

Review

# Biochar Acts as an Emerging Soil Amendment and Its Potential Ecological Risks: A Review

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**Abstract:** Biochar, known as “Black Gold”, has become a novel approach with potential benefits for soil amendment, such as improving soil physicochemical properties, reducing greenhouse gas emissions, and enhancing soil fertility. The previous research studies mainly focus on exploring different methods for the improvement of biochar enriched nutrients as fertilizers; however, the migration and transformation mechanisms of these nutrients induced by biochar are yet to be extensively investigated. This paper provides an overview of recent advances in the application and mechanisms of biochar for soil amendment focusing on soil properties and nutrients improvement. Biochar positively alters microbial-mediated reactions in the soil C and N cycles, i.e., mineralization of C and N, and N<sub>2</sub> fixation, thus enhancing maximizing C and N use efficiency and reducing the potential losses. Moreover, biochar provides reactive surfaces where P and K ions are retained in soil microbial biomass and in exchange sites, leading to increasing the availability of P and K to plants uptake. In addition, the toxic substances and potential ecological risks of biochar were also reviewed and discussed, thereby providing a baseline reference and guiding significance for future biochar applications as promising soil amendments.

**Keywords:** biochar; soil properties; nutrient improvement; ecological risks



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## 1. Introduction

As a crucial member of ecosystems, soils have played a critical role in biochemical transformation, element cycling, and supporting plants [1]. Moreover, soils are also essential for food safety because they determine the possible composition of food and substantially support the food chain [2,3]. It was reported that 33% of the global soils were facing soil degradation [4], which led to a decline in soil structural stability and the ability of soils to maintain and store carbon, and increasing erosion risks and global threats [5,6]. Maximillian et al. [7] also reported that all of the world’s topsoil might become unproductive within 60 years if the current rates of loss continue. The main factors of soil degradation include loss of organic matter in the soil, soil acidification, a decrease in soil fertility and aggregate, elements imbalance, and other issues [8–11], which in turn induced to alter the biogeochemical processes of ecosystems, adversely affect organisms [12–14]. Given the magnitude of the soil degradation and its significance to sustainable agriculture, it’s urgent for worldwide scientists to find a novel option that can effectively remediate soils.

Biochar, known as “Black Gold”, is a carbon-rich solid material derived from the thermochemical conversion of biomass (e.g., plant, manure, and sludge) under oxygen limitation [15]. It has been shown by numerous studies that biochar is used as a novel approach with potential benefits to agriculture and the environment [16–18]. After pyrolysis, biochar became more hydrophobic and recalcitrant due to the formation of aromatic structures,

and a negative emission potential of biochar [19]. Earlier published reviews on biochar included a summary of the negative effects of biochar addition on soil physicochemical properties (e.g., pH, soil bulk density, soil porosity, and organic matter) [18,20–23]. Biochar amendment has been reported to positively influence soil C stability, especially for soil that lacks organic matter [24]. Biochar acts, therefore, as an emerging and attractive option to effectively improve fertilizer utilization performance. Besides, biochar produced by pyrolysis itself contains N, P, and K, and biochar contributed to N mineralization by regulating microbial-mediated reactions [25,26].

Biochar's application led to a comparatively higher bio-available K fraction due to formation of water soluble kalinite ( $\text{KHCO}_3$ ) minerals [27]. Moreover, previous studies have exhibited that biochar can not only significantly increase the content of available P in soils, but also promote the availability of exogenous P in acidic soils [28]. Therefore, application of nutrient-rich biochars was vital for the restoration of degraded and/or nutrients deficit soils.

To the best of our knowledge, no systematic assessment is available to provide an overview of the mechanisms of biochar application on soil nutrient improvement. A deeper insight into the mechanisms of nutrition release and transportation induced by biochar in the biochar-soil-plants system is also necessary. In this paper, four sections have been proposed and aimed to enhance the understanding of the mechanisms of biochar as a soil amendment, including (1) The positive effects of biochar on soil properties, e.g., pH, cation exchange capacity (CEC), soil bulk density, water retention, and soil enzyme activity. (2) The mechanisms of biochar in the soil nutrients (C, N, P, and K) improvement; (3) Factors effects of biochar on soil nutrient improvement; (4) The toxic substances and adverse effects of biochar on the organisms were also reviewed and discussed, aiming to provide theoretical reference for practical land use of biochar.

## 2. Basic Properties of Biochar

### 2.1. Elements

Biochar contains various elements, of which basic elements C, H, O, and N constitute the framework of biochar [29]. Alkali metal elements (K, Ca, Na, and Mg) and common metallic elements (Mn and Fe) are involved in the structural composition of biochar and are regarded as the critical sources of alkaline components of biochar [30]. In addition, mineral element P also exists in biochar and is an essential nutrient for botanic and microbial growth [31,32]. The raw materials and preparation condition control the elemental compositions of biochar. The content of C in plant-derived biochar is generally higher than that of sludge-biochar and manure-biochar, ranging from 39.75% to 90.21% (Table S1). It is believed that the dehydration and depolymerization reaction of plant biochar occurs with the rise of pyrolysis temperature, and lignin and cellulose are decomposed into smaller molecules, which increases the C content [33]. The content of C in sludge biochar is generally low, and concentrations range mainly from 4.69% to 23.4% (Table S1), which is mainly due to the high concentration of minerals in sludge. There are also exceptional cases reported that 53.5% C content of granular sludge biochar was prepared at 300 °C [34], which different sources of sludge may cause.

In contrast to C, the contents of H and O in biochars decreased at a higher pyrolysis temperature (Table S1). As the pyrolysis temperature increases, H and O are mainly dissipated in the form of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , CO, and hydrocarbon [35]. Typically, manure biochar contains higher concentrations of P and N [36]. As a nutrient-rich fertilizer, biochar has a vital application prospect for the remediation of nutrition-deficient soil and improving crop growth.

### 2.2. pH

The pH value of biochar produced from different sources is unique. As shown in Table S1, with the increase in pyrolysis temperature, the pH of biochar also increases. The following two aspects can explain this: (1) The residual inorganic minerals and alkaline

components in biochar, such as  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ,  $\text{KCl}$ ,  $\text{CaSO}_4$ , and nitrate, are significant factors leading to alkaline pH [37]; (2) Biochar produced from plants sources promotes the decomposition of acidic functional groups (e.g.,  $-\text{COO}-$  and  $-\text{OH}$ ) and the volatilization of organic acids during high temperatures pyrolysis. Thus, most agricultural and forestry wastes have a pH between 7.0 and 10.4 [18,38]. Due to the alkaline pH properties, biochar is often used to improve acidic soils.

### 2.3. Functional Groups

Many functional groups exist on the surface of biochar, which endow biochar with different physical and chemical characteristics, i.e., adsorption properties, hydrophilic and hydrophobic properties, and acid-base buffering properties [18]. The oxygen-containing functional groups on biochar are mainly carboxyl, lactone, phenolic hydroxyl, and carbonyl [39,40]. In the process of biochar preparation, the types and quantities of oxygen-containing functional groups produced by different feedstock at the same pyrolysis temperature are similar [18]. Leng et al. [41] reviewed the nitrogen-containing functional groups of biochar, pyridinic-N, pyrrolic-N, quaternary-N, amine-N,  $\text{NH}_4^+$ -N, Nitrile-N,  $\text{NO}_3^-$ -N, and  $\text{NO}_2^-$ -N were found on the surface of various biochar. In addition, Janu et al. [42] also found that the dominant parameters, e.g., pyrolysis temperature, specific surface area, ash fraction, and H/C ratio, impact the signals of the functional groups on the biochar.

### 2.4. Electrical Conductance (EC)

The EC values of biochar range from  $0.07 \text{ dS m}^{-1}$  to  $10.4 \pm 0.05 \text{ dS m}^{-1}$  (Table S1). The EC values of plant residues biochar and sludge biochars are generally higher than those of manure. The biochar's EC also depends on the pyrolysis temperature and the raw materials. Generally, biochar prepared at higher pyrolysis temperatures has a higher EC value. This phenomenon is mainly due to the loss of volatile substances, increasing residues, and ash in the pyrolysis process [43].

### 2.5. CEC

Typically, biochar has a CEC value in the range of  $6.4\text{--}46.62 \text{ cmol kg}^{-1}$  [44,45], and even reaching values as high as  $75\text{--}128.7 \text{ cmol kg}^{-1}$  [46] (Table S1). The large variability of CEC may be due to the distinct surface properties of biochar, which is highly affected by carbonization temperature and raw materials. Generally, the higher pyrolysis temperatures contribute to a higher CEC value of biochar. The feedstock of biochar is also an essential factor affecting CEC values. The trend of CEC is consistent with the trend of functional groups based on temperature [47]. High temperatures promote the oxidation of aromatic carbon and the formation of carboxyl functional groups. As external pH increases, more negative charges remain on the surface of biochar due to dissociation of biochar surface functional groups (e.g.,  $-\text{COOH}$  and  $-\text{OH}$ ), favoring the cation exchange between biochar and cationic ions, finally leading to the increase of CEC [48,49].

## 3. Effects of Biochar on Soil Properties

### 3.1. pH

Soil pH plays a vital role in plant growth. Low soil pH can lead to toxic effects on plants because elements such as Al which is toxic to plants are easily present as available at low soil pH [50]. According to Dai et al. [51], soils worldwide are mostly acidic (typically  $\text{pH} < 5.5$ ) and continue to suffer from soil acidification. Biochar is alkaline and is always used to amend soil pH, generally by increasing acidic soil's pH. Biochar contributed to increasing the soil pH, and the pH dynamic after biochar application is shown in Table 1. A meta-analysis carried out by Jeffery et al. [52] indicated that the biochars significantly increased soil pH (by up to 2.0 units) in acid soils. Kamali et al. [22] also reviewed that biochar increases the soil pH in different acidic soil types, such as alfisols, ultisols, and latosols. There are two main explanations for improving soil pH by biochar: (1) Biochars have various concentrations of alkaline ash. When biochar is directly applied to soil, the

alkaline components (e.g., hydroxides, carbonates, Mg, Ca, K, and Na oxides) are released into the soil in soluble form. Subsequently, these soluble substances can react with  $H^+$  and Aluminum monomers in acidic soils to raise soil pH [53–55]. (2) The functional groups on the surface of biochar (i.e., phenolic OH,  $-COOH$ , and alcoholic OH) can interact with basic cations in soils based on different reactivity and contribute to an increase of acidic soil pH as a pH buffering [56]. As Novak et al. [48] mentioned, the protonation–deprotonation process of the functional groups on the surface of biochar was the primary mechanism that modified the soil pH.

### 3.2. Soil Bulk Density

Soil bulk density indicates soil physical properties and is commonly measured after biochar supplement. The decline of soil bulk density with biochar addition would contribute to the decrease of soil compaction. The ideal soil bulk density differs for various crop production, resting with soil textural class [57]. Zhang et al. [18] have demonstrated that low soil bulk density will improve the soil structure and facilitate the release and retention of nutrients.

Biochar contributes to decreasing the soil bulk density (Table 1). Rombola et al. [58] showed that the soil bulk density decreased from  $1.44 \pm 0.10 \text{ g cm}^{-3}$  to  $1.38 \pm 0.06 \text{ g cm}^{-3}$  after orchard pruning biochar application. Khan et al. [59] also found that applying maize straw biochar decreased the soil bulk density in sandy loam. A meta-analysis containing published literature between 2010 and 2019 was conducted by Razzaghi et al. [60] to quantify the effect of biochar on soil bulk density. Biochar application decreased approximately 11% of soil bulk density in the coarse-textured and fine-textured soils and 7% in medium-textured soils. The results have shown that biochar amendment decreased average bulk density in various soil types. In addition, they also found that biochar consistently reduced bulk density in the same soil textural group, regardless of the type of experiment.

### 3.3. Soil Water Retention

Soil water retention has played a significant role in crop productivity [60]. The evidence has shown that biochar addition affects soil water retention, possibly due to hydrophilic domains, high porosity, and high specific surface area of biochar. The soil water retention dynamic after biochar application was shown in Table 1. Oladele et al. [61] found that rice husk biochar at the rate of  $12 \text{ t ha}^{-1}$  increased the soil water retention from 36.87% to 32.94% in sandy clay loam. Razzaghi et al. [60] reported that biochar increased field capacity by 51% and 13% in coarse-textured and medium-textured soils, respectively. Moreover, the plant-available water in coarse-, medium and fine-textured soils increased with biochar amendment by 45%, 21%, and 14%, respectively. In addition, Hussaina et al. [62] revealed that many factors, e.g., raw materials type, pyrolysis temperature, biochar particle size, soil type, and compaction state, strongly affected soil water retention.

### 3.4. CEC

CEC is an important index to measure the adsorption capacity of soil and solid materials for exchangeable cations. It is also an essential indicator of soil fertility for supplying nutrients for plants while reducing the nutrients leaching [63]. The soil CEC will increase due to increased soil cation exchange sites. The soils with higher CEC have more vital adsorption ability of Ca, K,  $NH_4^+$ , and Mg, which improves the utilization of nutrient ions in the soil and reduces the loss of nutrients [64]. Many studies have explored the effect of biochar on the CEC of soil (Table 1). Khan et al. [59] showed that maize straw biochar application increased the CEC from  $12.9 \text{ cmol kg}^{-1}$  to  $15.6 \text{ cmol kg}^{-1}$ ,  $17.4 \text{ cmol kg}^{-1}$ , and  $19.2 \text{ cmol kg}^{-1}$  with the addition rate at  $4 \text{ t ha}^{-1}$ ,  $12 \text{ t ha}^{-1}$ , and  $36 \text{ t ha}^{-1}$ , respectively. Hossain et al. [65] revealed that approximately 20–40% increase in total soil CEC and charge were found with biochar amendment. Even a small amount of biochar added to the soil will significantly increase the nutrients and alkaline cations in the soil. Chintala et al. [66] also

reported that biochar could increase soil CEC, both in acidic and alkaline soils, attributed to more anions on the surface of biochar.

### 3.5. Soil Enzyme Activity

Soil enzyme activity, which is the proximate agent of organic matter decomposition and indicator of microbial activity, reflects the intensity and direction of various biochemical processes in soils [67]. Biochar has played a vital role in soil microbial activity and community structure [18]. Plants can produce and release soil phosphatases to mineralize P from nucleic acids, phospholipids, and other ester phosphates [67]. Biochar application led to a significant increase of 27.85% in acid phosphatase activity compared to the treatment without biochar after 7 weeks. The soil phosphatase activity increased by biochar particle size [68]. Pandey et al. [69] found that biochar increased dehydrogenase by 27% compared with the control group, and urease activity increased by 7.4–39% with biochar addition. Jia et al. [70] and Pandey et al. [71] revealed that soil enzymes (e.g., urea, invertase, and dehydrogenase) were activated with different types and concentrations of biochar application. Song et al. [72] reported that biochar addition led to an increase of 13.9, 8.4, 21.7, 81.3, and 150.5% in urease, protease, alkaline phosphatase, catalase, and sucrase, respectively.

Recently, a meta-analysis performed by Liao et al. [73] revealed that the pyrolysis temperature potentially controlled the impact of biochar on the activities of soil nutrient acquisition enzymes. Generally, low-temperature biochar (derived at  $<500$  °C) contributes to triggering soil enzymes. However, the effect of high-temperature biochar (derived at  $\geq 500$  °C) on soil enzyme activity was weak. In addition, it was also found that soil and biochar characteristics played a secondary role in the process of biochar's influence on enzyme activity. The effect of biochar on soil enzyme activity is closely related to biochar properties and soil types [73]. Therefore, selecting appropriate biochar according to soil properties is the premise of improving soil enzyme activity.

**Table 1.** The soil properties changes with biochar application.

| Biochar Type            | Pyrolysis Conditions | Highlighted Properties (Biochar)                                 | Soil Type             | Highlighted Properties (Soil)   | Addition Rate   | Duration | pH          | CEC                                  | Bulk Density                   | Water Holding Capacity | Ref. |
|-------------------------|----------------------|--|-----------------------|---|---|----------|-------------|--------------------------------------|--------------------------------|------------------------|------|
| Orchard pruning biomass | 3 h at 500 °C        | 71.4% C, 0.7% N, 1.5% H, and 5.9% O (dry weight)                 | Sandy clay loam       | 70% sand, 15% silt and 15% clay.  | 0   | 9 months | 5.18 ± 0.30 | 11.8 ± 0.9 meq 100 g <sup>-1</sup>   | 1.44 ± 0.10 g cm <sup>-3</sup> | -                      | [58] |
|                         |                      |  |                       |   | 16.5 t ha <sup>-1</sup> in 2009 and further 16.5 t ha <sup>-1</sup> in 2010 | 9 months | 6.76 ± 0.18 | 24.3 ± 1.8 meq 100 g <sup>-1</sup>   | 1.38 ± 0.06 g cm <sup>-3</sup> | -                      |      |
|                         |                      |  |                       |   | 16.5 t ha <sup>-1</sup>   | 9 months | 6.54 ± 0.25 | 18.32 ± 1.05 meq 100 g <sup>-1</sup> | 1.42 ± 0.07 g cm <sup>-3</sup> | -                      |      |
|                         |                      |  |                       |   | 0   | 1 year   | 5.25 ± 0.15 | 11.5 ± 1.5 meq 100 g <sup>-1</sup>   | 1.45 ± 0.06 g cm <sup>-3</sup> | -                      |      |
|                         |                      |  |                       |   | 16.5 t ha <sup>-1</sup> in 2009 and further 16.5 t ha <sup>-1</sup> in 2010 | 1 year   | 6.59 ± 0.20 | 24.1 ± 1.8 meq 100 g <sup>-1</sup>   | 1.38 ± 0.25 g cm <sup>-3</sup> | -                      |      |
|                         |                      |  |                       |   | 16.5 t ha <sup>-1</sup>   | 1 year   | 6.32 ± 0.14 | 18.14 ± 0.83 meq 100 g <sup>-1</sup> | 1.40 ± 0.03 g cm <sup>-3</sup> | -                      |      |
| Peanut shells biochar   | 650 °C for 6 h       | -  | Silt loam acidic soil | 5.58% clay, 49.5% silts, and 44.92% sand  | 2% (w/w)  | 42 d     | 6.11 ± 0.15 | -                                    | -                              | -                      | [74] |
|                         |                      |  |                       |   | 4% (w/w)  | 42 d     | 6.67 ± 0.16 | -                                    | -                              | -                      |      |
|                         |                      |  |                       |   | 6% (w/w)  | 42 d     | 6.91 ± 0.18 | -                                    | -                              | -                      |      |
| Maize straw biochar     | 350–550 °C           | -  | Sandy loam            | Bulk density 1.41 g mL <sup>-1</sup> , water holding capacity 0.38 cm <sup>3</sup> cm <sup>-3</sup> | 0 tons ha <sup>-1</sup> biochar   | 1 year   | 7.26        | 12.9 cmol kg <sup>-1</sup>           | 1.45 g cm <sup>-3</sup>        | -                      | [59] |
|                         |                      |  |                       |   | 4 t ha <sup>-1</sup>  | 1 year   | 7.39        | 15.6 cmol kg <sup>-1</sup>           | 1.43 g cm <sup>-3</sup>        | -                      |      |
|                         |                      |  |                       |   | 12 t ha <sup>-1</sup>   | 1 year   | 7.54        | 17.4 cmol kg <sup>-1</sup>           | 1.40 g cm <sup>-3</sup>        | -                      |      |
|                         |                      |  |                       |   | 36 t ha <sup>-1</sup>   | 1 year   | 7.64        | 19.2 cmol kg <sup>-1</sup>           | 1.36 g cm <sup>-3</sup>        | -                      |      |
| Grains husks and paper  | 500 °C               | Total C 531 g kg <sup>-1</sup> and total N 14 g kg <sup>-1</sup> | Haplic Luvisol        | 9.13 g kg <sup>-1</sup> soil organic carbon and pH 5.71   | 0 t ha <sup>-1</sup>  | 1 year   | -           | 153.93 ± 6.45 Mmol kg <sup>-1</sup>  | -                              | -                      | [75] |
|                         |                      |  |                       |   | 10 t ha <sup>-1</sup>   | 1 year   | -           | 160.15 ± 10.40 Mmol kg <sup>-1</sup> | -                              | -                      |      |
|                         |                      |  |                       |   | 20 t ha <sup>-1</sup>   | 1 year   | -           | 177.70 ± 13.33 Mmol kg <sup>-1</sup> | -                              | -                      |      |

Table 1. Cont.

| Biochar Type      | Pyrolysis Conditions | Highlighted Properties (Biochar) | Soil Type                | Highlighted Properties (Soil)        | Addition Rate         | Duration | pH   | CEC                         | Bulk Density | Water Holding Capacity | Ref. |
|-------------------|----------------------|----------------------------------|--------------------------|--------------------------------------|-----------------------|----------|------|-----------------------------|--------------|------------------------|------|
| Rice husk biochar | 350 °C for 1.25 h    | pH 8.50 and 51.13% TOC           | Typic Paleustalf Alfisol | 68.8% sand, 25.1% clay and 6.1% silt | 0                     | 2 years  | 5.27 | 7.18 cmol kg <sup>-1</sup>  | -            | 32.94%                 | [61] |
|                   |                      |                                  |                          |                                      | 3 t ha <sup>-1</sup>  | 2 years  | 6.54 | 9.69 cmol kg <sup>-1</sup>  | -            | 32.94%                 |      |
|                   |                      |                                  |                          |                                      | 6 t ha <sup>-1</sup>  | 2 years  | 6.66 | 9.91 cmol kg <sup>-1</sup>  | -            | 34.87%                 |      |
|                   |                      |                                  |                          |                                      | 12 t ha <sup>-1</sup> | 2 years  | 6.73 | 12.30 cmol kg <sup>-1</sup> | -            | 36.87%                 |      |
| Sawdust           | 350 °C for 4 h       | -                                | Loamy sand               | 65.3% sand, 25.4% silt, 9.3% clay    | 0                     | 11 weeks | 6.85 | 13.48 cmol kg <sup>-1</sup> | -            | -                      | [76] |
|                   |                      |                                  |                          |                                      | 10 t ha <sup>-1</sup> | 11 weeks | 7.24 | 17.63 cmol kg <sup>-1</sup> | -            | -                      |      |
|                   |                      |                                  |                          |                                      | 20 t ha <sup>-1</sup> | 11 weeks | 7.30 | 21.57 cmol kg <sup>-1</sup> | -            | -                      |      |

## 4. Effects of Biochar Addition on Soil Nutrients

### 4.1. C

Soil carbon has played an essential role in food security, environmental health, and ecosystem functioning, especially in global climate change mitigation. The United Nations Sustainable Development Goals (SDGs) highlight C sequestration and soil fertility improvement and set reasonable targets for nations to achieve by 2030. The SDGs emphasize the need for soil security to improve soil fertility and provide adequate and balanced nutrients for plants [77].

Generally, the organic carbons (OC) in biochar consist of at least two C pools, i.e., labile and stable OC, which exhibit low and high ability to resist mineralization [33]. Biochar produced at low temperature ( $\leq 400$  °C) has higher labile OC (e.g., low molecular weight aliphatic compounds) than at high temperature ( $>400$  °C) [78]. As summarized by Han et al. [79], the mineralization rate of biochar application in soil increased with time, and the amount of mineralization was as high as 15–20%. The mineralization of biochar depends on the biochar feedstock type and pyrolysis temperature. Manure and crop-produced biochar had a higher mineralized OC percentage than wood-derived biochar. The percentage of mineralized OC decreased with increasing pyrolysis temperature [79], possibly due to the increased portion of aromatic C and the higher degree of aromatic condensation in biochar, as reported previously [17].

The biochar amendment greatly influenced the soil total carbons (TC) as an exogenous carbon source. A global meta-analysis on the effect of biochar on soil carbon pools presented by Chagas et al. [80] reported that biochar addition rate is the most important factor which affects soil TC than other factors, e.g., raw material, pyrolysis temperature, biochar C content, experiment duration, experiment type, climate zone, soil pH, and soil texture. The higher biochar rate applied in the soil led to a significant increase in soil TC, with a range from 28.9% to 140.0%. Yin et al. [81] also explored the effect of biochar amendment on the soil total organic carbon (TOC) and labile OC. The amendments of biochar derived from wood (pyrolysis at 650 °C) significantly increased soil TOC. Yan and Liu [82] reported a similar result, biochar with a high carbon content (39.98–41.47%) led to the increase of soil TOC. Yan and Liu [82] also proved that different particle sizes do not significantly impact the TOC content in soil. This result might be because biochar with different particle sizes was almost identical in the composition ratio of their carbon-containing substances.

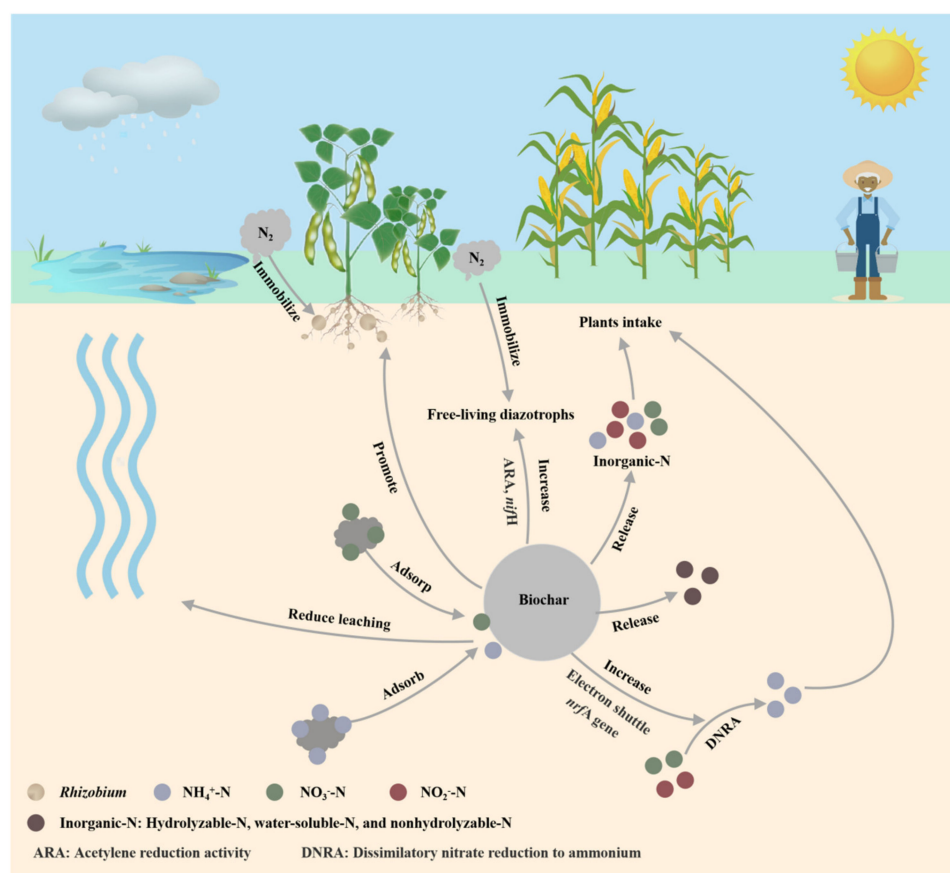
Biochar contributes to increasing soil microbial biomass carbons (MBC). Liu et al. [83] reported that soil MBC increased by 12–24% with biochar application. An overall increase of 25% induced by biochar in soil MBC was obtained via a meta-analysis [80]. The effect of biochar on soil MBC depends on the soil type. Liu et al. [83] showed that biochar addition significantly increases soil MBC content in acid soils compared to neutral or alkaline soil conditions. Perhaps this is because biochar is primarily alkaline, its application to acidic soils acts as a buffer, thus increasing the microbial population [84]. Soil MBC was also significantly impacted by the soil C content, biochar rate, and climatic zone [80].

Soil dissolved organic carbon (DOC) plays a vital role in the C cycle [85]. The pure spruce woodchips biochar [86] and Wood pellet biochar [87] contribute to increasing soil DOC. Hernandez-Soriano et al. [88] also reported that biochar increased humic-like fluorescent components in DOC from soil leachate. Biochar amendment to the soil could change DOC contents and composition, in turn, affect overall water quality. However, Liu et al. [89] reported that DOC increase with biochar application was temporary, and this effect quickly disappeared with the aging of the biochar. This finding suggested there was little risk of biochar application altering soil water quality through DOC leaching [80].

Biochar is vital in improving soil TC, TOC, BMC, and DOC. Factors such as soil C content, biochar rate, soil type, and experiment duration affect soil C dynamics with biochar application [80]. Therefore, selecting appropriate biochar and addition rate according to soil type and experimental conditions is essential for soil C improvement.

#### 4.2. N

In biochar, the content of N ranges from  $<0.10\%$  to  $9\%$  and decreases as the pyrolysis temperature increases (Table S1). Lang et al. [90] revealed that the volatilization of N is the primary way of the loss of total N, and  $21\text{--}71\%$  of N in the form of HCN,  $\text{NH}_3$ , and HCNO migrated into gaseous pyrolysis products [91,92]. This also means that pyrolysis temperature plays a critical role in the content of N of biochar. As described by Liu et al. [28], the N in biochar is mainly divided into inorganic N (hydrolyzable-N water-soluble-N, and nonhydrolyzable-N) and organic N (including  $\text{NH}_4^+$ -N,  $\text{NO}_2^-$ -N, and  $\text{NO}_3^-$ -N which are easy to absorb and intake by plants and bacteria) (Figure 1). Factors affecting the conversion of nitrogen in biochar preparation, such as biomass materials, pyrolysis temperature, heating rate and time, and atmosphere, were reviewed in detail by Yuan et al. [93].



**Figure 1.** The mechanisms of biochar application on N improvement in soil [94–97].

Several studies have reported that biochar application could increase soil total nitrogen (TN) content [94,98]. Consistently, increasing biochar application rates led to extra soil total N accumulation from  $0.09$  to  $0.30 \text{ g kg}^{-1}$  compared to the control. There is a significant linear correlation between the TN content, and the amount of biochar added, indicating that the amount of biochar is an important factor affecting the TN content in the soil. In addition, the concentrations of different N forms (e.g.,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , microbial biomass nitrogen, and dissolved organic nitrogen) also increased with biochar addition during the incubation, among which the peak value of  $\text{NO}_3^-$  was lagging behind  $\text{NH}_4^+$  [99]. Joseph et al. [100] also revealed that soil N content is directly increased through biochar supplement and indirectly achieved via the N transportation of manure biochar by insects.

As a promising soil amendment, biochar effectively reduced N loss due to its high adsorption capacity to  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N [101] (Figure 1). Nano-biochar effectively reduced soil nitrate loss ( $13.6\text{--}59.8\%$ ) compared to the control [102]. Similarly, a study in

which different rates of 0.5–4% (*w/w*) winter-pruned apple branches biochar reduced the leaching ratio of  $\text{NO}_3^-$ -N (9.9–68.7%) and nitrogen oxides flux (6.3–19.2%) in the soil [103]. Nelissen et al. [26] demonstrated that  $\text{NH}_4^+$  is immobilized quickly by adsorption of maize biochar, which reduces available N and concomitantly minimizes potential soil N losses in the short-term study. A similar result was obtained by Yao et al. [104], biochar exhibited  $\text{NH}_4^+$  adsorption. Many acidic functional groups (e.g., phenols, carboxylic groups, and carbonyls), which have a negative charge, have been found on the biochar surface and adsorb  $\text{NH}_4^+$ -N via electrostatic attraction [105]. Ventura et al. [106] also reported that biochar significantly decreased  $\text{NO}_3^-$  leaching by 75% in an apple orchard. Compared to  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N is more strongly held by biochar due to the higher CEC of most biochars. In addition, more outstanding negative surface charges carried by biochar may lead to weak adsorption of  $\text{NO}_3^-$ -N [107]. Amonette and Joseph. [108] and Montes-Morán et al. [105] found that chromenes, ketones, pyrones, etc., functional groups on the surface of biochar, can facilitate  $\text{NO}_3^-$ -N adsorption. Another possible chemisorption mechanism between biochar and  $\text{NO}_3^-$ -N via unconventional H-bonding was illustrated by Kammann et al. [109] and Lawrinenko et al. [110]. Nguyen et al. [111] also found a significant correlation between biochar CEC and  $\text{NH}_4^+$ -N adsorption through boosted regression tree analysis.

Soil application of biochar contributes to increasing N mineralization (Figure 1). Nelissen et al. [26] showed a 185–221% increase in gross N mineralization, 10–69% in nitrification, and up to a 508% increase in  $\text{NH}_4^+$  rates when the soil was amended with maize biochar. It is found that biochar produced at low pyrolysis temperature has a more apparent promoting effect on soil N mineralization and increased  $\text{NH}_4^+$  content compared to biochar produced at high pyrolysis temperature due to a more significant labile C fraction [26]. Generally, the biochar produced with high N feedstock content significantly promotes N mineralization [95]. Singh et al. [25] reported that manure biochar increased N mineralization compared to plant-based biochars due to the lower C/N ratio. In addition, Zimmerman et al. [112] found that the promotion of N mineralization by biochar is short-term. With the extension of application time, N mineralization decreased because organic substrates were adsorbed by biochar and soil to decrease their availability for microorganisms. The effects of biochar on soil N mineralization are mainly influenced by feedstock, pyrolysis temperature, incubation time, and the C/N ratio of biochar [100,111].

Biological  $\text{N}_2$  fixation (BNF) is a complementary N source for plants, and symbiotic bacteria contain the nitrogenase enzyme [113]. Generally, BNF consists of two primary pathways: symbiotic and free-living [114]. The positive effect of biochar toward stimulating BNF was more pronounced in the symbiotic relative to the nonsymbiotic BNF (35.8 vs. 28.1% increment over the control) [115]. Symbiotic  $\text{N}_2$ -fixation (SNF) occurred via a molecular “crosstalk” between plants (only limited to leguminous crops) and the  $\text{N}_2$ -fixing symbionts in plant roots [116]. Many kinds of literature have reported that BNF was enhanced with biochar supplement [94–97] (Figure 1). Azeem et al. [94] applied sugarcane bagasse biomass and pyrolysis at 350 °C in mash bean plots with the application rate of 10 t ha<sup>-1</sup>. An 83% increase in  $\text{N}_2$  fixation was found compared with the control treatments. The selection of suitable biochar according to the types of soils and plants can promote the BNF in root nodules or by association with free-living bacteria [117]. Horel et al. [118] also exhibit that biochar amendment contributes to improving the microclimate of microbial growth, which might lead to a significant decline of soil N, but a significant increase in  $\text{N}_2$  fixation rate in alder. Based on the results obtained by Anderson et al. [119], the population of  $\text{N}_2$  fixing microorganisms, i.e., Frankiaceae and Bradyrhizobium, increased with biochar supplement. A pot experiment with clay loam soil was carried out by Rondon et al. [120], and 31% greater  $\text{N}_2$  fixation by Rhizobium strains associated with bean plants was found with wood biochar amendment. On the other hand, free-living  $\text{N}_2$ -fixation (FNF), carried out by cyanobacteria in association with moss or other free-living diazotrophs in litter and soil, is nearly ubiquitous in terrestrial ecosystems [121]. Biochar with a 2% application rate significantly increased acetylene reduction activity (ARA) and *nifH* abundance in

56 days. Through the analysis of soil diazotrophic community composition, *Azotobacter*, *Bradyrhizobium*, and *Skermanella* were the most dominant genera. *Azotobacter*, a free-living diazotroph, reached the maximum in soil [99] (Figure 1). The variation in the diazotrophic community was associated with soil EC, DOC, and pH [99].

In addition, the enhancement of dissimilatory nitrate reduction to ammonium (DNRA) is well known as beneficial for the environment and agriculture because DNRA increases nitrogen retention in soil. According to Yuan et al. [122], adding rice straw biochar led to an increased DNRA with an increased rate of 0.2 to 0.7 mg kg<sup>-1</sup> NH<sub>4</sub><sup>+</sup>-N dry soil d<sup>-1</sup>. Moreover, biochar simultaneously increased the expression levels of the *nrfA* gene, which was the DNRA functional gene [123]. Through correlation analysis, the application of biochar enhanced DNRA due to its electron shuttle potential [123] (Figure 1). The capacity of biochar for paddy-soil N conservation and N<sub>2</sub>O mitigation is expected to amplify by improving the electron shuttle function of biochar [122,124].

#### 4.3. P

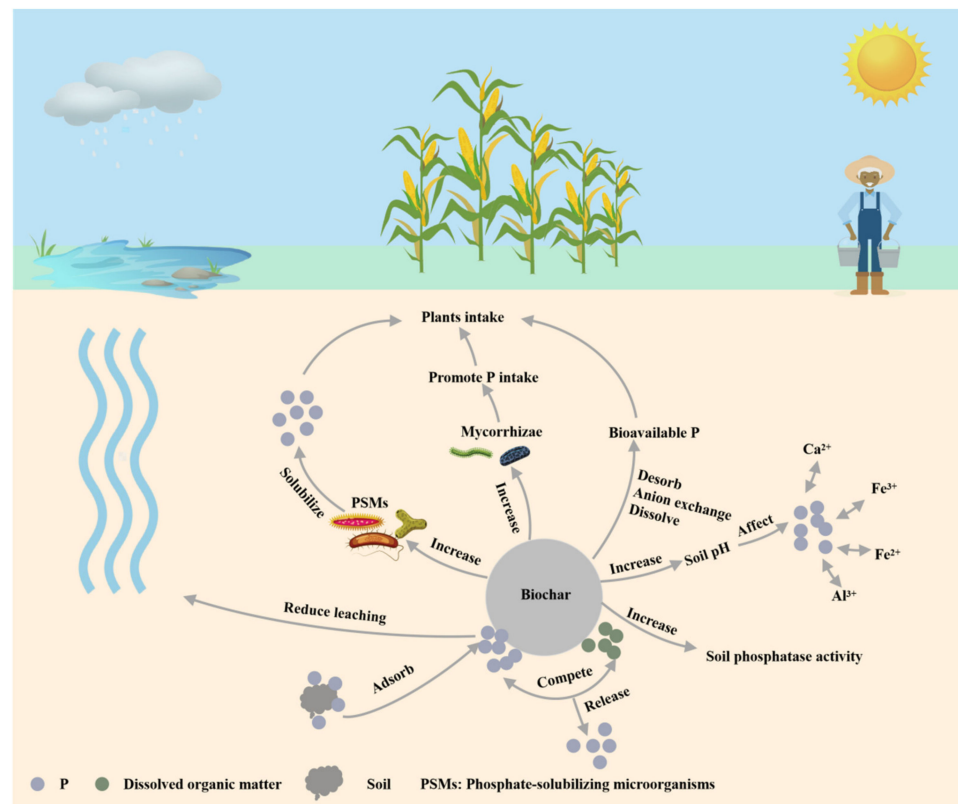
P is a decisive macronutrient element for all biological communities, without which plant growth and crop yields would be substantially limited [125]. Biochar has positively affected soil phosphorus transformation in agricultural soils [126]. Biochar contains the element P with the level of 0.01–6.1% (Table S1), and the total P content of biochar was influenced by the types of raw materials and pyrolysis temperature. As shown in Table S1, the P content in biochar derived from manure and sludge is higher than in plant biomass biochar.

Biochar has been provided with various P supplements to the soil as a P source. Different P forms, such as stable P (crandallite, wavellite, and poly-P), semi-labile P (CaHPO<sub>4</sub>, phytic acid, phospholipid, DNA, and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>), and labile P (orthophosphate), were found in biochar [127]. With the biochar addition to soil, the unstable P and part of semi-stable P were released first. Qian et al. [128] revealed that almost 50% of P was released in the forms of pyrophosphate and orthophosphate in the first 8 h. Furthermore, a similar result obtained by Jin et al. [36] showed that biochar supplement gave an orthophosphate release from 77.5–83.4% to 92.9–96.3%. The release patterns of P from biochar and its feedstock are quite different.

Through the comparative study of the P release rate in biochar and raw materials, Liang et al. [129] described P release from manure as fast desorption. However, manure biochar was initially controlled by diffusion and subsequently by stable P's slow and sustained dissolution. In addition, many environmental factors, e.g., soil pH, ionic strength, and soil microorganisms, had also been reported to affect the P release from biochar in soil [28,130,131]. Therefore, it is imperative to select reasonable biochar to improve the lack of P element in the soil and improve soil fertility according to the actual situation.

Numerous studies have shown that the application of biochar has led to an increase in soil available P via different mechanisms (Figure 2). (1) The biochar can release the bioavailable P to the soil due to desorption, anion exchange, or dissolution [127]. (2) Soil P complexation was influenced by biochar addition, mainly by modifying soil pH. Gao et al. [16] showed that the precipitation of P with Ca<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, and Al<sup>3+</sup> was affected by altering soil pH and activities of these cations. (3) The dissolved organic matter (DOM) released from biochar resulted in competition with P for sorption in soil and led to the increase of P release [24,132]. (4) Biochar promoted the available soil P by improving soil phosphate-solubilizing microorganisms (PSMs) biomass. In soil, PSMs are consistent with P-solubilizing fungi, P-solubilizing bacteria, and actinomycetes which can solubilize the P [133,134]. Jaafar et al. [135] reported that biochar gave PSMs a suitable habitat. Zheng et al. [136] indicated that the survival rate of PSMs and the available P content in biochar-emendation soil were higher than in the control. In addition, biochar can promote the P uptake by plants via the increase of mycorrhizae [137]. (5) Soil phosphatase activity was a significant influencing factor of available soil P with biochar application. Jin et al. [36] found that alkaline phosphomonoesterase increased by 28.5% in clay-loam soil and 95.1%

in silt loam soil with manure biochar supplement. To sum up, the application of biochar to enhance the available P is mainly by decreasing the complexation of P with soil components and promoting the P metabolism of soil.



**Figure 2.** The mechanisms of biochar application on P improvement in soil [24,127,132–137].

Although the presence of biochar contributed to releasing soluble P into the soil and increasing the available P in soil, little evidence has proven that biochar can reduce the leaching of P [104,138,139] (Figure 2). Biochar can decrease the leaching of P from soil to groundwater and surface water via increased P retention [140,141]. P has complex interactions with the soil-biochar system. The mechanism mainly involves pore filling, complexation, cation bridge, electrostatic attraction, competitive adsorption sites, and precipitation reaction [142,143]. In addition, Xu et al. [63] also showed that biochar decreased the leaching of P in soil due to the promotion of P intake by plants or the decrease of water loss from soil. In summary, adding biochar into soil led to an increase in the soil P available and a decrease in the leaching loss of soil P, and these positive effects are either direct or indirect. In particular, the interfacial interaction between biochar and soil components remains to be explored.

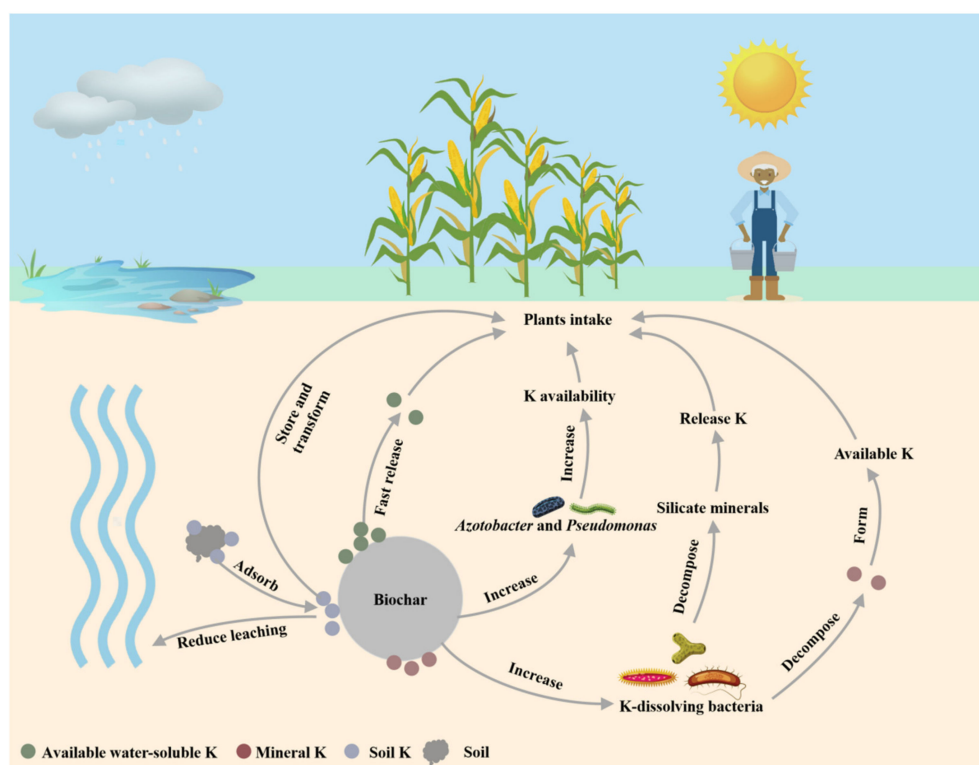
#### 4.4. K

Potassium is a vital macronutrient for plant growth, such as regulating plant metabolism and improving grain yields [144,145]. In recent years, the potassium content in the soil has decreased dramatically due to exhaustive contemporary agriculture and a lack of timely potassium supply [31]. Therefore, the search for new potassium fertilizer substitutes has a good application prospect because imported potassium fertilizer is relatively expensive.

Many studies have investigated biochar as a new type of K fertilizer for soil improvement [31,146,147]. As shown in Table S1, the amount of potassium in biochar ranges from 0.60 to 42.40 mg kg<sup>-1</sup>. It was found that potassium in biochar increases gradually with pyrolysis temperature but volatilizes in the form of gas when the temperature is above 600 °C [148]. The available water-soluble K, such as K<sub>2</sub>SO<sub>4</sub>, KCl, KNO<sub>2</sub>, and KNO<sub>3</sub>, ac-

counts for 50–58% of total potassium in biochar. Mineral K, mainly presented as the forms of layer-K and complex-K, comprises the remaining 42–50% [28].

The improvement of K in soil by biochar is firstly manifested in the supplement of K in soil (Figure 3). Oram et al. [149] found that biochar application increased K availability and increased the competitive ability of red clover to grass and plantain. With the increase in biochar level, the contents of soluble and available potassium in soil increased significantly. With 60 Mg ha<sup>-1</sup> biochar addition, the contents of soluble and available potassium increased by 10% and 27%, respectively, compared with the control group. Moreover, biochar also increased the soil potential buffering capacity of potassium in calcareous sandy soil [150]. However, the contents of soluble and available potassium in the soil increased significantly even at low levels of biochar addition [150]. It can be explained by that free nutrient cations are produced during biochar pyrolysis, and biochar application to the soil will improve the availability of base cations (such as potassium) [151,152].



**Figure 3.** The mechanisms of biochar application on K improvement in soil [146,147,153–155].

Generally, biochar provides soil and crops with potassium in the short term [89]. Limwikran et al. [153] revealed that 8–64% of the K in biochar is rapidly dissolved in water, of which 0–40% is rapidly released into the soil. After the application of biochar to soil, the loss of water-soluble potassium from biochar mainly occurred within one week, whereas insoluble K was relatively slow. Most of the water-soluble K is lost within eight weeks in biochar, such as durian shell, mangosteen shell, eucalyptus wood, and pineapple peel [153]. However, recent studies have shown that biochar still promotes soil K improvement under long-term application [31]. Farmyard manure and woodchip biochar significantly increased soil available K contents compared to CK and led to higher grain K contents and K use efficiency than their feedstock treatments during both years [31]. The soil K showed significant positive correlations with biological and grain yields [31]. Through a four-year biochar study, Zhang et al. [146] found that biochar increased the K availability due to the enhancement of the activity of *Azotobacter* and *Pseudomonas* (Figure 3). Xia et al. [147] also reported that the biochar supplement significantly increased the content of K-dissolving bacteria which can decompose silicate minerals and release K that can be directly used by plants [154] (Figure 3). Based on the gene prediction, biochar led to positive alterations

in bacterial function, which involved amino acid transport, production and translation of energy, and ribosomal structure.

In addition, biochar has a high adsorption capacity and can adsorb K lost in the soil, thus providing a stable potassium source for plant growth [146,155] (Figure 3). Among them, soluble potassium and mineral potassium are absorbed by plants or stored in the soil as available potassium through different transformation pathways. Water-soluble potassium is directly absorbed by plants in the form of potassium ions to meet their short-term metabolic demand for K [28].

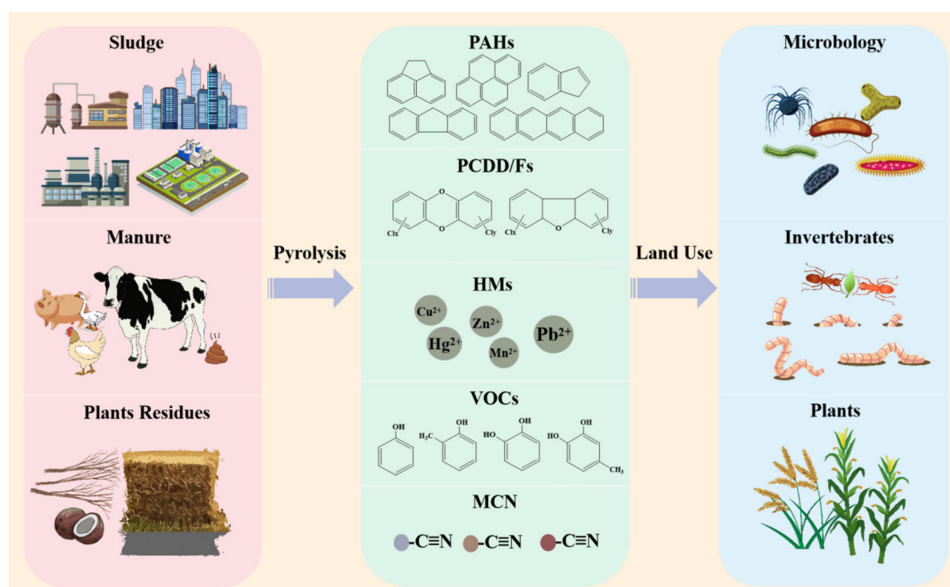
The effects of biochar on soil nutrient also vary over time. Jílková et al. [156] investigated the effects of biochar on soil nutrients in different incubation time and found that biochar supported microbial activity for several days or weeks at the beginning of the incubation until its stock of readily available nutrients had been depleted. They revealed that the biochar can only be used as a slow-release nutrients fertilizer during the six-month incubation period. Xia et al. also reported that peanut shell biochar improved soil K level after 30 months of application [147]. However, biochar application has no significant differences in soil nutrients, microbial growth, mycorrhizal colonization or weed emergence compared to the unamended soil after 3 years incubation [157]. Whilst biochar amendment is unquestionably a strategy for the improved soil nutrient levels or crop performance, it seemed to be short lived. Therefore, it is necessary to need more long-term field studies to provide data that can meaningfully inform agronomic management decisions.

## 5. The Adverse Effects of Biochar on Soil Organisms

### 5.1. Toxic Substances of Biochar

Biochar may be an essential source that introduces organic and inorganic contaminants (mainly HMs) to the soil system, leading to toxic effects on biota (Figure 4). Some of these contaminants exist naturally in biochar pyrolysis materials, and some are formed during the pyrolysis process, including improper or incomplete pyrolysis [158,159]. Many efforts have been made to identify these contaminants in biochar, and the toxic substances of biochar have summarized in Table 2. The PAHs are the main chemical composition of these contaminants in biochar, with the total PAHs content ranging from 1.609–355.2 mg kg<sup>-1</sup> [160]. Moreover, the biochar prepared at low-temperature processes has a lower content of 3–4 ring PAHs than that of biochar prepared at high temperatures. Lyu et al. [161] and Hale et al. [160] explored the concentration of PCDD/Fs in nearly 20 biochars prepared from different temperatures and raw materials and found that a total PCDD/Fs range from 50 pg g<sup>-1</sup> to 610 pg g<sup>-1</sup> and toxic dioxin concentration range from 0.005 pg g<sup>-1</sup> to 1.20 pg g<sup>-1</sup>. The volatile organic compounds (VOCs), mainly consisting of organic acids, aldehydes, furans, ketones, alcohols, and phenols, were generated during pyrolysis. Buss et al. [162] found that the prominent member of VOCs in softwood pellets biochar is phenols, with a concentration from 20 to 240 µg g<sup>-1</sup>. Recently, the MCN was reported as the critical toxic compound in biochar, and CN- contents were detected from 1.0 to 251 mg kg<sup>-1</sup>. The higher concentrations in corn protein biochar, food waste, and phycocyanin biochar are 23,251, 40,286, and 85,870 mg kg<sup>-1</sup>, respectively [163]. The PTEs, which mainly include Cu, Pb, Zn, Hg, Mn, Ni, As, Cr, Cd, etc., are other primary contaminants in biochar. PTEs can be found in various biochar derived from different feedstock, e.g., sludge, manure, and plant biomass [164,165].

More importantly, the toxic substrate in biochar depends on the pyrolysis raw material and temperature. In generally, sludge biochar contains more heavy metals and plant-derived biochar contains more PAHs. Sørmo et al. [166] reported that biochar derived with a high salt content raw material contained a significant amount of dioxins. High temperature has a stronger fixation effect on HMs on biochar and reduces their leaching. The PAH content in biochar generally decreases as the pyrolysis time and temperature increase [167]. Therefore, before applying biochar, it is necessary to strictly monitor the concentration of pollutants and select the appropriate dosage to reduce ecological risks.



**Figure 4.** A general view of the contaminants present in biochar regarding to their effect towards living organisms.

**Table 2.** Main pollutants of biochar obtained under different biomass and preparation conditions.

| Pollutants Types | Biochar Types     | Pyrolysis Conditions | Concentration   | Ref.   |  |
|------------------|-------------------|----------------------|---|--|--|
| PAHs             | Sewage sludge     | 500 °C for 3 h       | Total PAHs: 2263 µg kg <sup>-1</sup>  | [168]  |  |
|                  |                   | 600 °C for 3 h       | Total PAHs: 1730 µg kg <sup>-1</sup>  |  |  |
|                  |                   | 700 °C for 3 h       | Total PAHs: 1449 µg kg <sup>-1</sup>  |  |  |
|                  | Sewage sludge     | 500 °C               | Total PAHs: 612 to 766 µg kg <sup>-1</sup>  | [169]  |  |
|                  |                   | 350 °C for 2 h       | Total PAHs: 3.72 ± 0.422 mg kg <sup>-1</sup>  | [170]  |  |
|                  | Straw             | 500 °C for 2 h       | Total PAHs: 5.48 ± 1.02 mg kg <sup>-1</sup>   |  |  |
|                  |                   | 650 °C for 2 h       | Total PAHs: 4.94 ± 0.315 mg kg <sup>-1</sup>  |  |  |
|                  |                   | 200 °C               | Nap: 2.5 mg kg <sup>-1</sup><br>Flu: 8.5 mg kg <sup>-1</sup><br>Phe: 32 mg kg <sup>-1</sup><br>Pyr: 15.46 mg kg <sup>-1</sup><br>BaA: 2.01 mg kg <sup>-1</sup><br>CHR: 246.23 mg kg <sup>-1</sup><br>BbF: 1.51 mg kg <sup>-1</sup><br>BkF: 1.07 mg kg <sup>-1</sup> | [171]  |  |
|                  | Paper mill sludge | 300 °C               |   | Nap: 8.5 mg kg <sup>-1</sup><br>Flu: 39.5 mg kg <sup>-1</sup><br>Phe: 55.5 mg kg <sup>-1</sup>   |  |
|                  |                   |                      |   | Pyr: 12.64 mg kg <sup>-1</sup><br>BaA: 24.2 mg kg <sup>-1</sup><br>CHR: 157.42 mg kg <sup>-1</sup><br>BbF: 3.61 mg kg <sup>-1</sup><br>BkF: 2.43 mg kg <sup>-1</sup> |  |
|                  |                   |                      | Nap: 860 mg kg <sup>-1</sup><br>Flu: 343.5 mg kg <sup>-1</sup><br>Phe: 913 mg kg <sup>-1</sup>  |  |  |
| 400 °C           |                   |                      | Pyr: 492.3 mg kg <sup>-1</sup><br>BaA: 224.7 mg kg <sup>-1</sup><br>CHR: 534.9 mg kg <sup>-1</sup><br>BbF: 195.39 mg kg <sup>-1</sup><br>BkF: 172.3 mg kg <sup>-1</sup>   |  |  |

Table 2. Cont.

| Pollutants Types | Biochar Types | Pyrolysis Conditions | Concentration  | Ref.  |
|------------------|---------------|----------------------|--|-------|
|                  |               | 500 °C               | Nap: 372.5 mg kg <sup>-1</sup><br>Flu: 1198 mg kg <sup>-1</sup><br>Phe: 3700 mg kg <sup>-1</sup><br>Pyr: 1394.7 mg kg <sup>-1</sup><br>BaA: 769.5 mg kg <sup>-1</sup><br>CHR: 859.02 mg kg <sup>-1</sup><br>BbF: 2310 mg kg <sup>-1</sup><br>BkF: 2182 mg kg <sup>-1</sup>   |       |
|                  |               | 600 °C               | Nap: 4.5 mg kg <sup>-1</sup><br>Flu: 79 mg kg <sup>-1</sup><br>Phe: 197 mg kg <sup>-1</sup><br>Pyr: 165.8 mg kg <sup>-1</sup><br>BaA: 17.5 mg kg <sup>-1</sup><br>CHR: 127.5 mg kg <sup>-1</sup><br>BbF: 134.29 mg kg <sup>-1</sup><br>BkF: 121.8 mg kg <sup>-1</sup><br>Flu: 16.5 mg kg <sup>-1</sup><br>Phe: 60 mg kg <sup>-1</sup><br>Pyr: 21 mg kg <sup>-1</sup><br>BaA: 25 mg kg <sup>-1</sup><br>CHR: 12.28 mg kg <sup>-1</sup><br>BbF: 9.01 mg kg <sup>-1</sup><br>BkF: 8.2 mg kg <sup>-1</sup> |       |
|                  |               | 700 °C               | CHR: 12.28 mg kg <sup>-1</sup><br>BbF: 9.01 mg kg <sup>-1</sup><br>BkF: 8.2 mg kg <sup>-1</sup>  |       |
|                  |               | 300 °C for 3 h       | 2 ring PAHs: 5.7 mg kg <sup>-1</sup><br>3 ring PAHs: 4.8 mg kg <sup>-1</sup><br>4 ring PAHs: 1.8 mg kg <sup>-1</sup><br>5 ring PAHs: 0.6 mg kg <sup>-1</sup><br>6 ring PAHs: 0.8 mg kg <sup>-1</sup>   | [172] |
|                  |               | 400 °C for 3 h       | 2 ring PAHs: 6.0 mg kg <sup>-1</sup><br>3 ring PAHs: 4.0 mg kg <sup>-1</sup><br>4 ring PAHs: 3.1 mg kg <sup>-1</sup><br>5 ring PAHs: 1.3 mg kg <sup>-1</sup><br>6 ring PAHs: 1.0 mg kg <sup>-1</sup>   |       |
|                  | Sewage sludge | 500 °C for 3 h       | 2 ring PAHs: 6.9 mg kg <sup>-1</sup><br>3 ring PAHs: 1.4 mg kg <sup>-1</sup><br>4 ring PAHs: 0.3 mg kg <sup>-1</sup><br>5 ring PAHs: 0.6 mg kg <sup>-1</sup>   |       |
|                  |               | 600 °C for 3 h       | 2 ring PAHs: 1.3 mg kg <sup>-1</sup><br>3 ring PAHs: 2.4 mg kg <sup>-1</sup><br>4 ring PAHs: 2.4 mg kg <sup>-1</sup>   |       |
|                  |               | 700 °C for 3 h       | 2 ring PAHs: 1.0 mg kg <sup>-1</sup><br>3 ring PAHs: 0.5 mg kg <sup>-1</sup><br>4 ring PAHs: 0.4 mg kg <sup>-1</sup>   |       |
|                  | Corn stover   | 350 °C               | Total PAHs: 1609 µg kg <sup>-1</sup>   | [160] |
|                  |               | 450 °C               | Total PAHs: 1959 µg kg <sup>-1</sup>   |       |
|                  |               | 550 °C               | Total PAHs: 1770 µg kg <sup>-1</sup>   |       |
|                  | Wood pellets  | 500 °C for 30 min    | Total PAHs: 33,700 µg kg <sup>-1</sup>   | [173] |
|                  |               | 250 °C for 3 h       | Total PCDD/Fs: 2.7 × 10 <sup>2</sup> pg g <sup>-1</sup>  | [161] |
|                  |               | 300 °C for 3 h       | Total PCDD/Fs: 6.1 × 10 <sup>2</sup> pg g <sup>-1</sup>  |       |
| PCDD/Fs          | Sawdust       | 400 °C for 3 h       | Total PCDD/Fs: 3.6 × 10 <sup>2</sup> pg g <sup>-1</sup>  |       |
|                  |               | 500 °C for 3 h       | Total PCDD/Fs: 67 pg g <sup>-1</sup>   |       |
|                  |               | 700 °C for 3 h       | Total PCDD/Fs: 50 pg g <sup>-1</sup>   |       |

Table 2. Cont.

| Pollutants Types | Biochar Types         | Pyrolysis Conditions                                 | Concentration   | Ref.  |
|------------------|-----------------------|--|---|-------|
|                  | Food waste            | 300 °C   | Total 2,3,7,8-substitutes dioxin concentration: 13.3 pg g <sup>-1</sup> | [160] |
|                  |                       | 400 °C   | Toxic dioxin concentration: 1.20 pg g <sup>-1</sup>                     |       |
|                  |                       | 500 °C   | Total 2,3,7,8-substitutes dioxin concentration: 12.2 pg g <sup>-1</sup> |       |
|                  |                       | 600 °C   | Toxic dioxin concentration: 0.15 pg g <sup>-1</sup>                     |       |
|                  | Digested dairy manure | 600 °C   | Total 2,3,7,8-substitutes dioxin concentration: 0.39 pg g <sup>-1</sup> |       |
|                  |                       |  | Toxic dioxin concentration: 0.008 pg g <sup>-1</sup>                    |       |
|                  | Pine wood             | 900 °C   | Total 2,3,7,8-substitutes dioxin concentration: 7.5 pg g <sup>-1</sup>  |       |
|                  |                       |  | Toxic dioxin concentration: 0.16 pg g <sup>-1</sup>                     |       |
|                  | Lodgepole pine        | -  | Total 2,3,7,8-substitutes dioxin concentration: 8.0 pg g <sup>-1</sup>  |       |
|                  |                       |  | Toxic dioxin concentration: 0.13 pg g <sup>-1</sup>                     |       |
|                  | Laurel oak            | 650 °C   | Total 2,3,7,8-substitutes dioxin concentration: 10.7 pg g <sup>-1</sup> |       |
|                  |                       |  | Toxic dioxin concentration: 0.15 pg g <sup>-1</sup>                     |       |
|                  | Eastern gamma grass   | 650 °C   | Total 2,3,7,8-substitutes dioxin concentration: 10.5 pg g <sup>-1</sup> |       |
|                  |                       |  | Toxic dioxin concentration: 0.18 pg g <sup>-1</sup>                     |       |
|                  | Pine wood             | 800 °C   | Total 2,3,7,8-substitutes dioxin concentration: 1.5 pg g <sup>-1</sup>  | [162] |
|                  |                       |  | Toxic dioxin concentration: 0.02 pg g <sup>-1</sup>                     |       |
|                  | Switch grass          | 800 °C   | Total 2,3,7,8-substitutes dioxin concentration: 2.4 pg g <sup>-1</sup>  |       |
|                  |                       |  | Toxic dioxin concentration: 0.02 pg g <sup>-1</sup>                     |       |
|                  | Switch grass          | 900 °C   | Total 2,3,7,8-substitutes dioxin concentration: 0.5 pg g <sup>-1</sup>  |       |
|                  |                       |  | Toxic dioxin concentration: 0.005 pg g <sup>-1</sup>                    |       |
|                  | Paper mill waste      | 600 °C   | Total 2,3,7,8-substitutes dioxin concentration: 0.8 pg g <sup>-1</sup>  |       |
|                  |                       |  | Toxic dioxin concentration: 0.008 pg g <sup>-1</sup>                    |       |
|                  |                       |  | Total 2,3,7,8-substitutes dioxin concentration: 2.2 pg g <sup>-1</sup>  |       |
|                  |                       |  | Toxic dioxin concentration: 0.22 pg g <sup>-1</sup>                     |       |
|                  |                       |  | Total 2,3,7,8-substitutes dioxin concentration: 0.6 pg g <sup>-1</sup>  |       |
|                  |                       |  | Toxic dioxin concentration: 0.006 pg g <sup>-1</sup>                    |       |
|                  |                       |  | Phenol: 110 µg g <sup>-1</sup>  |       |
|                  |                       |  | 3-methyl-1,2-cyclopentadione: 91 µg g <sup>-1</sup>                     |       |
|                  |                       |  | 2-methylphenol: 130 µg g <sup>-1</sup>                                  |       |
|                  |                       |  | 3/4-methylphenol: 200 µg g <sup>-1</sup>                                |       |
|                  |                       |  | 3,4-dimethylphenol: 240 µg g <sup>-1</sup>                              |       |
|                  |                       |  | 4-ethylphenol: 110 µg g <sup>-1</sup>                                   |       |
|                  |                       |  | 3-ethyl-5-methylphenol: 64 µg g <sup>-1</sup>                           |       |
|                  |                       |  | 4-ethyl-3-methylphenol: 110 µg g <sup>-1</sup>                          |       |
|                  |                       |  | 1,2-benzenediol: 66 µg g <sup>-1</sup>                                  |       |
|                  |                       |  | 4-methyl-1,2-benzenediol: 45 µg g <sup>-1</sup>                         |       |
|                  |                       |  | Phenol: 49 µg g <sup>-1</sup>   |       |
|                  |                       |  | 4-methyl-1,2-cyclopentadione: 60 µg g <sup>-1</sup>                     |       |
|                  |                       |  | 2-methylphenol: 60 µg g <sup>-1</sup>                                   |       |
|                  |                       |  | 3,4-methylphenol: 92 µg g <sup>-1</sup>                                 |       |
|                  |                       |  | 3,4-dimethylphenol: 120 µg g <sup>-1</sup>                              |       |
|                  |                       |  | 2-methoxy-5-methylphenol: 23 µg g <sup>-1</sup>                         |       |
|                  |                       |  | 4-ethylphenol: 61 µg g <sup>-1</sup>                                    |       |
|                  |                       |  | 3-ethyl-5-methylphenol: 20 µg g <sup>-1</sup>                           |       |
|                  |                       |  | 4-ethyl-3-methylphenol: 59 µg g <sup>-1</sup>                           |       |
|                  |                       |  | 1,2-benzenediol: 49 µg g <sup>-1</sup>                                  |       |
|                  |                       |  | 4-methyl-1,2-benzenediol: 31 µg g <sup>-1</sup>                         |       |
| VOCs             | Softwood pellets      | At 500 for 20 min<br>(a liquid contaminated biochar) |   |       |
|                  |                       | At 500 for 20 min<br>(a gas contaminated biochar)    |   |       |

Table 2. Cont.

| Pollutants Types | Biochar Types                                    | Pyrolysis Conditions                | Concentration                             | Ref.  |
|------------------|--|-------------------------------------|---|-------|
| MCN              | Food waste                                       | 800 °C for 1 h                      | 40,286 mg kg <sup>-1</sup>                | [163] |
|                  | Soybean residue                                  | 800 °C for 1 h                      | 17.4 mg kg <sup>-1</sup>                  |       |
|                  | Rapeseed residue                                 | 800 °C for 1 h                      | 9.6 mg kg <sup>-1</sup>                   |       |
|                  | Phycocyanin                                      | 800 °C for 1 h                      | 85,870 mg kg <sup>-1</sup>                |       |
|                  | Algae protein                                    | 800 °C for 1 h                      | 10.3 mg kg <sup>-1</sup>                  |       |
|                  | Vinasse  | 800 °C for 1 h                      | 6.9 mg kg <sup>-1</sup>                   |       |
|                  | Corn protein                                     | 800 °C for 1 h                      | 9.3 mg kg <sup>-1</sup>                   |       |
|                  | Wheat straw                                      | 800 °C for 1 h                      | 1.0 mg kg <sup>-1</sup>                   |       |
|                  | Corn straw                                       | 800 °C for 1 h                      | 105.4 mg kg <sup>-1</sup>                 |       |
|                  | Cow dung   | 800 °C for 1 h                      | 5.9 mg kg <sup>-1</sup>                   |       |
|                  | Kitchen waste                                    | 800 °C for 1 h                      | 15.9 mg kg <sup>-1</sup>                  |       |
|                  | Fungi residue                                    | 800 °C for 1 h                      | 251.1 mg kg <sup>-1</sup>                 |       |
|                  | Biogas residue                                   | 800 °C for 1 h                      | 50.9 mg kg <sup>-1</sup>                  |       |
|                  | Corn protein with K <sub>2</sub> CO <sub>3</sub> | 800 °C for 1 h                      | 23,251 mg kg <sup>-1</sup>                |       |
| Heavy metals     | Sewage sludge                                    | 300 °C                              | Zn: 10,400.17 ± 97.21 mg kg <sup>-1</sup> | [164] |
|                  |  |                                     | Cu: 316.55 ± 20.08 mg kg <sup>-1</sup>    |       |
|                  |  |                                     | Cr: 297.37 ± 9.88 mg kg <sup>-1</sup>     |       |
|                  |  |                                     | Ni: 217.32 ± 6.27 mg kg <sup>-1</sup>     |       |
|                  |  |                                     | Cd: 0.793 ± 0.103 mg kg <sup>-1</sup>     |       |
|                  |  |                                     | Mn: 1859.43 ± 20.75 mg kg <sup>-1</sup>   |       |
|                  |  | 400 °C                              | Zn: 11,134.92 ± 69.83 mg kg <sup>-1</sup> |       |
|                  |  |                                     | Cu: 347.53 ± 18.39 mg kg <sup>-1</sup>    |       |
|                  |  |                                     | Cr: 314.35 ± 11.37 mg kg <sup>-1</sup>    |       |
|                  |  |                                     | Ni: 238.57 ± 8.21 mg kg <sup>-1</sup>     |       |
|                  |  |                                     | Cd: 0.852 ± 0.091 mg kg <sup>-1</sup>     |       |
|                  |  |                                     | Mn: 2082.52 ± 33.62 mg kg <sup>-1</sup>   |       |
| 500 °C           | Zn: 12,550.41 ± 93.04 mg kg <sup>-1</sup>        |                                     |   |       |
|                  | Cu: 374.05 ± 23.01 mg kg <sup>-1</sup>           |                                     |   |       |
|                  | Cr: 360.75 ± 8.78 mg kg <sup>-1</sup>            |                                     |   |       |
|                  | Ni: 260.14 ± 5.08 mg kg <sup>-1</sup>            |                                     |   |       |
|                  | Cd: 0.928 ± 0.055 mg kg <sup>-1</sup>            |                                     |   |       |
|                  | Mn: 2256.54 ± 52.01 mg kg <sup>-1</sup>          |                                     |   |       |
| 600 °C           | Zn: 13,080.32 ± 70.55 mg kg <sup>-1</sup>        |                                     |   |       |
|                  | Cu: 392.15 ± 10.55 mg kg <sup>-1</sup>           |                                     |   |       |
|                  | Cr: 376.82 ± 7.99 mg kg <sup>-1</sup>            |                                     |   |       |
|                  | Ni: 272.39 ± 2.09 mg kg <sup>-1</sup>            |                                     |   |       |
|                  | Cd: 0.866 ± 0.042 mg kg <sup>-1</sup>            |                                     |   |       |
|                  | Mn: 2319.54 ± 41.27 mg kg <sup>-1</sup>          |                                     |   |       |
| 700 °C           | Zn: 14,109.92 ± 91.39 mg kg <sup>-1</sup>        |                                     |   |       |
|                  | Cu: 426.92 ± 20.02 mg kg <sup>-1</sup>           |                                     |   |       |
|                  | Cr: 411.96 ± 10.11 mg kg <sup>-1</sup>           |                                     |   |       |
|                  | Ni: 299.49 ± 7.44 mg kg <sup>-1</sup>            |                                     |   |       |
|                  | Cd: 0.139 ± 0.027 mg kg <sup>-1</sup>            |                                     |   |       |
|                  | Mn: 2525.01 ± 72.13 mg kg <sup>-1</sup>          |                                     |   |       |
| 400 °C for 2 h   | Water-soluble Cu: 1.21 mg kg <sup>-1</sup>       |                                     |   |       |
|                  | Water-soluble Zn: 0.17 mg kg <sup>-1</sup>       |                                     |   |       |
|                  | DTPA-Cu: 23.44 mg kg <sup>-1</sup>               |                                     |   |       |
|                  | DTPA-Zn: 122.89 mg kg <sup>-1</sup>              |                                     |   |       |
|                  | Water-soluble Cu: 2.38 mg kg <sup>-1</sup>       |                                     |   |       |
|                  | Water-soluble Zn: 0.81 mg kg <sup>-1</sup>       |                                     |   |       |
| Pig manure       | 700 °C for 2 h                                   | DTPA-Cu: 31.05 mg kg <sup>-1</sup>  |   |       |
|                  |  | DTPA-Zn: 129.24 mg kg <sup>-1</sup> |   |       |

Table 2. Cont.

| Pollutants Types | Biochar Types | Pyrolysis Conditions | Concentration   | Ref.  |
|------------------|---------------|----------------------|---|-------|
|                  | Pig manure    | 300 °C               | Cr: 513.40 ± 3.50 mg kg <sup>-1</sup><br>Mn: 1390.6 ± 5.30 mg kg <sup>-1</sup><br>Cu: 673.40 ± 3.80 mg kg <sup>-1</sup><br>Zn: 4310.30 ± 16.00 mg kg <sup>-1</sup>    | [165] |
|                  |               | 350 °C               | Cr: 518.10 ± 7.70 mg kg <sup>-1</sup><br>Mn: 1430.60 ± 6.40 mg kg <sup>-1</sup><br>Cu: 780.90 ± 6.20 mg kg <sup>-1</sup><br>Zn: 4670.90 ± 29.10 mg kg <sup>-1</sup>   |       |
|                  |               | 400 °C               | Cr: 521.70 ± 4.90 mg kg <sup>-1</sup><br>Mn: 1510.30 ± 1.30 mg kg <sup>-1</sup><br>Cu: 824.60 ± 7.50 mg kg <sup>-1</sup><br>Zn: 4950.80 ± 26.30 mg kg <sup>-1</sup>   |       |
|                  |               | 450 °C               | Cr: 553.50 ± 10.30 mg kg <sup>-1</sup><br>Mn: 1580.00 ± 8.50 mg kg <sup>-1</sup><br>Cu: 838.70 ± 7.30 mg kg <sup>-1</sup><br>Zn: 5040.70 ± 33.40 mg kg <sup>-1</sup>  |       |
|                  |               | 500 °C               | Cr: 666.20 ± 9.40 mg kg <sup>-1</sup><br>Mn: 1660.40 ± 6.70 mg kg <sup>-1</sup><br>Cu: 950.70 ± 5.30 mg kg <sup>-1</sup><br>Zn: 5630.00 ± 28.30 mg kg <sup>-1</sup>   |       |
|                  |               | 550 °C               | Cr: 559.50 ± 5.20 mg kg <sup>-1</sup><br>Mn: 1520.30 ± 4.30 mg kg <sup>-1</sup><br>Cu: 810.20 ± 1.90 mg kg <sup>-1</sup><br>Zn: 4900.80 ± 37.20 mg kg <sup>-1</sup>   |       |
|                  |               | 600 °C               | Cr: 476.90 ± 2.50 mg kg <sup>-1</sup><br>Mn: 1550.20 ± 8.50 mg kg <sup>-1</sup><br>Cu: 901.50 ± 6.60 mg kg <sup>-1</sup><br>Zn: 5160.80 ± 51.50 mg kg <sup>-1</sup>   |       |
|                  |               | 650 °C               | Cr: 569.70 ± 11.30 mg kg <sup>-1</sup><br>Mn: 1860.80 ± 9.10 mg kg <sup>-1</sup><br>Cu: 981.80 ± 16.10 mg kg <sup>-1</sup><br>Zn: 6010.80 ± 40.10 mg kg <sup>-1</sup> |       |
|                  |               | 700 °C               | Cr: 819.90 ± 10.30 mg kg <sup>-1</sup><br>Mn: 1920.60 ± 2.30 mg kg <sup>-1</sup><br>Cu: 1080.70 ± 9.60 mg kg <sup>-1</sup><br>Zn: 7720.30 ± 46.70 mg kg <sup>-1</sup> |       |

FLO-fluorene. PHE-phenantrene. ANT-anthracene. FLA-fluoranthene. PYR-pyrene. BaA-benzo(a)anthracene. CHR-chrysene. BbF-benzo(b)fluoranthene. BkF-benzo(k)fluoranthene. BaP-benzo(a)pyrene. DahA-dibenzo(ah)anthracene. BghiP-benzo(ghi)perylene. IcdP-indeno(cd)pyrene.

Once these pollutants are introduced to soil, potential risks to humans and ecology (e.g., phytotoxicity, cytotoxicity, ecotoxicity, etc.) will occur. In addition, the negative effect of biochar on microbiology and plants has received more attention in recent years

### 5.2. Negative Effects of Biochar on Microbiology

As an essential member of the soil environment, the structure and number of microbial communities are also important indicators of soil quality and crop production. Although many studies have reported that biochar can promote microbial diversity and increase the number of microbial communities after soil amendment [175,176], the toxic effect of biochar on microorganisms is still a problem that cannot be ignored. As shown in Table 3, biochar's adverse effects on microbiology were summarized.

**Table 3.** The negative effect of biochar on soil organisms.

| Negative Impacted Groups | Biochar Feedstock                                       | Pyrolysis Conditions   | Soil Type                             | Addition Rate                                       | Incubation Time     | Negative Effects   | Ref.  |
|--------------------------|---|--|---------------------------------------|---|---------------------|--|-------|
| Microbiology             | Maize corn cob  | 450–500 °C   | Sandy loam                            | 5 t·ha <sup>-1</sup>                                | 2, 14 and 24 months | The application of biochar significantly reduced soil microbial biomass (phospholipid fatty acid, PLFA).   | [177] |
|                          | Rice straw  | At 500 °C for 3 h.   | Hydromorphic paddy soil               | 10, 15 and 20% (w/w)                                | 3–4 days            | The biochar significantly reduced fungi in soil by 22.2–30.2% compared with control.   | [178] |
|                          | Corn stover, ponderosa pine wood chips, switchgrass     | The reactor temperature ramps from 150 °C to 850 °C with residence time of 4 h and 4 min | Sandy, mixed, frigid entic hapludolls | 10 g kg <sup>-1</sup> , and 50 g kg <sup>-1</sup> . | 120 days            | The short-term incubation study showed that biochar had negative effects on microbial activity (FDA and DHA) and some enzymes including β-glucosidase and protease.  | [66]  |
|                          | Rice straw  | At 500 °C for 2 h  | Clay loam texture                     | 22.5 t ha <sup>-1</sup>                             | 48 h                | The addition of biochar limited the growth of methanotrophs and nitrifiers.  | [179] |
|                          | Sewage sludge   | At 500 °C, 600 °C, and 700 °C for 5 h  | Loamy sand                            | 1% (w/w)  | 6 months            | Biochar derived at 500 °C has a higher toxic effect on <i>Aliivibrio fischeri</i> than that at 600 °C and 700 °C.  | [169] |
|                          | Switchgrass, mixed hardwood, and mixed softwood pellets | 500 °C, 700 °C, 800 °C   | -                                     | 10% (w/w)   | 6 weeks             | Mycorrhizal fungi were inhibited by biochar addition.  | [180] |
|                          | Solid residue from biogas production                    | 400, 600 and 800 °C  | Artificial soil                       | 0.5–5% (w/w)  | -                   | Depending on the temperature at which it was produced, biochar caused mortality of <i>F. candida</i> at a level from 20 to 30% (0.5% dose) and from 30 to 50% (5.0% dose), and reproduction inhibition occurred from 70 to 100% (0.5% dose) and 100% (5.0% dose) for all temperatures. | [181] |
|                          | Rice husk   | >480 °C  | Pristine agricultural soil            | 0.5–50% (w/w)                                       | 90 days             | Biochar amendment reduced fungal population with shift in community structure and abundance, over time.  | [182] |
| Invertebrates            | Walnut shells and corn cobs                             | At 250 °C, 400 °C, and 600 °C for 4 h  | -                                     | 2% (w/w)  | 75 days             | Application of biochars to the soil decreases Proteobacteria richness (23–29%).  | [183] |
|                          | Rice husk   | >480 °C  | -                                     | 0.5–50% (w/w)                                       | 90 days             | The growth of the exposed earthworms was strongly reduced by biochar, especially for 50% biochar addition.   | [182] |
|                          | Sewage sludge   | At 500 °C, 600 °C, and 700 °C for 5 h  | Loamy sand                            | 1% (w/w)  | 6 months            | Biochar exhibited toxic activity towards <i>Folsomia candida</i> after six months incubation, and biochar produced at higher temperatures exhibited lower toxicity than that prepared at lower temperature.  | [169] |

Table 3. Cont.

| Negative Impacted Groups   | Biochar Feedstock                                       | Pyrolysis Conditions                  | Soil Type           | Addition Rate                  | Incubation Time   | Negative Effects  | Ref.  |
|----------------------------|---|---------------------------------------|---------------------|--------------------------------|---|---|-------|
| Plants                     | Wheat straws  | At 500 °C for 4 h                     | Artificial soil     | 10% (w/w)                      | 28 days   | About 10% of biochar applications induced DNA damage to earthworms.   | [184] |
|                            | Wood  | 700 °C                                | Sandy loam cambisol | 10% (w/w)                      | -   | Reproduction rates of earthworms reduced by 38% in comparison to unamended soil.  | [185] |
|                            | Rice husk   | ~600 °C                               | Sandy loam cambisol | 10% (w/w)                      | -   | Reproduction rates of earthworms reduced by 27% compared to unamended soil.   |       |
|                            | Walnut shells and corn cobs                             | 250 °C, 400 °C, and 600 °C for 4 h    | -                   | 2% (w/w)                       | 75 days   | Most of six biochars significantly increased the concentrations of $\Sigma$ 16PAHs in Chinese cabbage by 30.10–74.22%.  | [183] |
|                            | Beech, hazel, oak, birch                                | 500 °C                                | -                   | 100 and 120 t ha <sup>-1</sup> | -   | A general reduction of wheat biomass was observed.  | [186] |
|                            | Rice husk   | >480 °C                               | -                   | 0.5–50% (w/w)                  | 90 days   | Biochar led to the direct toxic influence on the roots of <i>Oryza sativa</i> and <i>Solanum lycopersicum</i>   | [182] |
|                            | Sewage sludge   | At 500 °C, 600 °C, and 700 °C for 5 h | Loamy sand          | 1% (w/w)                       | 6 months  | The biochar exhibited toxic activity towards <i>Lepidium sativum</i> after six months incubation, and biochar produced at higher temperatures exhibited lower toxicity than that prepared at lower temperature. | [169] |
|                            | Switchgrass, mixed hardwood, and mixed softwood pellets | 500 °C, 700 °C, 800 °C                | -                   | 10% (w/w)                      | 6 weeks   | Biochar amendment tended to reduce the aboveground biomass of <i>Allium porrum</i> ‘Musselburgh’.   | [180] |
|                            | Corn stover   | At 600 °C for 20 min                  | -                   | 2, and 5% (w/w)                | 28 days   | The addition of biochar contributed to weight loss in <i>Aporrectodea caliginosa</i> .  | [187] |
|                            | Mixed wood sievings                                     | At 500 °C for 20 min                  | Haplic Cambisols    | 8% (w/w)                       | 1 month   | The biochar led to a decline of <i>Lactuca sativa</i> biomass.  |       |
| Paper sludge + wheat husks | At 500 °C for 20 min                                    | Haplic Cambisols                      | 8% (w/w)            | 1 month                        | About 33% lower stem length of <i>Lactuca Sativa</i> was found after biochar amendment. | [188]   |       |
| Sewage sludge              | At 500 °C for 20 min                                    | Haplic Cambisols                      | 8% (w/w)            | 1 month                        | The biochar reduced 15–38% of the stem length and root (dry weight).                    |   |       |

Andrés et al. [177] applied biochar from maize corn cob at 450–500 °C to amend sandy loam soil. The biochar significantly reduced soil microbial biomass with an additional 5 t ha<sup>-1</sup>. Similar results were also obtained by Li et al. [178] and Nan et al. [179]. The biochar led to an adverse impact on microbial and enzymatic activity. In addition, biochar prepared at low temperatures is more toxic to microorganisms than derived at high temperatures. Tomczyk et al. [169] reported that biochar derived from sewage sludge at 500 °C contributed to a higher toxic effect on *Aliivibrio fischeri* than that at 600 °C and 700 °C. In addition, Palansooriya et al. [189] reported that possible adverse effects of biochar application on the soil microbial community might depend on the feedstock type, distinct types of charred material, soil types, and dosage. According to Godlewska et al. [167], the toxic effect of biochar on microbiology mainly occurred through the changes in soil properties and releasing heavy metals or organic chemicals in biochar. Biochar amendment led to the increase of soil pH, which broke the balance between fungi and bacteria due to the insensitivity of fungi to the pH [190]. Du et al. [191] investigated the toxic effect of DOMs in biochar prepared from sewage sludge at different temperatures and revealed that DOMs solutions of sludge biochar prepared at 300 °C (SSB<sub>300</sub>) and 400 °C (SSB<sub>400</sub>) contained more toxic pollutants due to a significant luminescence inhibitory on *Vibrio qinghaiensis* Q67. Further positive control experiments showed that the toxicity of DOM solution of SSB<sub>300/400</sub> to *Vibrio qinghaiensis* Q67 was equivalent to 7.92 mg L<sup>-1</sup> and 6.18 mg L<sup>-1</sup> of 3–5 dichlorophenol. DOMs solutions of biochar prepared at 500–800 °C showed the nearly same degree of luminescence quenching effect, suggesting that the DOMs from sludge biochar obtained at the pyrolysis temperature over 500 °C had no obvious potential risk on the *Vibrio qinghaiensis* Q67 [191].

### 5.3. Negative Effects of Biochar on Invertebrates

Earthworms are widely distributed on earth and are the most crucial member of belowground soil biomass, with approximately 60–90% [192]. Earthworms were reported to influence soil's physical, chemical, and biological properties and were reviewed by Xiao et al. [193], that took part in potential toxic elements (PTEs) biogeochemical cycling in soils. Earthworms are able to consume these contaminants by ingestion of soil particles and passive diffusion through the skin [184]. Several studies have proven that biochar's application led to a negative effect on earthworms. The adverse effects of biochar on invertebrates are summarized in Table 3. Anyanwu et al. [182] showed that biochar derived from rice husk significantly reduced the exposed earthworm growth after 90 days of incubation. Bielská et al. [185] also obtained similar results, wood biochar prepared at 700 °C and rice husk derived at ~600 °C decreased reproduction rates of earthworms by 38% and 27% after 30 days, respectively, in comparison to unamended soil. Godlewska et al. [167] reviewed that biochar negatively influence earthworms, mainly due to toxic substances present in biochar. In recent years, the toxicity of biochar to earthworm mainly includes epidermal damage, oxidative stress, and DNA damage, and intestinal injury. Han et al. [194] reported that 5% rice straw-derived biochar negatively affected earthworm skin, not only involving fracture irregular arrangement in microvilli and thickening of upper stratum corneum, but also a fault zone between stratum corneum and epidermis occurred. Environmental persistent free radicals in biochar may pose a potential environmental risk because they can induce the formation of reactive oxygen species (ROS) with high phytotoxicity and cytotoxicity within environmental media [167]. Biochar addition disturbed antioxidant enzyme activities and increased malondialdehyde content, which revealed that earthworm suffer oxidative stress, also showing a potential vermitoxicity of biochar on earthworms. A 5% application not only led to decrease in activities of digestion-related enzymes including Na<sup>+</sup>-K<sup>+</sup>-ATPase and cellulose, but also facilitated some abnormalities of intestinal epithelial tissue [195].

In addition, in recent years, *Folsomia candida* was treated as a model organism to investigate the toxic effect of biochar on the soil system. Tomczyk et al. [169] exhibited that sewage sludge biochar prepared at 500 °C, 600 °C, and 700 °C led to toxic activity towards

*Folsomia candida* with an additional rate of 1% in loamy sand soil after six months. Thus, it can be seen that biochar has strong biotoxicity to invertebrates in the soil.

#### 5.4. Negative Effects of Biochar on Plants

The application of biochar on soil is mainly due to its usefulness in agriculture. The toxic effect of biochar on plants was regarded as an essential indicator to measure biochar's impact on a particular soil's toxicity. Although many kinds of literature have reported the positive effects of biochar on plants, such as improving plant growth and reducing the accumulation of harmful substances in plants [183,190], the toxic effects of biochar on plants still cannot be ignored. The adverse effects of biochar on plants in amend-soil are summarized in Table 3.

As is known that germination, root and shoot length, and produced plant biomass are the most frequently evaluated eco-toxicological parameters for plants. Du et al. [191] investigated the toxicity of DOMs in biochar toward pak choi seed by the germination test. They found that DOMs derived from low temperatures led to higher inhibition of germination. The seed germination index (SGI) significantly increased with pyrolysis temperature. DOMs solutions of sludge biochar derived at 800 °C (SSB<sub>800</sub>) had a maximum SGI of 85.8%. Anyanwu et al. [182] showed that rice husk biochar led to a direct toxic impact on the roots of *Oryza sativa* and *Solanum lycopersicum* after 30, 60, and 90 d. With the increase in pyrolysis temperature, the inhibitory effect on root growth gradually weakened, and DOMs solutions of SSB<sub>800</sub> showed a slight inhibition effect at approximately 14.2% [191]. The inhibition of mycorrhizal fungus that occurred by biochar might be why biochar amendment reduced root growth [180]. In addition, there is evidence that biochar exhibited toxic activity toward plants. Tomczyk et al. [169] exhibited that sewage sludge biochar led to harmful activity to *Lepidium sativum*. Zhang et al. [183] also found that biochar prepared from walnut shells and corn cobs increased the concentrations of  $\Sigma$ 16PAHs in Chinese cabbage by 30.10–74.22%, with 2% biochar addition after 75 days of incubation. Interestingly, the significant reduction of Proteobacteria after biochar amendment most likely resulted in the decrease in dissipation of PAHs. Some evidence has shown that Proteobacteria could be associated with the biodegradation of low solubility and bioavailable hydrocarbons, particularly PAHs. In addition, the richness of Bacteroidetes which were also related to the biodegradation of PAHs decreased [183].

In addition, the toxic effects of biochar on plants can be associated with the addition rates of biochar. Méndez et al. [196] reported that higher addition rates of sewage sludge biochar led to the higher bioavailable fraction content of HMs in biochar-amended soils. With 4% and 8% addition rates, the bioavailable fraction content of Cu, Ni, Pb, and Zn was from 1.5 to 1.6, 3.0 to 3.5, 1.6 to 1.8, and 1.2 to 1.5-times higher, respectively, compared to soil without biochar addition. Visioli et al. [197] investigated the effects of different addition rates (0.5, 1, 2, 5, 10, 20, 50%) of biochar on the plant growth and revealed that EC and Cu negatively affected both germination and root elongation at a biochar application rate of  $\geq 5\%$  (w/w), EC and Cu altered both germination and root elongation at 5% addition rate, together with Zn at 10% and elevated pH at 20%. Moreover, high rates (20 and 50%) of biochar decreased the Germination.

At present, the toxic effects of biochar on the soil-plant system are also limited. The comprehensive mechanisms by which biochar negatively affects the environment at the microcellular and molecular levels should be further explored. In the future, we should focus on exploring the toxic effects of biochar at the cellular and molecular levels to reveal the underlying mechanisms at the molecular level. Much more effort should be made to comprehensively evaluate the potentially negative impacts during biochar amendment and develop high-efficiency strategies for mitigation of biochar contaminants release.

## 6. Conclusions

As an emerging soil amendment, biochar positively impacts soil's physical and chemical properties. It is crucial in improving acid soil, soil water holding capacity, CEC, and

enzyme activity. More importantly, biochar is involved in soil nutrient transportation and improvement. Biochar could significantly increase soil C content, including TC, OC, MBC, and DOC. Biochar also releases N, P, and K elements directly to the soil. Moreover, biochar promotes the mineralization of N, P, and K and increases the abundance of responsive metabolic bacteria to achieve nutrient supplementation. In addition, the adsorption of N, P, and K in soil by biochar further enhanced the retention of these elements in the soil. In order to effectively use biochar as a substitute for chemical fertilizers, it is necessary to understand the composition and morphology of the elements in biochar and the properties of the modified soil. The physicochemical properties of biochar are primarily affected by raw materials, pyrolysis temperature, pyrolysis time, and other factors. The application of biochar in soil involves a slow degradation process. Its physical and chemical properties and eco-environmental benefits have different effects with time, and its impact on the eco-environment needs a long-term and large-scale study. In addition, biochar contains many pollutants, such as PAHs, PCDD/Fs, VOCs, MCN, and HMs, which have toxic effects on organisms after being applied to the soil. Thus, much more effort should be made to comprehensively evaluate the potential negative impacts at the microcellular and molecular levels during biochar amendment and develop high-efficiency strategies for the mitigation of biochar contaminants release.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en16010410/s1>, Table S1: Differences in physical and chemical properties of different types of biochar. References [198–212] are cited in the Supplementary Materials.

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