrast, positively charged soil inorganic colloids can limit the migration of MB/NB via charge neutralization. The behavior of MB/NB aggregation is also affected by natural OM, such as humic acid (HA). For example, HA can be adsorbed onto the surface of MB/NB via 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 (Gui et al., 2021). 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 (approximately 5 mg/L) and divalent cations were present at high concentrations to induce cation bridging, the aggregation of biochar colloids in soil was enhanced (Yang et al., 2019). In addition, for pyrolysis temperature, MB/NB rich in functional surface groups (i.e., low-temperature pyrolyzed MB/NB) is generally less likely to accumulate in the soil solution, thereby having high fluidity in the soil (Yang et al., 2019; Cely et al., 2015). In summary, biochar particles can form a stable suspension in soil solutions, especially in acidic soils with low alkali saturation. Dissolved OM can further enhance the stability of MB/NB, thereby enhancing the potential transport of MB/NB by soil water. Therefore, considering the transportation and fate of MB/NB, when biochar is applied to agriculture or environmental remediation, the biochar raw material, preparation temperature, and composition of soil colloids should 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 in the soil and crops (Xia et al., 2020; Liu et al., 2019a).

### 3.1. Soil physical and chemical properties

The pH, structure, porosity, mobility, bioavailability of toxic elements, and other properties of the soil can be changed by biochar (Lee et al., 2010; Wang et al., 2019c). Because as the pyrolysis temperature increases, the amount of acidic functional groups on the surface of the biochar decreases with the loss of O, thereby causing the pH of the biochar to gradually increase from neutral or acidic to alkaline (Wang et al., 2019c). The increase in soil pH due to biochar may limit the supply of certain nutrients (such as $NH_4^+$) to the original soil (Zhang et al., 2019a). El-Naggar et al., (2019b) reported the failure of woody plants to establish and survive owing to the high accumulation of charcoal and micronutrient deficiency caused by increased soil pH from soil biochar application. The biochar-induced increase in soil pH may also promote the hydrolysis of N-acyl-homoserine lactone (AHL), a signaling molecule used by gram-negative bacteria for cell–cell communication, thereby resulting in a decrease in the bioavailability of AHL (Gao et al., 2016). Eventually, communication between the bacterial cells is inactivated. Yang and Lu (Yang and Lu, 2021) evaluated the effects of five different types of biochar on the physical properties of paddy soil using field experiments and found that the addition of biochar to the soil significantly reduced the tensile strength. As the amount of biochar increased, the degree of soil tensile strength decreased. The soil tensile strength under 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, compared with that of the control group. 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 (Li et al., 2019b). Biochar application to soil may have a negative impact not only on the soil but on other related environmental aspects as well. For example, biochar may inhibit the soil nutrient supply and crop productivity by reducing plant nutrient absorption (El-Naggar et al., 2019c). Biochar can also 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. (2020) found that the application of straw biochar significantly increased the bioavailability of As in soil by 101.6%.

### 3.2. Crops

The positive effects of biochar on crop growth are well known; however, we found that biochar still poses potential risks under specific situations; this section summarizes and analyzes those situations. 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) (Lehmann et al., 2011). During 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 (Gelardi et al., 2019). The PAH content in the soil with biochar amendment is higher (Fig. 6a) than that of soil without biochar (Rombola et al., 2019). For instance, Wang et al. Wang et al. (2018) found that 75.0% of Chinese cabbage (*Brassica chinensis*) and 87.5% of pak choi (*Brassica campestris*) samples had benzo[a]pyrene TEQ values

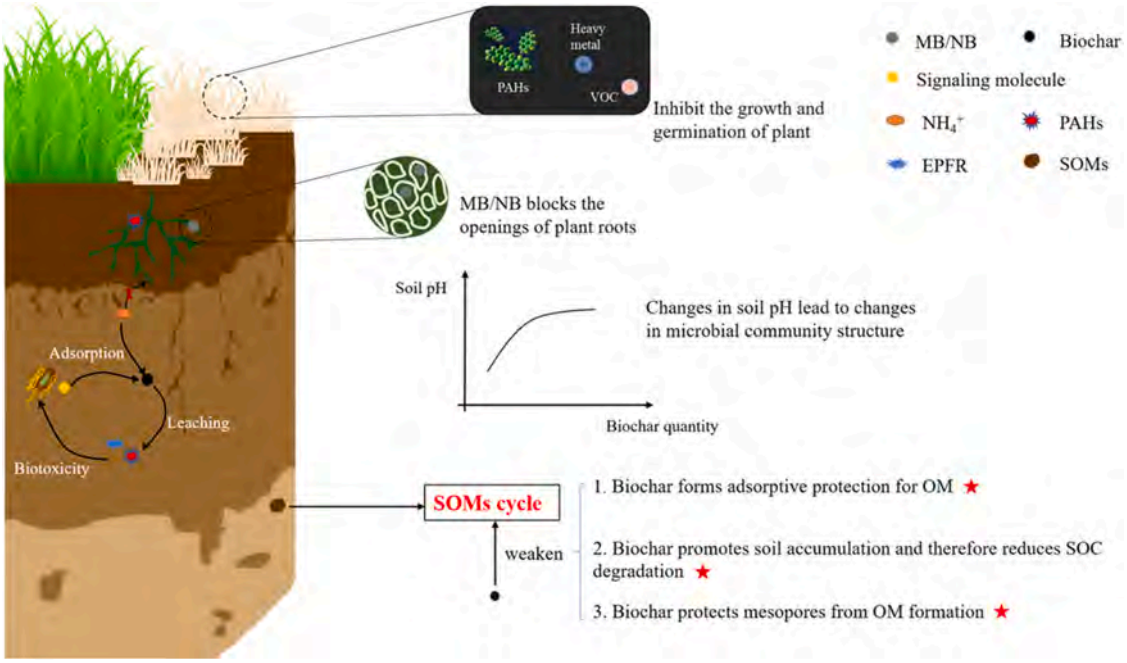


**Fig. 5.** Schematic diagram of the potential negative environmental impact of biochar in the soil environment.

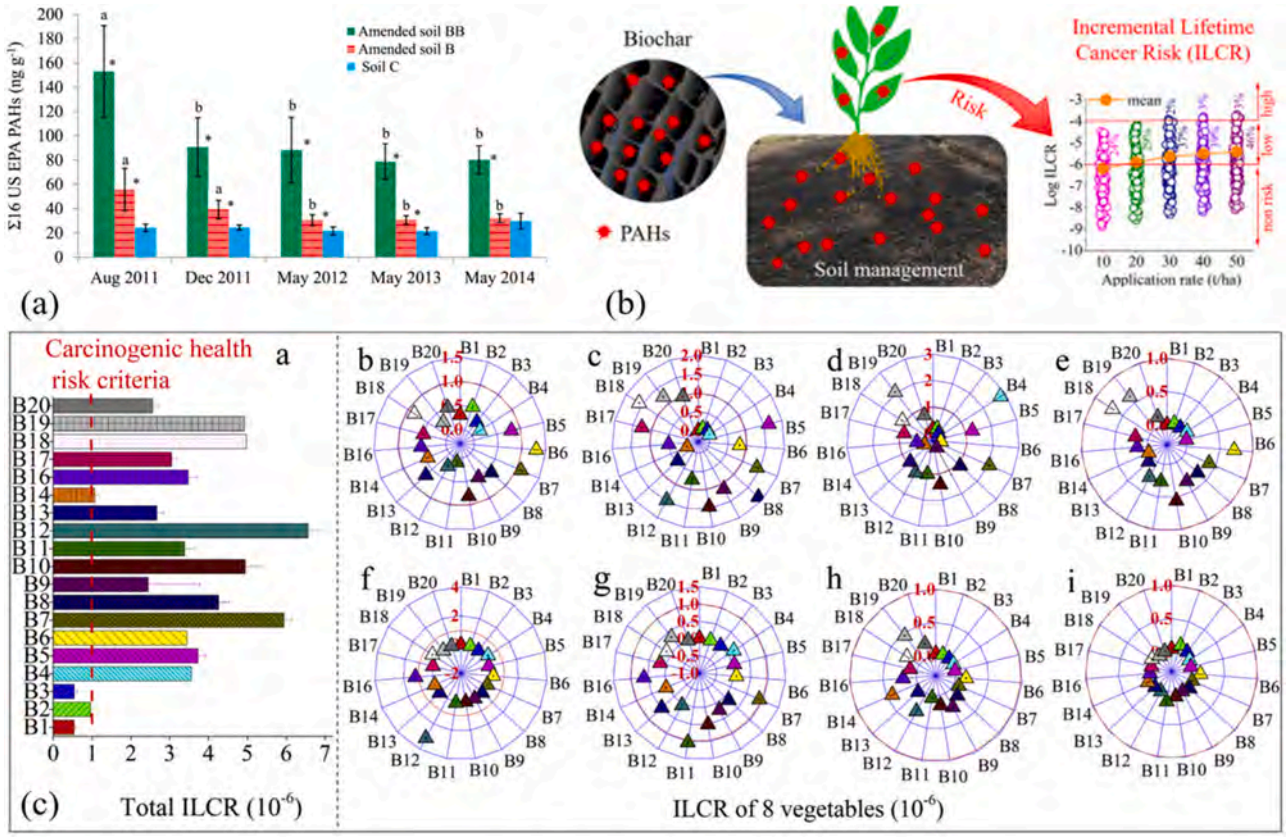


**Fig. 6.** Biotoxicity of PAHs in biochar. (a) The application of biochar results in an increase in the content of PAHs in the soil. (b) PAHs in biochar are enriched by plants and enter the food chain. (c) The human body may ingest PAHs due to the intake of vegetables grown in the soil after biochar modification, which may cause a (ILCR).

(a) Reproduced with permission from ref (Rombola et al., 2019). Copyright 2018 Elsevier. (b) Reproduced with permission from ref (Wang et al., 2019a). Copyright 2019 Elsevier. (c) Reproduced with permission from ref (Wang et al., 2018). Copyright 2018 Elsevier.

higher than the maximum contaminant level. This indicates that the crops concentrate the PAHs leached from biochar, which negatively affects their growth, and in turn, threatens human and animal health (Fig. 6b and c). To verify this, Wang et al. (2018) 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. The negative environmental impact of metals contained in biochar on plants in the soil has also received close attention. Visioli et al. (2016) demonstrated that electrical conductivity and Cu negatively affected both germination and root elongation at a biochar application rate of $\geq$ 5% (w/w), Zn affected both at a biochar application rate of $\geq$ 10%, and elevated pH affected both at a biochar application rate of $\geq$ 20%. Moreover, in all species, root elongation was more sensitive than germination, and strongly decreased at high rates of grape marc biochar application ($>$ 10%) and wheat straw biochar application ($>$ 50%), whereas root length in cucumber and sorghum was affected at a low conifer and poplar biochar application rate of 0.5%, with marked impairment at application rates of $>$ 5.0% of all biochars. This could be explained by the fact that cell division/elongation at the root tip is 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 (Lian and Xing, 2017). Liao et al. (2014) 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 prepared 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 (Odinga et al., 2020). In addition, low molecular weight organic molecules (LOM) accumulate on the surface of biochar and condense in the pores during biochar production. The growth of animals and plants can be repressed by high concentrations of LOM compounds (Joseph et al., 2014). A germination test showed that VOCs in biochar had an inhibitory effect on the germination and growth of cress (Buss and Mašek, 2014), possibly because the re-condensation of VOCs during biochar pyrolysis resulted in a high content of mobile phytotoxic compounds.

In addition to the PAHs, heavy metals, and EPFRs contained in biochar, NB has been widely used in agriculture and poses potential risks to agricultural production (Ramadan et al., 2020). Zhang et al. (2020a) prepared six types of biochar via 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 the 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, and significantly reduced the bud length and biomass. This phenomenon occurred because phenolic compounds were deposited on the NB during biochar pyrolysis, which have a cytotoxic effect on fibroblasts and thus a negative impact on the plants (Oliveira et al., 2019; Sigmund et al., 2017). The pyrolysis temperature also affects the toxicity of MB/NB; the MB/NB obtained from low-temperature biochar contains higher concentrations of highly unsaturated phenolic compounds and polyphenols than the MB/NB obtained from high-temperature biochar (Fig. 7) (Wang et al., 2018). In addition, the ability of low-temperature MB/NB to release PAHs is

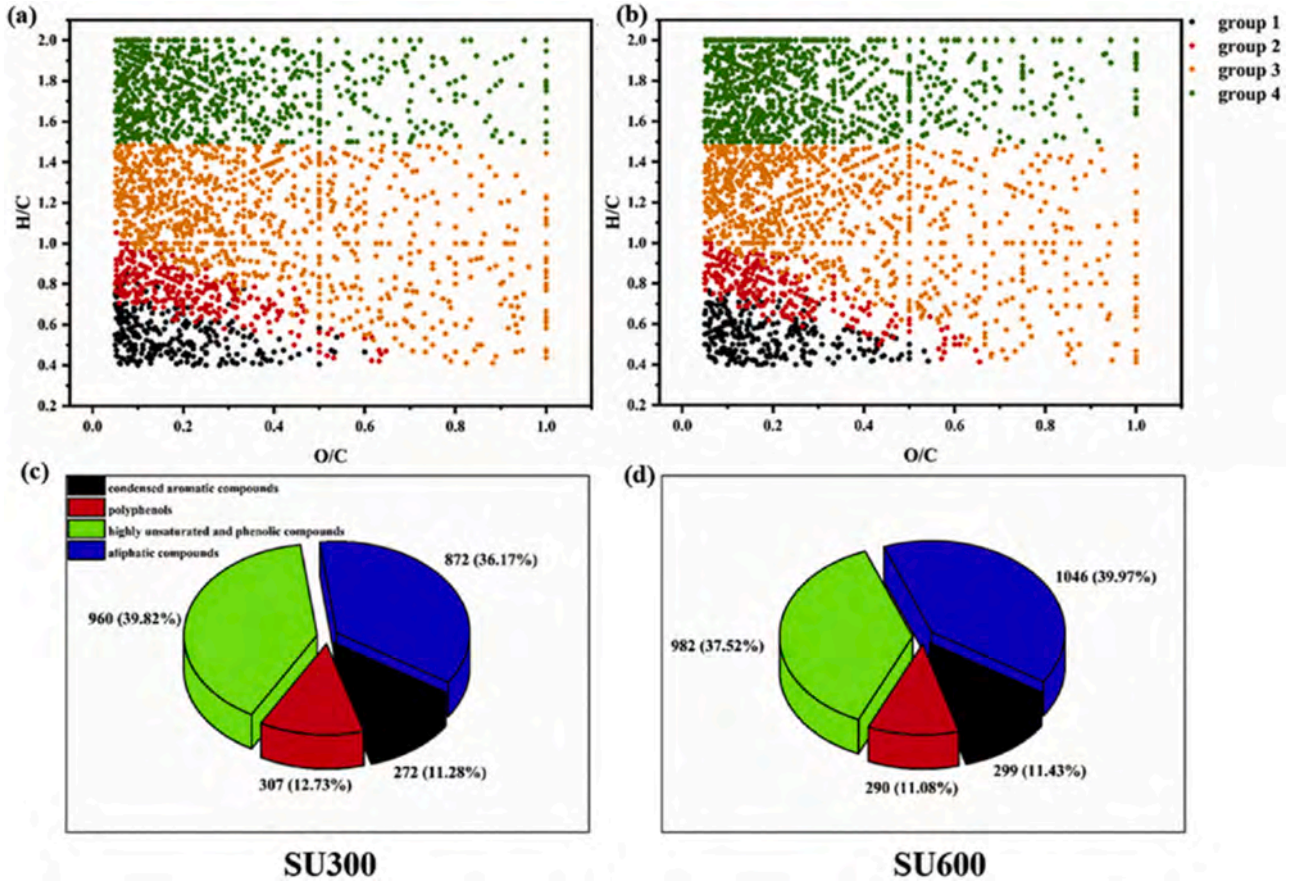


**Fig. 7.** Van Krevelen diagrams of low-temperature MB/NB(a) and high-temperature MB/NB; (b) and relative percentage of four groups in low-temperature MB/NB; (c) and high-temperature biochar(d).
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higher than that of high-temperature MB/NB, thereby making low-temperature MB/NB more biotoxic (Zhang et al., 2019b). Moreover, the toxicity of biochar depends on its raw biomass. Because the pyrolysis of lignin can produce a large quantity of phenolic compounds (Jung et al., 2016), NB obtained from biomass with a high lignin content poses higher potential environmental risks. However, whether the main source of toxicity of MB/NB is the adsorbed harmful substances or the biochar itself, the effect of size must be further explored.

Kim et al. (2015a) reported that it was difficult to obtain N from the soil because of its increased distribution on the biochar surface, and showed that as biochar application increased, lettuce growth was further delayed. Rajkovich et al. (2012) also found no growth-promoting effect of corn with more than 2% biochar addition, regardless of the biochar type. The reason for the lack of beneficial effects at higher application rates was that the available nutrients were reduced. The reduction of plant nutrient elements in the soil by biochar due to adsorption has been verified in previous studies. Novak et al. (2010) 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. This indicated that N could be adsorbed onto the surface of the biochar, thereby resulting in the inhibition of plant growth by reducing the available inorganic N. Similar conclusions have been reported in other studies (El-Naggar et al., 2019c; Bruun et al., 2012; Hussain et al., 2017). The biochar composition also affects its N fixation ability. As the content of mineralizable components (volatile substances) in biochar increases, the N content fixed by biochar from the environment also increases, thereby suggesting a lower available N content for plant growth (Deenik et al., 2010). In conclusion, the negative impact of biochars competing for nutrient elements required by plants in soil environments is possibly due to an improper amount of biochar application, as well as the use of biochar with high contents of mineralizable components. The adsorption of nutrients and the adsorption of plant hormones cannot be ignored. Phytohormones, which are signal molecules, have a regulatory effect on plant growth and development. However, it has been found that biochar has an immobilizing effect on plant hormones, thereby inhibiting plant growth (Lehmann et al., 2011; Akiyama et al., 2005; Jain and Nainawatee, 2002; Zhu et al., 2017). Moreover, recent studies have reported that rice husk biochar could increase the solubility, mobility, and phytoavailability of toxic elements (such as Sb, As, Cd, Zn, and Ni). This might be due to the wider range of the redox potential ($E_H$) (−12 mV to +333 mV) and pH (4.9-8.1) in the biochar treated soil than the un-treated soil ($E_H$ = – 30 mV to + 218 mV; pH = 5.9-8.6) (i.e., biochar could increase the potential mobility of the toxic elements under oxic acidic conditions). Therefore, application of such rice husk biochar to soil might stimulate the release of the toxic elements (such as As, Co, and Mo) under flooding conditions, which might increase the environmental and health risks in such wetland ecosystems (Rinklebe et al., 2020; El-Naggar et al., 2019a, 2018b).

Based on the above discussion, it can be concluded that the three main reasons for the potential risks of biochar to crops 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 research on the causes of various pollutants in biochars presented 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 agricultural fields; (2) MB/NB, especially from biomass with a high lignin content or produced at

low temperatures, may have toxic effects on crops owing to the presence of phenolic compounds on its surface; and (3) biochar with high contents of mineralizable components may absorb nutrients (such as N, P, and inorganic salts) and plant hormones from the soil, thereby leading to reduced plant access to important nutrients.

### 3.3. Soil organisms

Biochar addition to soil can have a direct or indirect negative impact on soil microorganisms. Indirect effects are mediated by changes in the environment (Marks et al., 2014), such as pH, or other factors related to the ecological tolerance range of the exposed species. For instance, biochar application changes the pH of the soil, and because some signaling compounds in fungi (such as farnesol) are not sensitive to pH, the ratio between fungi and bacteria becomes imbalanced (Gao et al., 2016; Khodadad et al., 2011). This indicates that the influence of biochar on the structure of the microbial community depends on the type of biochar as well as complex and changeable mechanisms.

In contrast, direct effects of biochar affect microbial activity by releasing heavy metals or organic chemicals, and can be mediated by multiple exposure pathways (ingestion or touch) (Liu et al., 2019a). For instance, PAHs unintentionally generated during biochar pyrolysis have mutagenic effects on salmonella/microsomes (Anjum et al., 2014), and EPFRs can reduce the contents of some cellular enzymes (Balakrishna et al., 2009). The negative impact of PAHs is caused by chemical stress on the microbial community at a higher soil nutrient level (Wang et al., 2020a). For EPFRs, the negative impact originates from the EPFRs themselves that cause the transfer of electrons between the biochar surface and specific cells during the remediation process, thereby changing the microbial community structure. Additionally, EPFRs may have potential toxicity to specific soil microorganisms (Odinga et al., 2020; Balakrishna et al., 2009).

The inhibitory effect of biochar on microbial activity increases as the pyrolysis temperature increases owing to the changes in the structure and chemical composition of biochar, especially the C 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 latter (Gondek et al., 2016). The biotoxic compounds adsorbed onto biochar inhibit the growth of microorganisms (Lehmann et al., 2011). Studies have found that biotoxic compounds (e.g., catechol) are strongly adsorbed by high-temperature biochar derived from ash-rich corn stover (Borraccino et al., 2001; Kasozi et al., 2010). Biotoxic compounds have been found to desorb from biochar material used to prepare the agar growth medium toxic to

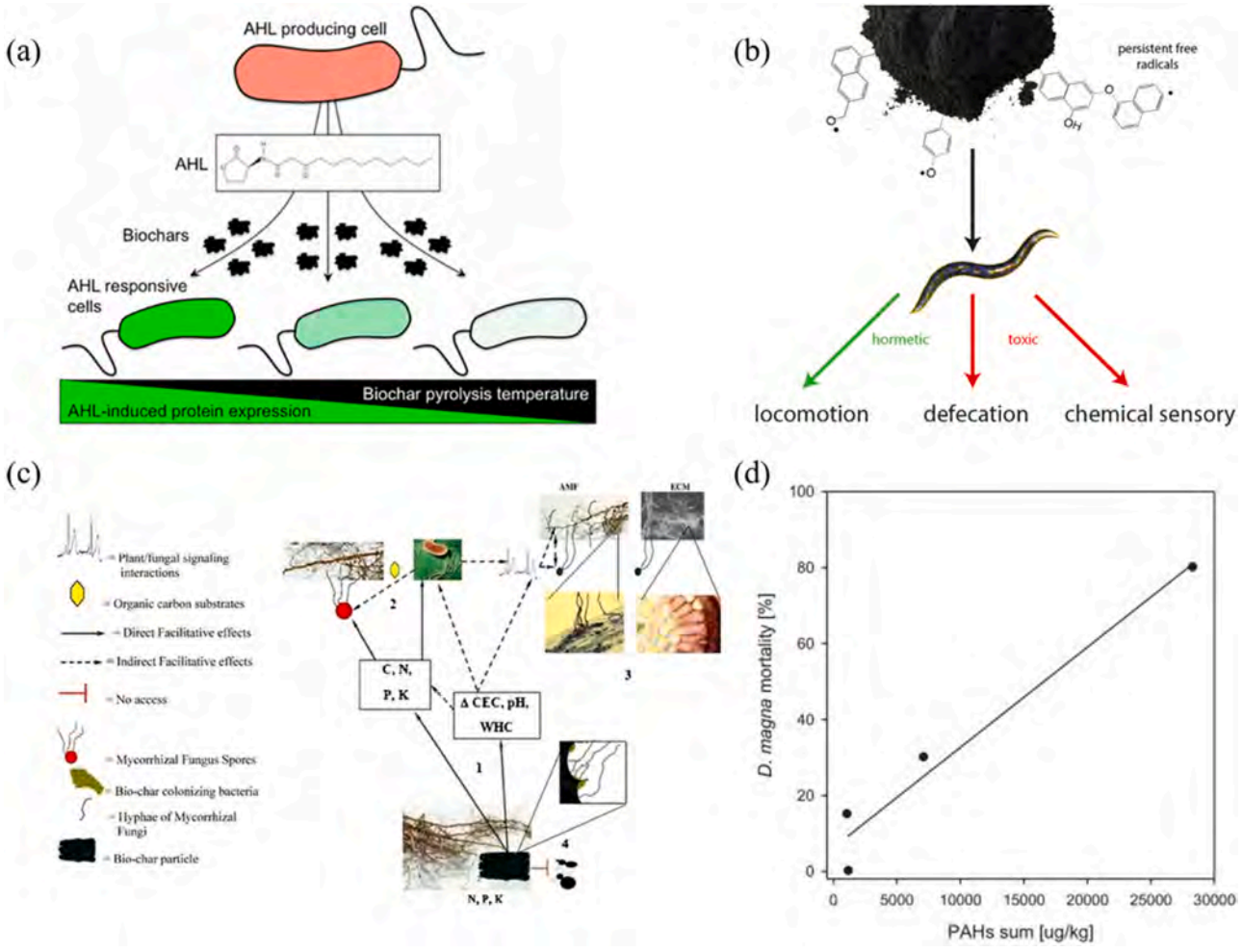


**Fig. 8.** The negative impact of biochar on microorganisms. (a) Biochar adsorbs signal molecules (such as AHL) and promotes its hydrolysis to change the microbial community structure. (b) Microbial decay resulting from EPFR in biochar. (c) Biochar changes the physical and chemical properties of the soil and then changes the microbial community structure in the soil (Warnock et al., 2007). (d) PAHs content is in direct proportion to the mortality rate of biological D. Magna. Therefore, PAHs contained in biochar have chemical stress effect on microorganisms in soil.
(a) Reproduced with permission from ref (Zhang et al., 2019a). Copyright 2019 Elsevier. (b) Reproduced with permission from ref (Lieke et al., 2018). Copyright 2018 ACS publications. (c) Copyright 2007 Springer. (d) Reproduced with permission from ref (Oleszczuk et al., 2013). Copyright 2013 Elsevier.

*Bordetella pertussis*, indicating that the growth-inhibiting substance was retained by the biochar (Lehmann et al., 2011).

Biochar has both positive and negative effects on arbuscular mycorrhizal (AM) fungi and exogenous mycorrhizal fungi, the most common types of mycorrhizal fungi in soil; the negative effects are mainly due to alternations in nutrients (Rousk et al., 2010; Wallstedt et al., 2002). Warnock et al. (2010) found that the relative abundance of AM decreased after biochar application. AM fungi are known to have an intergrowth relationship with more than 80% of plants on land (Jain and Nainawatee, 2002). Studies have shown that the signal transduction process of flavonoids is disturbed by the adsorption of flavonoids on biochar (Akiyama et al., 2005), which poses a threat to the growth and survival of soybean plants, AM fungi plants, and AM fungi (Jain and Nainawatee, 2002). Biochar not only affects the transmission of signaling molecules between microorganisms and plants, but 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) (Masiello et al., 2013).

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 (Lehmann et al., 2011), (2) promoting the adsorption and hydrolysis of signaling molecules to interrupt the interspecies communication of microorganisms (Fig. 8a) (Zhu et al., 2017), (3) releasing harmful components (e.g., PAHs, heavy metals, and organic pollutants) that are biologically toxic to microorganisms (Gondek et al., 2016), (4) decreasing the ability of mycorrhizal fungi to colonize plant roots via the persistent adsorption of signaling compounds, (Warnock et al., 2007) (5) changing the physical and chemical properties of the soil (Fig. 8c) (Rousk et al., 2010), and (6) increasing the amount of pollutants adsorbed by microorganisms.

Biochar also poses a potential threat to soil organisms. For instance, high concentrations of biochar negatively affect the survival of invertebrates in the soil (Fig. 8b). Furthermore, the presence of EPFRs in biochar may be neurotoxic to soil organisms (Pan et al., 2019). For instance, EPFRs in biochar can trigger neurotoxic effects in *Caenorhabditis elegans*, thereby inhibiting its life characteristics (movement and defecation) in the soil (Lieke et al., 2018). *Caenorhabditis elegans* also serves as food for *Bacteroides nematodes* and plays an important role in soil productivity and nutrient cycling; a decrease in the population of *C. elegans* would inevitably affect the hunting and growth of *B. nematodes* (Jean et al., 2016). In addition, because biochar adsorbs pesticides applied for agricultural production, organisms such as earthworms and mites can indirectly ingest pesticides by the casual predation of biochar particles (Jones et al., 2011). In the worst-case scenario, pesticides may be released inside the insect gut, exposing insects to toxic pesticide concentrations. However, there is no direct evidence to prove that biochar increases the exposure of soil organisms to pesticides. This effect should be explored in future studies. Moreover, small-size biochar not only increases the adsorption of contaminants, but also is more easily ingested by organisms, thereby indicating that MB/NB has a stronger negative impact on organisms. The activity of applied pesticides, such as herbicides, is reduced by biochar (Jones et al., 2011; Hussain et al., 2017), which could lead to the excessive use of pesticides in agricultural production and cause pesticide accumulation, thereby leading to more serious negative environmental impacts (Khalid et al., 2020). Therefore, in view of the toxic effects of biochar on soil microorganisms and organisms, caution should be exercised when using biochar 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, namely (1) the original unstable OM in soil is adsorbed onto the surface of biochar to form adsorbent protection (Cheng and Reinhard, 2008). (2) Biochar can prevent OM adsorbed in the mesopores from mineralization by isolating microorganisms and enzymes outside the mesopores. It can also greatly reduce the activity of laccase (a type of phenol oxidase that can use molecular O to catalyze the oxidation of aromatic compounds) and inactivate laccase via adsorption in its mesopores, thereby preventing OM mineralization (Zimmerman et al., 2004). (3) Biochar also promotes the formation of soil mineral aggregates, which reduces its degradation as well as that of soil organic carbon (SOC) to a certain extent (Jastrow et al., 2007). 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 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) (Xu et al., 2013). As such, inorganic N and P can be released from biochar and become a source of nutrients. Chen et al., (2017a) reported that the leaching of $NH_4^+$ from biochar into an aquatic environment accounted for 0.30–4.92% of the total $NH_4^+$ concentration. Similarly, Park et al. (2015) observed that the amount of phosphate released by sesame straw-derived biochar was high. The content of released phosphate changed from 62.6 mg/g to 168.2 mg/g with an increase in pyrolysis temperature. The low binding affinity of phosphate to biochar with a low Ca and/or Mg content may be responsible for the high levels of $PO_4^{3-}$ released in water (Zhang et al., 2020b). Additionally, the abundant ions in water not only weaken the pollutant adsorption ability of biochar, but also promote the release of inorganic N/P adsorbed onto the biochar. For instance, Novais et al. Novais et al. (2018) reported that a pure water solution extracted more than 20% of P from used poultry manure and sugarcane straw biochar after four extraction rounds, whereas $HCO_3^-$ 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, the use of a biochar with a lower content of endogenous N/P is recommended (i.e., attention should be paid 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 $Pb^{2+}$ and $Cd^{2+}$ from sewage. However, in the first 20 min after the addition of CPBC, the content of available P in the solution increased because of the dissolution of $Ca_5(PO_4)_3Cl$ (Deng et al., 2019b).

### 4.2. Pollutant migration

There are also potential environmental risks of co-transportation in the use of carbonaceous nanocomposites because the biochar nanocomposite can act as an active carrier (Song et al., 2019). Biochar and its adsorbed pollutants can infiltrate the surface and groundwater via surface runoff, ditches, or irrigation (Chen et al., 2019a), thereby posing potential environmental risks to aquatic environments such as groundwater and rivers (Wang et al., 2013b). The co-migration ability of the nanocomposites is also affected by the biochar source. Under the same experimental conditions, the enhancement of the $Cd^{2+}$ migration ability by biochar–$Fe_3O_4$ nanocomposites derived from wheat straw was significantly higher than that derived from sawdust (Chen et al., 2019a). This could be explained by the fact that biochar with a high content of mineral components (such as calcium carbonate) is beneficial for $Cd^{2+}$ adsorption (Wu et al., 2018), thereby increasing the diffusion and

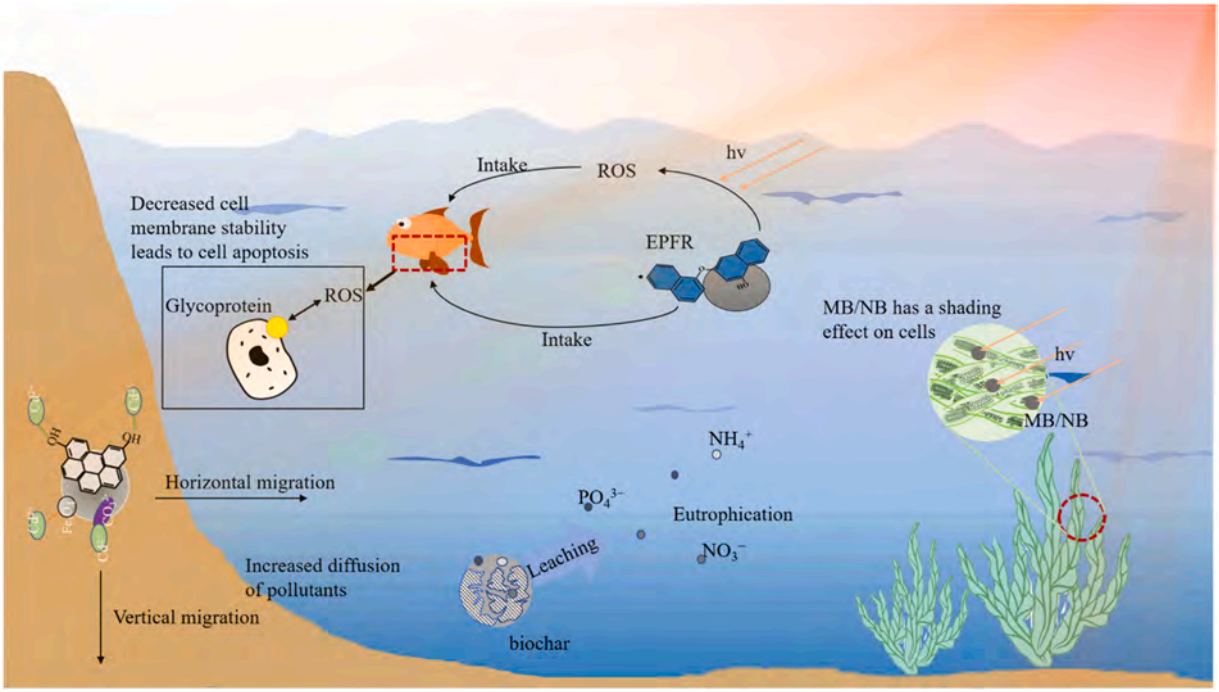


**Fig. 9.** Schematic diagram of potential negative environmental impact of biochar in aquatic environment.

transfer of $Cd^{2+}$ in the environmental media.

MB/NB is known to exhibit higher mobility and accessibility owing to surface reactivity and polarity, thereby accelerating the transfer and diffusion of environmental pollutants (Wang et al., 2013b). Because more polar groups are present in MB/NB, they have higher dispersibility in natural water (Liu et al., 2018b) and a stronger co-migration effect on pollutants in the aquatic environment. 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, preparation methods for amendment materials, and methods for controlling the potential co-migration of pollutants and carbonaceous nanocomposites in the underground environment should be the focus of future research.

### 4.3. Aquatic organisms

By exploring the degree of toxicity of biochar on a series of organisms, Oleszczuk et al. (2013) found that biochar had the greatest impact on crustaceans, and the 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 (2016) added biochar produced from wheat straw at 400 °C or 700 °C to bed sediments at a rate of 3% (w/w), and its effects on the growth and root and stem biomass of *Vallisneria spiralis* were studied. After 54 days, the presence of 700 °C biochar not only resulted in a lower *V. spiralis* biomass but also reduced root length compared with the plants in the control experiment. Additionally, EPFRs in biochar were found to generate hydroxyl free radicals in aquatic environmental media, which could also induce the generation of ROS (i.e., hydroxyl free radicals) in aquatic plant cells and cause damage to cells and organs (Odinga et al., 2020). For instance, Zhang et al. (2019c) found that three prepared biochars significantly promoted the generation of cellular ROS in *Streptococcus obliquus*. The ROS levels induced by 800 mg/L of biochar obtained at 300, 400, 500, and 600 °C were 120%, 134%, 125%, and 113% higher than the control, respectively. Except for ROS, when the concentration of biochar was greater than 200 mg/L, the SOD activity of all exposed groups was also significantly higher than that of the control group. This indicates that the redox balance of *S. obliquus* is disrupted by biochar. Meanwhile, it was found that the chlorophyll-*a* (Chl-*a*) concentration in *S. obliquus* was decreased by biochar. Biochar prepared at 500 °C had a high inhibition rate (89%) for Chl-*a* at a concentration of 500 mg/L. Steinberg et al. (2003) reported that the photosynthetic O content of *Ceratophyllum demersum* was reduced by EPFRs. This could be explained by the fact that the semiquinone free radicals formed in biochar influence the electron transfer chain by acting as electron scavengers in the humus and the plants growing in the media, hindering O production from plant photosynthesis (Odinga et al., 2020). Liu et al. (2018b) produced NB via the collapse of pores and fracture of the biochar skeleton, and found that MB/NB and its associated pollutants may pose an exposure risk to aquatic organisms owing 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 and to indirect effects, such as shading effects of MB/NB on the cells (negatively influencing light absorption and photosynthesis) and the adsorption of nutrients on MB/NB (Freixa et al., 2018). 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, thereby posing a potential environmental risk (Rhema et al., 2017). MB/NB is widely present in aquatic media because it flows into surface water or groundwater systems owing to its high migration capacity. Moreover, the various pollutants carried by MB/NB continue to accumulate after entering the aquatic environment. Because of the various interactions between MB/NB and environmental media, the adsorbed pollutants may be released, posing 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 (Freixa et al., 2018).

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

The potential negative impacts of biochar application on the atmospheric environment are mainly reflected in the change in the atmospheric greenhouse effect and the increase in air particulate concentrations (Fig. 10).

### 5.1. Atmospheric greenhouse effect

Biochar plays an important role in the atmosphere by affecting $CH_4$, $N_2O$, and other GHG emissions (Cayuela et al., 2014). However, some studies have shown that the application of biochar also has a negative impact on GHG emissions, which in turn poses potential environmental risks (Lehmann et al., 2011; Ribas et al., 2019; Xu et al., 2020). The N dynamics are affected by the soil pH, aeration, and biochar type (Lin et al., 2017; Yanai et al., 2007). When biochar is applied to the soil, it may affect soil $N_2O$ emissions by influencing the activity of microorganisms (Deng et al., 2019a). For example, the addition of straw-derived biochar to soil regulates the surrounding pH, which can enhance the growth of ammonia-oxidizing bacteria and thus increase the nitrification rate, thereby causing an increase in soil $N_2O$ emissions (Lin et al., 2017). 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 $N_2$ occurs, leading to $N_2O$ uptake and promoting $CH_4$ production (Ribas et al., 2019). The ash concentration of biochar also affects $N_2O$ emissions because high-salt biochar will cause a "salting-out effect," leading to high $N_2O$ emissions (Heincke and Kaupenjohann, 1999). Luz et al. (2013) found a positive correlation between $N_2O$ emissions and ash concentrations in a study on nine biochars under denitrification conditions. Therefore, the importance of the concentration of mineral components in biochar in relation to GHGs requires further research. Biochar derived from different raw materials may have different effects on the $N_2O$ concentration in the atmosphere owing to the different interactions between microbes and biochar with various properties (Niu et al., 2018). For instance, Xu et al. (2020) found that straw-derived biochar significantly reduced soil $N_2O$ emissions by 51.4–93.5%, whereas the use of biochar derived from camellia husk increased soil $N_2O$ emissions. Meanwhile, different contents of $NH_4^+$-N and $NO_3^-$-N in biochar led to different levels of $N_2O$ emissions in the soil (Zwieten et al., 2010). Regarding the impact of soil texture on $N_2O$ emissions, biochar can significantly reduce $N_2O$ emissions in finer soils, whereas the average use of biochar in coarse soils can increase $N_2O$ emissions by 53% (under high moisture conditions) (Cayuela et al., 2014). The impact of soil pH has a significant impact on the $N_2O/N_2$ emission ratio; $N_2O/N_2$ increases with the decreasing soil pH in the saturated soil (Clough et al., 2004). Therefore, it is not possible to accurately determine the $N_2O$ concentration in the atmosphere around biochar-modified soils. More research on the effects of biochar in different types of agricultural systems with various climatic conditions on $N_2O$ emissions is necessary.

Biochar mainly affects the decomposition ability of microbial communities in the soil by influencing their species and activity. Therefore, terrestrial OC emitted to the atmosphere in the form of $CO_2$ is reduced, thereby reducing the greenhouse effect (Rousk et al., 2010). However, Zimmerman et al. (2011) found in a 1 year field experiment that all other types of biochar-soil mixtures released more $CO_2$ than related soils without biochar and had higher initial $CO_2$ release rates. This was probably because biochar, especially freshly prepared biochar produced at low temperatures, is inherently unstable, thereby contributing to the loss of degradable C in the mixture. The mechanism most often proposed involves the growth of r-strategist microbes that are adapted to respond quickly to newly available C sources, re-mineralize soil nutrients, and co-metabolize more refractory OM, such as soil humic materials, in the process (Kuzyakov, 2010). Regarding the effect of soil texture and biomass sources on soil $CO_2$ emissions, three types of biochar (straw, umbrella wood, and grass) were applied to sandy loam and sandy soil in a short-term incubation experiment conducted by El-Naggar et al. (2018a). The results showed that the sandy loam soil had 2–3 times higher $CO_2$ emissions than those of the sandy soil due to the higher microbial community abundance in the sandy loam soil. Rice straw biochar treatment induced the highest $CO_2$ emission rate in sandy soil, which was attributed to the high content dissolved aliphatic OC of rice straw biochar. Wang et al. (2016) conducted a meta-analysis based on 116 observations, and the results showed that after the addition of

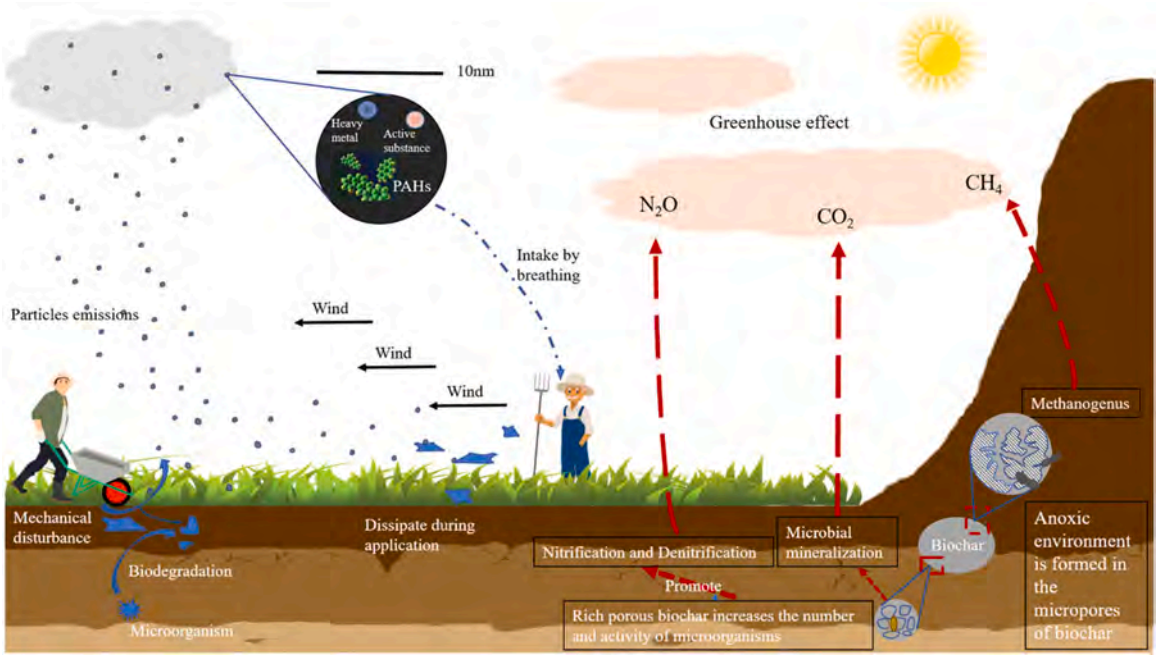


**Fig. 10.** Schematic diagram of the potential negative environmental impact of biochar in the atmospheric environment.

biochar, sandy soils with poor soil fertility usually showed increased $CO_2$ emissions owing to the stimulation of microbial activity in soils. Furthermore, one study reported that biochar could change the utilization of C by microorganisms in the soil. Coupled with the catalytic reduction of minerals or free radicals and the adsorption of $NH_3$, the main role of fungi or bacteria in the soil GHG emission process may change (Zimmerman et al., 2011). Considering the contribution rate of $CH_4$ and $N_2O$ to the greenhouse effect, the impact of biochar requires more comprehensive analysis methods, such as LCA.

### 5.2. Particulate concentrations in the atmospheric environment

Biochar application may increase $PM_{10}$ emissions (Li et al., 2018; Ravi et al., 2016). The typical characteristics of biochar are: low bulk density, large surface area, and variable particle size distribution; these facilitate biochar release into the atmosphere by natural or mechanical interference and contribute to the measured $PM_{10}$ (El-Naggar et al., 2019b; Gelardi et al., 2019). Aged biochar is more likely to be broken into small particles because of its reduced mechanical strength (Spokas et al., 2014). Compared with bulk biochar, small and light particles of biochar can easily enter the atmosphere under natural wind conditions, thereby resulting in an increased $PM_{10}$ concentration (Gelardi et al., 2019). Ravi et al. (2016) reported that $PM_{10}$ emissions were generally higher from all soils studied 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, thereby resulting in the amended soil being more susceptible to dust emission (Gelardi et al., 2019; Li et al., 2018). $PM_{10}$ is hazardous to human health because it can be deposited in the lungs and can enter the alveoli and blood. The particulates deposited on the alveoli damage them as well as the mucous membranes, thereby causing a series of pathologies such as chronic rhinitis and bronchitis (Yang et al., 2017). Because of adsorption of pollutants onto biochar in large quantities, the adsorbed pollutants may be discharged into the air along with the biochar and may be released from the biochar into 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 (Gelardi et al., 2019). 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 life cycle owing to potential adverse human health impacts (Ibarrola et al., 2012; Sparrevik et al., 2013). However, there is a lack of relevant research on several associated topics, namely the possibility of biochar emission in the form of dust, the possibility of the intake of the pollutants in biochar after its release, and the bioavailability of biochar after adsorption. In agricultural settings, this airborne release may occur during the application of biochar to the soil or via natural wind-driven erosion or mechanical farming events after it has been incorporated into the soil (Gelardi et al., 2019). Therefore, particular attention must be paid to the problems caused by dust emissions when applying biochar to actual agricultural production.

MB/NB formed from larger biochar particles 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 owing to its nature and characteristics (Sigmund et al., 2017). Sgro et al. (2009) observed the cytotoxic cell internalization of fine biochar particles. However, Sigmund et al. (2017) did not observe the internalization of biochar in NIH 3T3 mouse fibroblast cells. This indicated 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, and increased as the particle size decreased (Kong et al., 2013). Therefore, compared with bulk biochar, MB/NB poses a higher biological risk via biological inhalation. The presence of semiquinone and phenoxyl radicals may lead to activated species in combustion-generated particles and ambient fine PM (Odinga et al., 2020; Lyu et al., 2018b). The generated active substances accumulate in the human respiratory tract and induce the production of ROS, thereby causing oxidative stress and threatening human health (Lyu et al., 2018b).

## 6. Detection, assessment, and avoidance of environmental risks posed by biochar

### 6.1. Risk detection and assessment in the soil environment

#### 6.1.1. Phytotoxicity

Biochar in soil has toxic effects on plants. When biochar is applied to soil, it is necessary to evaluate its phytotoxicity. Biochar phytotoxicity research is mainly based on germination experiments, which have several shortcomings, such as long experiment times, unclear internal mechanism, and other uncontrollable factors (Luo et al., 2018; Malfatti et al., 2021; Onofri et al., 2018). It is difficult to compare and summarize different studies because the results of such studies vary depending on the species (Luo et al., 2018). Therefore, phytotoxicity analysis based on a quantitative index is of practical significance with regard to the application of biochar. Ruzickova et al. (2021) proposed that in the presence of organic compounds in biochar, the ratio of OC to elemental carbon can be evaluated to determine whether biochar is phytotoxic (based on the recognition that biochar is phytotoxic because of the presence of organic compounds (Bargmann et al., 2014)). The phytotoxicity of biochar in soil can also be predicted by the ratio of aliphatic organic compounds to aromatic organic compounds (AL/AR) (e.g., an AL/AR value of $< 0.5$ indicates the domination of aliphatic compounds, which are involved in biochar toxicity). Kong et al. (2019) proposed the detection and evaluation of the phytotoxicity of biochar from the perspective of metabolism. In their experiment, the toxicology of sewage sludge-derived biochar to wheat was investigated by integrating metabolomics and physiological analysis. A total of 514 peaks were detected in the wheat root extract, of which 211 were identified. The analyzed metabolites were classified into amino acids, organic acids, and sugars. It was found that the sewage sludge-derived biochar obtained at 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 the biochar was phytotoxic, and that many amino acids, including valine, alanine, isoleucine, proline, oxyproline, orthovaline, ornithine, puthumine, and aminomalonic acid, were downregulated by more than four times under biochar exposure compared with the control group. This mainly occurred because the enhancement of oxidative stress caused by biochar in the organism was manifested in the downregulation of amino acid metabolism (Xiangang et al., 2015). 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

Section 3.3 explains the negative effects of biochar on soil microbial communities. The phosphorus lipid fatty acid (PLFA) method is mainly used to detect the impact of biochar on microorganisms (Wang et al., 2020a; Wei et al., 2020). The PLFA method is based on modern biochemical theory, and is an effective method for analyzing soil microbial communities without the need for separation or culturing (Zhang et al., 2021). Owing to the mutagenic substances (e.g., PAHs and dissolved OC) present in biochar, it is necessary to conduct in-depth research on the genetic changes in microorganisms. Qiu et al. (2019) used 16S ribosomal ribonucleic acid sequencing to analyze the dynamic changes in bacterial community composition in compost with the addition of biochar, and found that the relative abundance of actinomycetes increased in the late composting period, whereas the relative abundance of red caterpillars decreased sharply. A differential operational taxonomic unit abundance analysis was conducted to determine the effect of biochar addition on microbial community separation. It was

found that the addition of biochar increased the abundance of specific microbial populations in the compost. Moreover, to gain a more comprehensive understanding of microbial community changes, high-throughput sequencing, network technology, denaturing gradient gel electrophoresis, and other methods can be combined and applied to investigate the impacts of biochar. For example, Qiu et al. (2019) found that biochar has a negative impact on the number and activity of Microbacteriaceae and *Aeromicrobium* via high-throughput sequencing and network technology. However, most quantitative analysis methods have 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 focus on the use of standard and universal microbial community measurements and 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 on aquatic organisms are mostly conducted via laboratory-level toxicity simulation experiments. Toxicity detection and evaluation of fish are particularly important in aquatic environments of economic significance. Abakari et al. (2020) reared tilapia (*Oreochromis niloticus*) in the presence of biochar and evaluated the toxicity of biochar to tilapia via its performance parameters (e.g., fish growth parameters, fish welfare indicators, proximal analysis of fish back muscle, and determination of antioxidant and immune enzyme activities). The risk substances (i.e., biochars) that enter the aquatic environment via various channels may also act on and damage algae (Lu et al., 2021). Therefore, algae are also one of the main organisms for evaluating the toxicity of biochar to aquatic organisms. Zhang et al. (2019c) proposed four quantitative indicators via the acute toxicity test of *S. obliquus* (model aquatic algae), namely cell growth (inhibition), Chl-*a* (decrease in concentration), ROS content (upregulation), and SOD content (upregulation). Finally, the biotoxicity of biochar to aquatic algae was determined via a comprehensive evaluation of these indicators. Mondal et al. (2016) measured the cell density of the microalgae *Scenedesmus* sp. (a model organism representing phytoplankton and eukaryotes) via a growth inhibition toxicity test to evaluate the aquatic toxicity of biochar. 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 (*Photobacterium phosphoreum* T3 spp.) after treatment with biochar was detected by Zhang et al. (2019c), and it was found that the luminescence inhibition rate increased as the biochar concentration increased. Polymerase chain reaction (PCR) involves in vitro amplification of specific deoxyribonucleic acid fragments (Barkallah et al., 2020). In toxicology studies of protozoa, phytoplankton, zooplankton, and fish, the results obtained using PCR have provided a scientific basis for the ecological risk assessment of pollutants (Qian et al., 2009; Soetaert et al., 2007). However, there are few studies on the application of PCR in the field of biochar aquatic toxicity detection. Therefore, more attention should be given to this subject in future research.

### 6.3. Risk detection and assessment in the atmospheric environment

The PM produced during the pyrolysis of biochar not only increases the concentration of atmospheric PM, but may also have a toxic effect on organisms (Gelardi et al., 2019). Therefore, the capture and toxicity determination of PM emitted from the pyrolysis of biochar is essential (Wang et al. 2019b). Dunnigan et al. (2017) used a cascade impactor made of stainless steel with a size range of 0.1–10.0 μm to collect PM produced by the combustion of raw pyrolysis volatiles. A gas chromatograph-mass spectrometer was then 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 μg PAH/g PM) and 800 °C (882 μg PAH/g PM). In addition, between raw pyrolysis volatile production temperatures of 400 °C and 800 °C, the benzo(a)pyrene TEQ of the PM increased from 19.1 μg PAH/g PM to 149.1 μg PAH/g PM. Therefore, running the pyrolysis–combustion process at a lower pyrolysis temperature has the potential for low PM toxicity. In intensive agricultural areas, agricultural dust is the largest contributor to PM in the air (Gelardi et al., 2019). 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. (2018) used dust generators to simulate possible dust conditions under farming conditions (a large 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 involved the measurement of the benzene polycarboxylic acid (BPCA) produced by the digestion of $HNO_3$ 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. Anton et al. (2009) indicated that biochar can be used to quantify pyrolyzed carbonaceous substances on different substrates. Therefore, the separation technology of various carbonaceous substances, such as CTO-375 (a technique for determining black C with chemothermal oxidation at 375 °C in active air flow) (Zencak et al., 2007), BPCA (Li et al., 2018), $Cr_2O_7$ (Hammes et al., 2007), and thermal–optical transmittance/reflectance (Park et al., 2015), can be selectively applied to the separation of biochar, which will help to promote the development of an atmospheric environmental risk assessment involving biochar.

### 6.4. Life cycle assessment

As discussed in this review, although biochar has benefits, its potential risks cannot be ignored. Therefore, in practical applications, it is necessary to systematically evaluate the risks and benefits of biochar in complex ecosystems. LCA is a widely recognized standardized method that has been extensively used to evaluate the efficiency of biochar systems (Owsianiak et al., 2018; Huang et al., 2020). LCA consists of four parts: target definition and scope, life cycle inventory analysis, life cycle impact assessment, and interpretation (Azzi et al., 2019). Using LCA, the environmental effects of biochar have been determined by calculating various indicators, such as net GHG emissions (i.e., GHG emission reduction due to biochar use minus the GHG emissions of biochar preparation, transportation, and other processes) (Dutta and Raghavan, 2014) and the global warming potential, which is used to measure the impact of GHG emissions from biochar systems on global warming (Struhs et al., 2020). The sensitivity index (i.e., sensitivity coefficient and critical point) is another indicator that can be used to draw a sensitivity analysis chart to understand the degree of influence of each factor in the biochar system on the overall environmental effect (Roberts et al., 2010). The N and P efficiency coefficients of the main fertilizers required for crop growth (biochar feedstock) have also been used to evaluate the eutrophication impact of biochar systems (Whitman et al., 2011). For instance, the net negative impact of biochar systems on acidification and eutrophication was assessed by Peters et al. (2015) using LCA. The effects of acidification and eutrophication increased as biochar production increased, which was mainly due to the increase in the amount of biomass that needed to be transported and treated per hectare. Compared with direct biomass combustion, biochar systems achieve GHG reduction at the expense of reduced energy efficiency and increased negative impacts. Esteves et al. (2019) also indicated 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 using modern ultra-low-emission pyrolysis equipment (Llorach-Massana et al., 2017). 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 (Matuštík et al., 2020). Similarly, biochar production systems in tropical rural areas have potentially significant negative impacts on the environment because of the high emissions of gases and aerosols during the production process, which cannot be compensated for by C sequestration (Sparrevik et al., 2013; Smebye et al., 2017). Although many studies have evaluated the benefits of biochar production using LCA, the biochar life cycle results depend on the choice of method and assumptions considered (Muñoz et al., 2017). Therefore, the differences between studies make it difficult to directly compare the corresponding research results or to obtain causality that is applicable to all or even most biochar systems.

### 6.5. Risk avoidance measures

Based on the above-mentioned detection and tracking technologies, supplemented by modern biochar improvement and optimization technologies, it can be deduced there is an urgent need to reduce or eliminate toxicity risks in the field of biochar research. This would be beneficial not only 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 concentrations of harmful substances should be selected. Feedstock containing plant biomass is recommended because it contains fewer PAH precursors (Quilliam et al., 2013b). In terms of the pyrolysis rate, slow pyrolysis is recommended. Biochar produced at a slow rate has lower ecological risks than that produced at fast rates, which is mainly reflected in the lower content of harmful substances in biochar produced at low temperatures and slow rates, as well as the limited soil nutrient immobilization ability and stronger mineralization ability of the biochar (El-Naggar et al., 2019c; Bruun et al., 2012). Biochar prepared at low temperatures has a lower content of harmful substances (e.g., PAHs) and lower ecotoxicity than that prepared at high temperatures. Moreover, the concentration of PAHs usually decreases with increasing pyrolysis time and temperature (Hale et al., 2012).

In the process of biochar application to soil, the physical and chemical properties of the medium (e.g., soil moisture and aeration) should be determined first. For instance, owing to the low soil water content, soil dust emissions have been found to increase after biochar application. Li et al. (2018) suggested that tilling after wetting biochar-amended plots effectively reduced 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. We suggest that biochar should be added to soil as large particles, which have lower sorption (due to the reduced surface area-to-volume ratio), thereby reducing the capacity for ingestion or transfer to crops or animals. The amount of biochar has an overall potentially negative impact on the growth of plants. Therefore, it is necessary to determine the appropriate amount of biochar for practical applications. For example, Baronti et al. (2010) found that greater than 1.7% (more than 60 t/ha) biochar application to soil resulted in a decrease in the dry matter yield of perennial ryegrass. Li et al. (2020) found that adding 1% (w/w) or 3% (w/w) biochar can reduce the soil loss rate by simulating rainfall events, whereas adding 7% (w/w) biochar can increase the soil loss rate.

When using biochar in aquatic environments, in addition to the requirements mentioned above for the selection of feedstock, biochar with lower N and P contents and a lower mineral content is more suitable (Xu et al., 2013; Wu et al., 2018). 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 (Liu et al., 2018b). Biochar fixation technology can be used to avoid the environmental risks posed by smaller particles. For example, biochar can be prepared as macroscopic materials such as sheets with large volumes or biochar foam, thereby effectively inhibiting its long-distance migration and achieving effective recovery (Qiangu et al., 2021). In addition, considering that the biotoxicity of EPFRs in aquatic environments is higher than that of EPFRs in soils (i.e., soil exhibits high complexation and EPFRs can induce the generation of hydroxyl free radicals), combined with the reasoning stated in Section 2.1.1, we recommend the use of hardwood lignin, which contains fewer precursor substances than softwood lignin. Regarding modified biochar, studies tend to use magnetic biochar to facilitate recovery from the aquatic environment (Ye et al., 2020).

Although studies have been conducted on the corresponding avoidance measures discussed above, multiple issues have not been resolved. For example, Zhang et al. (2019c) confirmed that biochar has 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 has correspondingly larger environmental risks owing to the presence of O-containing functional groups and heavy metals (Kim et al., 2015a; Sun et al., 2018). Therefore, substantial improvements can be made to technologies for biochar risk avoidance measures, which is worthy of further investigative research.

## 7. Conclusions and outlook

Biochar poses potential environmental risks to soil, water, and atmosphere owing to its harmful components, adverse surface properties or structure, and chemical characteristics at micro-/nano-dimensions. The wider application of biochar has potential environmental uncertainties. Complicated connections between physical properties and unpredictable chemical interactions exist between biochar and various aspects of the environment to which it is applied, thereby resulting in a wide variety of possible negative impacts. Therefore, the following points should be considered in future research:

(1) To achieve an optimal environmental remediation performance of biochar, it is necessary to further investigate the relationships between certain production factors (e.g., biomass sources and preparation conditions) and the environmental risks of biochar in subsequent studies. LCA can be used to assess the potential environmental risks of biochar.
(2) The comprehensive mechanisms of the negative impacts of biochar on the environment at the microcellular and molecular levels should also be further studied. The interaction between biochar and various environmental media in the biosphere (i.e., the atmosphere, water, and soil) and the overall negative environmental impact of biochar on the entire ecosystem (that is, at the macroscopic scale) also require further exploration.
(3) The internal mechanism(s) of the negative impact of MB/NB on the environment must be explained in future studies (e.g., whether the main source of MB/NB toxicity originates from the harmful substances adsorbed onto the biochar or from its size).
(4) In terms of the effects of the discharge of biochar as dust during application, some knowledge gaps exist, including whether the desorption of attached pollutants is possible, whether desorbed contaminants are inhaled by humans after entering the atmosphere, and 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, including LCA, systematic toxicological assessment, and epidemiological investigation. 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 ecosystem complexity and the changeability of biochar, more research must be conducted to understand the basis of

simple evaluation mechanisms for describing the behavior of biochar in the ecological environment. Considering that certain environmental differences and related systematic errors are difficult to eliminate (such as those related to climate, soil type, raw materials, or pyrolysis devices), various testing and evaluation methods should be unified considering certain aspects to make accurate comparisons. For example, the feedstock and environmental characteristics of biochar in the same region are generally similar. In addition, 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, professional knowledge and capabilities are required for the practical application and management of biochar. The International Biochar Initiative has formulated standards for the safe use of biochar in soil and issued a white paper on the pollutant-biochar-component dioxin (i.e., the production, hazard analysis, and detection report requirements of dioxin). Other environmental media and environmentally harmful substances in biochar require corresponding standards and summaries, which would be of great significance for the sustainable development and safe application of biochar. Existing avoidance measures should also be standardized and unified. In addition, new methods need to be developed for preventing or ameliorating the potential environmental risks of biochar.

## Declaration of Competing Interest

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

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