

RESEARCH REVIEW

How biochar works, and when it doesn't: A review of mechanisms controlling soil and plant responses to biochar

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Abstract

We synthesized 20 years of research to explain the interrelated processes that determine soil and plant responses to biochar. The properties of biochar and its effects within agricultural ecosystems largely depend on feedstock and pyrolysis conditions. We describe three stages of reactions of biochar in soil: dissolution (1–3 weeks); reactive surface development (1–6 months); and aging (beyond 6 months). As biochar ages, it is incorporated into soil aggregates, protecting the biochar carbon and promoting the stabilization of rhizodeposits and microbial products. Biochar carbon persists in soil for hundreds to thousands of years. By increasing pH, porosity, and water availability, biochars can create favorable conditions for root development and microbial functions. Biochars can catalyze biotic and abiotic reactions, particularly in the rhizosphere, that increase nutrient supply and uptake by plants, reduce phytotoxins, stimulate plant development, and increase resilience to disease and environmental stressors. Meta-analyses found that, on average, biochars increase P availability by a factor of 4.6; decrease plant tissue concentration of heavy metals by 17%–39%; build soil organic carbon through negative priming by 3.8% (range –21% to +20%); and reduce non-CO₂ greenhouse gas emissions from soil by 12%–50%. Meta-analyses show average crop yield increases of 10%–42% with biochar addition, with greatest increases in low-nutrient P-sorbing acidic soils (common in the tropics), and in sandy soils in drylands due to increase in nutrient retention and water holding capacity. Studies report a wide range of plant responses to biochars due to the diversity of biochars and contexts in which biochars have been applied. Crop yields increase strongly if site-specific soil constraints and nutrient and water limitations are mitigated by appropriate biochar formulations. Biochars can be tailored to address site constraints through feedstock selection, by modifying pyrolysis conditions, through pre- or post-production treatments, or co-application with organic or mineral fertilizers. We demonstrate how, when used wisely, biochar mitigates climate change and supports food security and the circular economy.

KEYWORDS

carbon sequestration, GHG mitigation, heavy metals, priming effect, resilience, rhizosphere processes, soil carbon

1 | INTRODUCTION

Biochar is produced by thermal transformation of organic matter in an oxygen-limited environment. Research interest in biochar has grown markedly since 2000 (Figure S1), stimulated by early studies of Terra Preta soils in the Amazon that indicated potential for biochar amendment to simultaneously improve a broad range of soil properties and thus increase agricultural yields, while also contributing to climate change mitigation (Glaser et al., 2002; Lehmann et al., 2006).

A wide range of biochar types produced from feedstocks including woody residues, crop straw, animal manures, sewage sludge, and food wastes are pyrolyzed at temperatures (highest treatment temperature, HTT) ranging from around

350°C to over 750°C. Biochar properties vary widely, determined largely by feedstock, HTT, and residence time at HTT, as well as treatments applied before and after pyrolysis (Schimmelpennig & Glaser, 2012). A review of 5400 studies (Ippolito et al., 2020) found that wood-based feedstocks generally produced biochars with the highest surface area, straw-based feedstocks gave the highest cation exchange capacity (CEC), and manure feedstocks produced biochars with the highest N and P content. HTTs above 500°C produced biochars that were more persistent in soil, with higher ash contents and pHs.

Biochar trials have used a wide range of application rates and formulations (Text S1; Table S1; Figure S2; Figure S3). Higher rates (10–50 Mg ha⁻¹) have commonly been applied

where low-nutrient biochar is used as a soil conditioner to improve bulk soil chemical and physical properties, while lower rates ($<1 \text{ Mg ha}^{-1}$) have been used as a nutrient carrier to increase fertilizer use efficiency and decrease nutrient losses, and in mechanized planting (Table S1). Economic analyses suggest that formulations combining biochar with fertilizer (biochar compound fertilizer [BCF]), applied at low rates, are likely to be the most cost-effective approach for broadacre cropping in higher income countries (Robb et al., 2020).

Studies report a wide range of effects of biochars on physical, biological, and chemical soil properties and functions, and on plant growth. Reviews and meta-analyses show that biochar generally lowers soil acidity and increases buffering capacity; increases dissolved and total organic C, CEC, available nutrients, water retention, and aggregate stability; and reduces bulk density (El-Naggar et al., 2019; Lehmann & Joseph, 2015). Biochar can increase microbial activity, accelerate nutrient cycling, and reduce leaching and volatilization of nitrogen (Lehmann & Joseph, 2015).

In terms of plant performance, biochars can affect seed germination, plant growth, flowering, resistance to disease, and acclimation to abiotic stresses. Many studies report that biochar increases plant productivity, with an average yield increase of 10%–42% (Table 1), although negative effects have also been recorded (Jeffery et al., 2017; Macdonald et al., 2014; Ye et al., 2020). Studies reporting positive responses have commonly used biochar application rates of 5–20 Mg ha^{-1} (Table 1); however, applications of biochar–fertilizer mixes at low rates ($<1 \text{ Mg ha}^{-1}$ biochar) have also increased yields, particularly when applied as a band near the seed (Table S1). The effects of biochar on crop yields are discussed further in Section 4.

Besides agronomic benefits, biochar contributes to climate change mitigation: Biochar C persists in soil for one to two orders of magnitude longer than unpyrolyzed organic residues, providing long-term C sequestration when applied to soil. In addition, biochar can increase soil C levels by decreasing mineralization of existing soil organic matter (SOM; Wang et al., 2016) and newly added plant C (Weng et al., 2017). Furthermore, biochar can reduce emissions of the greenhouse gases (GHGs), nitrous oxide and methane (Van Zwieten, Kammann, et al., 2015).

The large body of literature that has accumulated over the last two decades has greatly increased our observational database of the effects biochar can have on soil properties and crop performance. In-depth mechanistic studies have brought focus to the importance of the rhizosphere in these effects. The objectives of this review are to synthesize the last 20 years of research on biochar to elucidate the underlying biochar–soil–plant processes, and mechanisms that lead to plant responses to biochar, and to provide recommendations for optimizing the use of biochar to increase plant yield, soil health, and climate change mitigation.

We first describe biochar–soil–plant interaction mechanisms, focusing on rhizosphere processes and implications for plant growth, concentrating on biochar applied to annual crops. Use of biochar in annual crops has been the most commonly studied application to date and is anticipated to be the most widespread future application of biochar. Subsequent sections review the implications of biochar for food security, climate change mitigation, and the role of biochar in the circular economy. We conclude with a summary of key processes, knowledge gaps, and recommendations for optimal biochar use.

2 | MECHANISMS OF BIOCHAR EFFECTS ON SOIL AND PLANTS

We consider the interactions between biochar, soil and plants in the context of the annual crop cycle:

- Stage 1: Short-term (1–3 weeks) reactions of biochar in soil, and effects on seed germination and seedlings
- Stage 2: Medium-term (1–6 months) creation of reactive surfaces on biochar, effects on plant growth and yield from seedling to harvest
- Stage 3: Long-term (>6 months) interactions as biochar “ages” in soil, and its effect on subsequent crop cycles.

Biochar is commonly applied at sowing or 1–3 weeks before sowing. Mechanisms involved when biochar is applied in conjunction with mineral and/or organic fertilizers, and as a BCF comprising biochar, fertilizer, minerals (e.g., gypsum, dolomite, diatomite, rock phosphate) and binder (e.g., clay, starch) are examined.

2.1 | Stage 1: Short-term reactions (1–3 weeks)

2.1.1 | Biochar reactions in soil

Chemical effects

The general properties of biochars are described in Text S2. After application to soil, water entering biochar pores dissolves soluble organic and mineral compounds on biochar outer and inner surfaces (Figure 1). These solutes increase dissolved organic carbon (DOC), cations, and anions in the soil solution (Silber et al., 2010), which increases the electrical conductivity and pH and reduces Eh (Joseph et al., 2015). The extent of changes in soil solution composition depends on the specific biochar and soil (Mukherjee & Zimmerman, 2013; Schreiter et al., 2020). Release of DOC and nutrient ions from biochar (Kim et al., 2013) is rapid over the first week and much slower over the following

TABLE 1 Summary of meta-analyses of yield response to biochar, and synthesis of findings

| Study | Number of studies included | Notes | Biochar dose giving optimal response (t/ha) | Crop factor reported | Grand mean change % | Synthesis of key findings |
|------------------------------|----------------------------|--|---|----------------------|---------------------|---|
| Jeffery et al. (2011) | 23 | First meta-analysis of biochar effects on yield, using pot and field studies. | 100 | Crop yield | 10 | <ul style="list-style-type: none"> • Greatest benefit in acidic and pH neutral soils suggesting liming effect as key driver • Greater effect in coarse-textured soils suggesting improved water and nutrient availability • Poultry litter feedstock showed the greatest positive benefit |
| Biederman and Harpole (2013) | 114 | Yield response presented for fertilized biochar treatment vs. fertilized control | ns | Crop yield | 42 | <ul style="list-style-type: none"> • Improved plant tissue P and K concentrations compared to fertilizer alone • Grass and manure feedstocks most effective especially at higher temperatures due to increased liming effect • Application rate was not a good predictor due to variable responses arising from different interactions |
| Crane-Droesch et al. (2013) | 84 | Predicted yield response based on the application of 3 Mg ha ⁻¹ biochar | 3 | Crop yield | 10 | <ul style="list-style-type: none"> • Soil CEC and SOC content are predictors of yield response • Greatest benefits in lowest-potential agricultural areas, which are predominantly found in the humid tropics • Benefits to yield increased yearly up until year 4 after application |
| Liu et al. (2013) | 103 | | <10–20 | Crop yield | 11 | <ul style="list-style-type: none"> • Greatest benefit in acidic soils (pH < 5) • Greatest benefit in sandy soils, followed by clay, then silt or loam-textured soils • Manure feedstock generally most effective, followed by wood, then crop residue |
| Thomas and Gale (2015) | 17 | Study focused on responses of trees | NA | Tree biomass | 41 | <ul style="list-style-type: none"> • Greater positive effect in tropical than in temperate systems, and in angiosperms than conifers • Limited number of studies exist but authors suggest significant opportunities during reforestation |
| Jeffery et al. (2017) | 111 | | NA | Crop yield | 13 | <ul style="list-style-type: none"> • An average 25% yield increase in the tropics with liming effect and fertilizer value as the key driver • Biochars containing higher nutrient contents had greater benefit to yield than lower nutrient biochars • The authors stressed the need to understand the constraint that is being addressed by biochar |

TABLE 1 (Continued)

| Study | Number of studies included | Notes | Biochar dose giving optimal response (t/ha) | Crop factor reported | Grand mean change % | Synthesis of key findings |
|---------------------|----------------------------|--|---|--------------------------|---------------------|---|
| Xiang et al. (2017) | 136 | Analysis focused on below ground effects | NA | Root biomass | 32 | <ul style="list-style-type: none"> No change in root N concentration but significantly increased root P concentration Benefits were greater for legumes and resulted in increased nodulation Higher temperature biochars had a greater effect and HTT was a more important indicator than feedstock type |
| Awad et al. (2018) | 50 | Study focuses on rice production | 1–10 | Crop yield | 16 | <ul style="list-style-type: none"> Greatest benefits observed in very acidic soil No significant differences in effects with biochar rate Soil texture did not have a major role in determining yield effect |
| Dai et al. (2020) | 153 | | NA | Crop yield | 16 | <ul style="list-style-type: none"> Liming, improved soil physical properties, and increased nutrient use efficiency were key mechanisms resulting in positive effects Interactions between soil properties and biochar properties were key to delivering positive effects Biochars with high ash content (e.g., higher nutrient content) applied into sandy and/or acidic soils likely to give greatest benefits. |
| Ye et al. (2020) | 56 | Comparison with unfertilized control Comparison with fertilized control | <5 5–10 | Crop yield Crop yield | 30 10 | <ul style="list-style-type: none"> The study separately assessed biochar response in comparison with fertilized and unfertilized controls, and showed that benefits to yield are additive to the fertilizer effect Soils with CEC < 100 mmol_c kg⁻¹ showed the greatest positive response Soils with SOC ≤ 20 g kg⁻¹ showed the greatest positive response Crops grown on soils with pH ≤ 6.5 always had a positive yield response to biochar addition |

Abbreviations: CEC, cation exchange capacity; NA, not applicable/ not investigated; ns, no response detected; SOC, soil organic carbon.

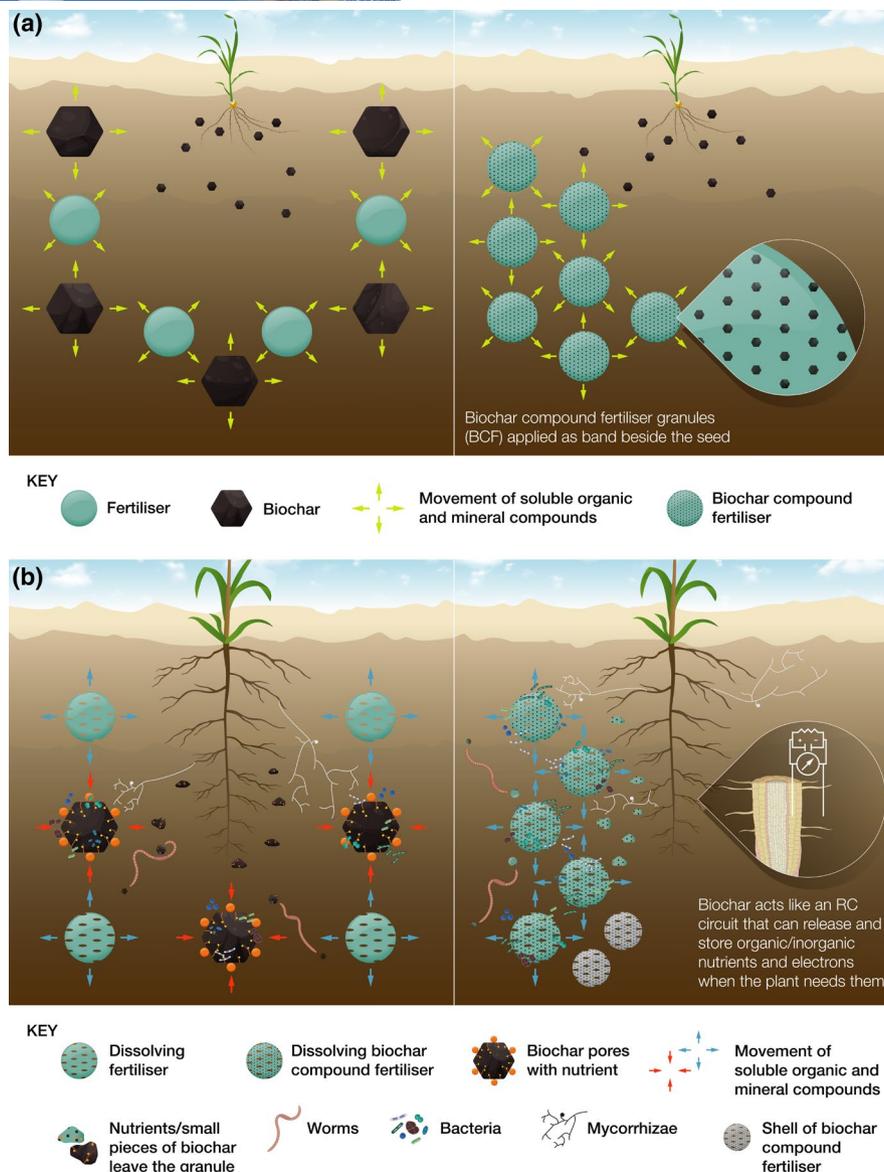


FIGURE 1 Summary of the processes that occur when biochar is applied to soil, based on two modes of application: (left) biochar and fertilizer applied together and incorporated through the soil prior to sowing, and (right) biochar compound fertilizer (BCF) comprising biochar mixed with fertilizer, minerals and a binder, granulated, applied to the soil as a band near the seed. (a) Stage 1: dissolution of biochar, interactions with seedlings; (b) Stage 2: reactive surface development on biochar, interactions with growing plants. RC, resistor and capacitor in parallel

weeks (Mukherjee & Zimmerman, 2013). Initial rapid dissolution can occur via dissolution of salts, ion exchange, submicrometer particle detachment, and preferential dissolution at crystal imperfections (Wang et al., 2020). After the initial rapid dissolution stage, continued dissolution is faster in acidic (Silber et al., 2010) and low-nutrient soils (Wang et al., 2020).

When biochar is applied in the form of BCF that combines biochar, minerals, and N and P compounds (e.g., urea, ammonium sulfate, diammonium phosphate), the physical and chemical reactions that occur during the production of the granules slow the rate and extent of dissolution of N compounds compared with dissolution of mineral fertilizers (Chen et al., 2017; Shi et al., 2020).

Fresh biochar typically has a low CEC, as the high temperatures during pyrolysis reduce the concentration of functional groups (e.g., $-\text{OH}$, $-\text{COOH}$, $-\text{CH}$, and $-\text{C}=\text{O}$). CEC of biochar is more difficult to measure than CEC of soils, due to its pH-dependent variable charge properties and the presence of soluble salts (Graber et al., 2017; Munera-Echeverri et al., 2018). Using methods considered suitable for biochar, CEC ranges from approximately 50 to 200 mmol kg^{-1} (Graber et al., 2017; Mitchell et al., 2013), and anion exchange capacity (AEC) is typically also less than 200 mmol kg^{-1} (Lawrinenko et al., 2017). As CEC of fresh biochar is relatively low compared with CEC of many soil components, applying biochar typically does not increase the soil CEC immediately (Kharel et al., 2019). However, the CEC and

AEC of biochar increase over time as additional functional groups form on biochar surfaces (see Section 2.3), increasing its ability to sorb and retain cations and anions (Hagemann, Joseph, et al., 2017; Hagemann et al., 2017; Rechberger et al., 2017; de la Rosa et al., 2018; Wang et al., 2019).

Low-temperature biochars (HTT < 450°C) and biochars produced in facilities with incomplete separation of pyrolysis vapors (Buss & Mašek, 2014; Buss et al., 2015) generally have higher contents of water-soluble organic compounds, particularly low molecular weight neutrals (alcohols, aldehydes, ketones, phenolics, karrikins), polyphenols/polyphenolic acids, and complex macromolecules, whereas high-temperature biochars (HTT > 450°C) have relatively lower levels of water-soluble compounds that are dominated by low-molecular weight acids and low-molecular weight neutrals (Graber et al., 2015; Reynolds et al., 2018; Taherymoosavi et al., 2018). Low-temperature biochars can be hydrophobic initially due to accumulation of aliphatic compounds in pores and on the surface; such compounds are usually lost during pyrolysis at higher temperatures. Hydrophobicity can inhibit water uptake by biochar particles (Gray et al., 2014), but this effect dissipates over time.

Most biochars are alkaline, with acid-neutralizing capacity up to 33% of agricultural lime (Van Zwieten, Kimber, Morris, Chan, et al., 2010) due to their carbonate, oxide, and hydroxide content. Biochar is a reductant, and therefore lowers soil redox potential (Joseph et al., 2015). An exception is flooded rice soils, where biochar application can increase Eh due to the release of O₂ from roots. Chew et al. (2020), Joseph et al. (2015), and Pignatello et al. (2017) detail the range of reactions that can take place on the external surfaces and in the pores of biochar (see also Section 2.2). Except in flooded soils, oxygen will diffuse into the pores and react with redox-active organic molecules (e.g., quinones; Yu & Kuzyakov, 2021) and minerals, particularly Fe and Mn. In acid soils, excess H⁺ reacts with basic minerals such as calcite and dolomite present within the C lattice of the biochar (Amonette & Joseph, 2009).

Biochars (especially those made at >400°C) can have a high content of free radicals, which can lead to the formation of reactive oxygen species (Pignatello et al., 2017; Ruan et al., 2019; Yu & Kuzyakov, 2021) and strongly accelerate oxidation reactions. This acceleration leads to oxidation not only of biochar itself but also of SOM and plant residues (Du et al., 2020) and is especially intensive in soils with fluctuating water level (Merino et al., 2020) or with high content of iron (oxyhydr)oxides (Merino et al., 2020; Yu & Kuzyakov, 2021).

Physical effects

Biochars commonly increase soil water holding capacity, particularly in coarse-textured soils, decrease bulk density, and increase porosity, with greater effects observed at rates

exceeding 40 Mg ha⁻¹ (see Section 3; Quin et al., 2014). Biochar can also impact water infiltration into soils, for example, moderating the reduction in infiltration rate that occurs during high-intensity rainstorms in soils prone to surface sealing, as seen at 2% w/w by Abrol et al. (2016). Reduced sealing leads to lower runoff and erosion rates. The effects were attributed to a biochar-related increase in soil solution Ca and decrease in Na, leading to decreased sodium adsorption ratio (Abrol et al., 2016).

Biochar particles have low density and are easily crushed (Abdullah & Wu, 2009). Cultivation and ingestion by soil fauna result in fragmentation and fracturing, creating very small particles (approximately <100 μm). These small particles are more mobile and can have higher reactivity, surface charge, radical content (Das et al., 2020; Yu & Kuzyakov, 2021) and surface area than larger particles (Yang et al., 2020), which can increase reactivity and nutrient availability (Wang et al., 2020). High mineral ash biochars and engineered biochars used in BCF generally contain high quantities of small mineral particles <100 μm (especially silica, alumina, Fe/O and CaCO₃, CaHPO₄, and Mg compounds) in or on the C matrix that are easily fragmented from the biochar and are mobile in soil.

2.1.2 | Effects on seed germination and early seedling growth

Reported impacts of biochar on germination and seedling growth range from inhibition to stimulation. Hormesis is commonly observed, that is, high rates of biochar can have a detrimental effect, while low rates can be stimulatory. Below we discuss the mechanisms likely to contribute to the range of effects on seed germination and early seedling development reported in the literature.

Seed germination begins with water imbibition and ends when the radicle emerges from the seed coat. The following are the main factors that determine whether biochar impacts seed germination: (i) release of salts from biochar to the soil solution; (ii) release of phytotoxins; (iii) release of germination-inducing hormones or karrikins; (iv) change in water holding capacity and porosity of the soil. These biochar-related factors are the reason that biochar feedstock, production HTT, and application amount have a range of impacts on germination speed and rate. The specific sensitivity of seeds of different plant species to salinity, toxins, hormone-like compounds and water availability also results in very variable results. For example, wood biochar (HTT 620°C) at 80 Mg ha⁻¹ in a pot trial inhibited germination of tomatoes, while biochar made from paper sludge and wheat husk (500°C) or sewage sludge (600°C), and applied at the same rate, had no effect on lentil, tomato, cress, cucumber, and lettuce seeds (Gascó et al., 2016). Other studies that applied a range of woody and manure biochars at rates of 10–40 Mg ha⁻¹

found positive or nil effect on germination (Das et al., 2020; Gascó et al., 2016; Khan et al., 2014; Mete et al., 2015; Van Zwieten, Kimber, Morris, Downie, et al., 2010). Some studies (e.g., Uslu et al., 2020) that reported negative effects of biochar on germination at very high rates (120 Mg ha⁻¹) applied biochar directly to seeds in a petri dish, in the absence of soil or other media, which is unlikely to reflect the effects of biochar in the field environment, where charged clay minerals, microbes, and organic compounds interact with biochar, and are likely to modify and buffer the response. Germination rates were not affected by the addition of BCF at <700 kg ha⁻¹ in pot or field trials, while seedling growth was the same or greater than with NPK fertilizer alone (Joseph, Graber, et al., 2013; Liao et al., 2020; Qian et al., 2014; Zheng et al., 2017). Aqueous extracts of some biochars have been found to stimulate germination and seedling growth (Taek-Keun et al., 2012).

Seed germination and early seedling development can be influenced as a result of the effects of biochar on soil physical properties (Section 2.1.1). For instance, by reducing soil bulk density and increasing soil aeration, biochar can provide oxygen for seed germination and improve seedling growth through lower resistance to root penetration and seedling emergence. These effects typically increase with higher biochar rates (Obia et al., 2018).

Chemical impacts of biochar on soils and soil water solution can also affect seed germination and early seedling development. For example, by raising the pH, alkaline biochars alleviate Al and heavy metal toxicity that can reduce root growth in acidic soils (Lauricella et al., 2021; Shetty et al., 2020; Van Zwieten, Rose, et al., 2015). At high application rates, biochars with high levels of soluble salts could inhibit germination and seedling growth through osmotic stress. Certain soluble organic compounds released from biochars can stimulate germination and plant growth (Sun, Drosos, et al., 2017). Kochanek et al. (2016) showed that biochars containing karrikins, a class of water-soluble organic molecules associated with plant response to fire, can accelerate germination and early growth of plants. These authors attributed the response to signaling molecules that stimulate plant development. The quantity of karrikins and germination response varied widely between biochars studied by Kochanek et al. (2016). French and Iyer-Pascuzzi (2018) found evidence that stimulation of the gibberellin pathway contributes to the observed promotion of germination and seedling growth by wood biochar in some tomato genotypes. Similarly, phenols and polyphenols released from biochar (Reynolds et al., 2018) can break seed dormancy, leading to germination, and also promote seedling growth (Mu et al., 2003; Stoms, 1982). Yet, some organic molecules released can be phytotoxic, so applying biochar a few weeks in advance of sowing supports seedling growth through the development of a beneficial rhizosphere microbiome (Jaiswal et al., 2018).

At very high rates of application (>50 Mg ha⁻¹), biochars derived from contaminated sludges or feedstock grown in contaminated soils can release heavy metals that inhibit germination (Das et al., 2020). Biochars contain polycyclic aromatic hydrocarbons (PAHs; Gascó et al., 2016; Weidemann et al., 2018), organic pollutants formed during incomplete combustion, that can inhibit germination at high rates. However, PAHs in biochar are generally of little or no concern for plant growth due to their strong binding by biochar, and furthermore, their concentration is usually below regulatory limits if biochar is made under slow pyrolysis conditions (Buss et al., 2015; Hale et al., 2012; Hilber et al., 2017).

At high biochar application rates in the absence of soil (volumetrically equivalent to >40 Mg ha⁻¹, in a petri dish), free radicals from biochar inhibit germination and seedling growth (Liao et al., 2014). However, at low biochar rates, low levels of free radicals could be beneficial, as reactive oxygen species can interact with plant hormones that trigger germination (Gomes & Garcia, 2013). Furthermore, free radicals associated with biochar have been found to degrade certain organic and inorganic pollutants (Ruan et al., 2019) which in turn could enhance germination and seedling growth. In addition, biochar can lower the production of reactive oxygen species by plants: Natasha et al. (2021) showed that the production of reactive oxygen species was lower, on average, by 33% in plants grown in soils contaminated with trace elements where biochar was applied (2%–10% w/w).

In summary, most biochars and biochar formulations do not inhibit germination and early growth of plants in soil unless applied at very high rates (e.g., >40–50 Mg ha⁻¹), and can promote germination and seedling growth at moderate rates. The mechanisms for the positive effects largely involve water-soluble organic compounds that stimulate germination and seedling growth, or reactions that deactivate inhibitory factors such as heavy metals and phytotoxic organic compounds. These effects vary between biochars: low temperature biochars have a higher content of water-soluble organic molecules that can promote germination and early growth at low application rates; these biochars are also likely to cause inhibition if applied at high rates. Negative effects on germination can result where high rates are applied due to release of soluble salts or phytotoxic levels of organic compounds, where biochar is contaminated, and where soil is absent. Biochars with high levels of soluble mineral compounds can also cause inhibition at high application rates.

2.2 | Stage 2: Medium-term reactions (1–6 months)

The effects of biochar in later periods differ from the first stage which is dominated by dissolution of compounds from biochar. In stage 2, plant roots intercept and interact with

biochar. Root hairs enter biochar pores, roots wrap around biochar (Joseph et al., 2010; Prendergast-Miller et al., 2014), and very small biochar particles can attach to root surfaces (Figure 1; Chew et al., 2020). Biochar affects the abundance of specific microorganisms especially in the rhizosphere, and the interactions between biochar, soil, plants, and the microbiome affect plant growth and health (Anderson et al., 2011; Jaiswal et al., 2015).

2.2.1 | Physical and chemical reactions in soil

The physical and chemical properties of biochar surfaces change significantly in Stage 2 through a range of biotic and abiotic processes that take place in the pores exposed after the rapid dissolution phase ends (Joseph et al., 2010). The surface area and porosity increase (Schreiter et al., 2020), and a fine layer of organic matter with a high concentration of C–O and C–N functional groups forms around the external and some of the internal pore surfaces of the biochar and BCF. This fine layer adsorbs cations (including heavy metals), anions, nanoparticulate minerals, and organic compounds through a range of binding mechanisms that include cation and anion exchange, ligand exchange, covalent bonding, complexation, chelation, precipitation, redox, and acid–base reactions, that together result in formation of organo-mineral layers (Hagemann, Joseph, et al., 2017; Joseph, Van Zwieten, et al., 2013). These layers are redox-active and mesoporous. Surfaces in nanopores bind molecules more tightly than larger pores (Pignatello et al., 2017). Some of the nutrients released from fertilizer, especially N and P, can react with the biochar pore surfaces and organo-mineral layers (Haider et al., 2020; Hestrin et al., 2019; Joseph et al., 2018; Kammann et al., 2015). Biochar pores may become filled with organic matter and minerals, protecting organic matter from microbial decomposition (Pignatello et al., 2017) and reduces availability of nutrients.

Microagglomerates that form on internal and external biochar surfaces, consisting of nanoparticulate minerals bound with organic molecules, have a significant concentration of –C–O, –C=O, –COOH, or –NH functional groups (Joseph et al., 2010). Recent research indicates that many of the reactions described above related to biochar occur on or in the microagglomerates.

Gases such as NH₃, N₂O, and CH₄ produced through biotic and abiotic reactions of fertilizers in soils and/or through chemical reactions on the surfaces of the biochar can diffuse into the nanopores (<50 nm), where they can react with oxidants and reductants, especially if the pores contain water, which reduces N loss and GHG emissions (Section 4.3; Chiu & Huang, 2020; Quin et al., 2015).

2.2.2 | Microbial responses

Meta-analyses have shown that biochar increases microbial biomass and activities (Pokharel et al., 2020), particularly in high-N soils (Zhang et al., 2018) and with biochars produced at low temperature from nutrient-rich feedstocks (Li et al., 2020). Biochars, particularly those made at low temperature from crop residues, cause shifts in microbial community composition, increasing the ratios of fungi to bacteria, and gram-positive to gram-negative bacteria (Zhang et al., 2018). The meta-analysis by Pokharel et al. (2020) identified that biochar increased microbial biomass C and the activities of the enzymes urease, alkaline phosphatase, and dehydrogenase by 22%, 23%, 25%, and 20%, respectively, with greatest effects in acidic fine-textured soils. This increase in enzyme activities as well as the shift in microbial community diversity and activity (Jaiswal, Elad, et al., 2018) are directly dependent on (i) pH increase after biochar addition, as soil acidity is the main factor regulating microbial composition (Rousk et al., 2010); (ii) increased aeration, and consequently, better conditions for fungi and aerobic bacteria, as well as oxidative enzymes; (iii) changes in metabolic needs due to the prevalence of large organic compounds, and consequently, shift in the community toward K-strategists (Cui et al., 2020), decrease in gram-negative bacteria, shift toward saprophytic fungi, and increase in peroxidases; and (iv) strong increase in hydrophobic compounds in soil that favors activity of fungi (Deng et al., 2021; Xia et al., 2020).

Li et al. (2020) noted a negative effect of high biochar rates (>50 Mg ha⁻¹) on microbial diversity, and suggested the following potential causes: (i) introduction of toxic components that inhibit some species; (ii) increase in the C:N ratios of SOM that limits microbial C utilization, possibly only in the short term and only to the extent that the organic C is metabolized; and (iii) disruption of microbial microenvironments. Note also that C:N ratio does not influence microbial metabolism of biochars (Torres-Rojas et al., 2020).

Fungi and bacteria inhabit the larger nutrient-rich pores of biochar (>2 μm) where they mine the nutrients in the biochar and those that have been absorbed from fertilizers. The adsorption of root exudates, microbial metabolites, and microbial necromass increases SOM levels and thus increases soil organic carbon (SOC; see Section 4.2). Small biochar particles can migrate to the root surface and can alter the abundance of specific root-associated bacteria (Chew et al., 2020; Kolton et al., 2011).

In low P soils, arbuscular mycorrhizal fungi (AMF) invade the pores of biochar, especially biochars with high P content on the pore surface, which can increase plant P uptake (Gujre et al., 2020; Solaiman et al., 2019; Vanek & Lehmann, 2015). Blackwell et al. (2015) found that a phosphorus-enhanced BCF increased root colonization to 75% compared with 20%

in mineral fertilizer and unfertilized control and increased P uptake efficiency.

Adsorption of microbial signaling molecules (especially acyl-homoserine lactone) on biochar surfaces can disrupt soil microbial communication, which could reduce the effects of pathogens (Gao et al., 2016; Masiello et al., 2013). Biochar can also adsorb pathogenic enzymes and toxic metabolites exuded by soil-borne pathogens, thus reducing the concentration of virulence factors in the root zone and lowering disease severity (Jaiswal et al., 2018).

2.2.3 | Plant responses

Nutrient responses

Much of the N within the biochar C matrix (e.g., heterocyclic-N) is unavailable to plants (Clough et al., 2013; Torres-Rojas et al., 2020), whereas most K in biochar is present in soluble forms, released in the short term after application to soil (Silber et al., 2010), and is readily available to plants. Meta-analyses have found that biochar application commonly increases P availability, particularly when applied to acidic or neutral soils, and for biochar produced from low C:N feedstocks (e.g., manure, crop residues), and produced at low temperatures (Gao et al., 2019; Glaser & Lehr, 2019). However, P availability can be low in Ca-rich and K-poor feedstocks such as sewage sludge (Buss et al., 2018, 2020; Torres-Rojas et al., 2020; Wang et al., 2019) because pyrolysis can convert plant-available organic P into inorganic P that is less available in the short term (Buss et al., 2020; Rose et al., 2019). The opposite has also been observed, with pyrolysis increasing plant-available P although decreasing water-extractable P (Wang et al., 2014; Zwetsloot et al., 2015, 2016). The effect of biochar on P availability is determined by microscale effects on soil pH and soil solution composition, especially Ca content (Buss, Assavavittayanon, et al., 2018; Buss et al., 2018). Biochar can retain nutrients, especially N, released as fertilizers dissolve, and nutrients already present in soil, reducing loss through leaching (Haider et al., 2020). For example, meta-analysis found that biochar reduces N leaching on average by 26%, though it can increase ammonia volatilization at biochar application rates $>40 \text{ Mg ha}^{-1}$ and with biochar pH > 9 (Haider et al., 2020; Liu, Zhang, et al., 2018). While the stimulation of microbial activity by easily-mineralizable components of biochar can reduce N availability through microbial immobilization (Clough et al., 2013), it also accelerates the mineralization of organic matter and nutrient cycling, and AMF root colonization, which can increase N and P uptake by plants, as discussed above (Solaiman et al., 2019) and can also improve root growth under water stress (Mickan et al., 2016).

Adsorption of root exudates by biochar may cause dissolution of mineral compounds in biochar pores (Wang et al.,

2020), which can increase nutrient availability, and can result in additional adsorption sites for organic molecules (Prendergast-Miller et al., 2014).

In flooded paddy soils, biochar and BCF particles can be encapsulated in an organo-mineral layer (Chew et al., 2020) on the root surface. BCF attached to the root or located in the rhizosphere of rice grown in flooded soils was observed to significantly alter the pH and Eh around the root, the root membrane potential (the potential difference between the inside of the root and the soil), and the abundance of specific microorganisms that increase nutrient availability (Chew et al., 2020). Thus, when biochar is in contact with root hairs, in the presence of microbes, it has the capacity to store and release nutrient ions and electrons (Chew et al., 2020; Sun, Levin, et al., 2017). The change in root membrane potential can facilitate uptake of nutrients when required by the plant. Chew et al. (2020) have represented these reactions as an RC circuit (Figure 1). Biochar directly mediates electron transfer by functioning as an electron shuttle and indirectly transfers electrons from the valence band to the conduction band in the Fe minerals by generating electron-hole pairs producing reactive oxygen species (O_2^- , H_2O_2 , HO^\cdot) by Fenton and Fenton-like reactions (Yu & Kuzyakov, 2021).

Chemolithotroph bacteria can grow on the surfaces of microagglomerates of clay and Fe nanoparticles and make S and Fe more available to plants (Ye et al., 2017). Microbes can form biofilms on biochar surfaces, and establish corrosion cells that increase the solubility of metal species (e.g., insoluble Al_2O_3 to soluble Al; Joseph, Van Zwieten, et al., 2013).

Effects on heavy metal uptake

Many studies have shown that biochar can reduce uptake of heavy metal(loid)s by plants. A meta-analysis found biochar addition to soils resulted in average decreases in plant tissue concentrations of Cd, Pb, Cu, and Zn by 38%, 39%, 25%, and 17%, respectively (Chen et al., 2018). Studies showing significant reduction in bioavailability of heavy metals have often applied high rates of biochar, in excess of 10 Mg ha^{-1} (Chen et al., 2018; Wang et al., 2020). The surface O-functional groups on biochar can immobilize heavy metals through ion exchange, precipitation, cation and anion metal attraction, reduction, electron shuttling, and physisorption (Figure 2; Ahmad et al., 2014; Ding et al., 2014; Liu, Xu, et al., 2018; Tan et al., 2015; Zheng et al., 2020). Alkalinity from biochar (the liming effect) increases pH of acid soils, increasing the negatively charged exchange sites on clay particles, attracting cationic metals (Figure 1). Manure biochars commonly contain higher Ca than plant-derived biochars, and thus can immobilize cationic heavy metals (e.g., Cd^{2+} and Cu^{2+}) through ion exchange (Lei et al., 2019). Stable precipitates formed in biochars with high P can immobilize Pb through the formation of $\beta\text{-Pb}_9(\text{PO}_4)_6$, whereas higher alkalinity and calcite

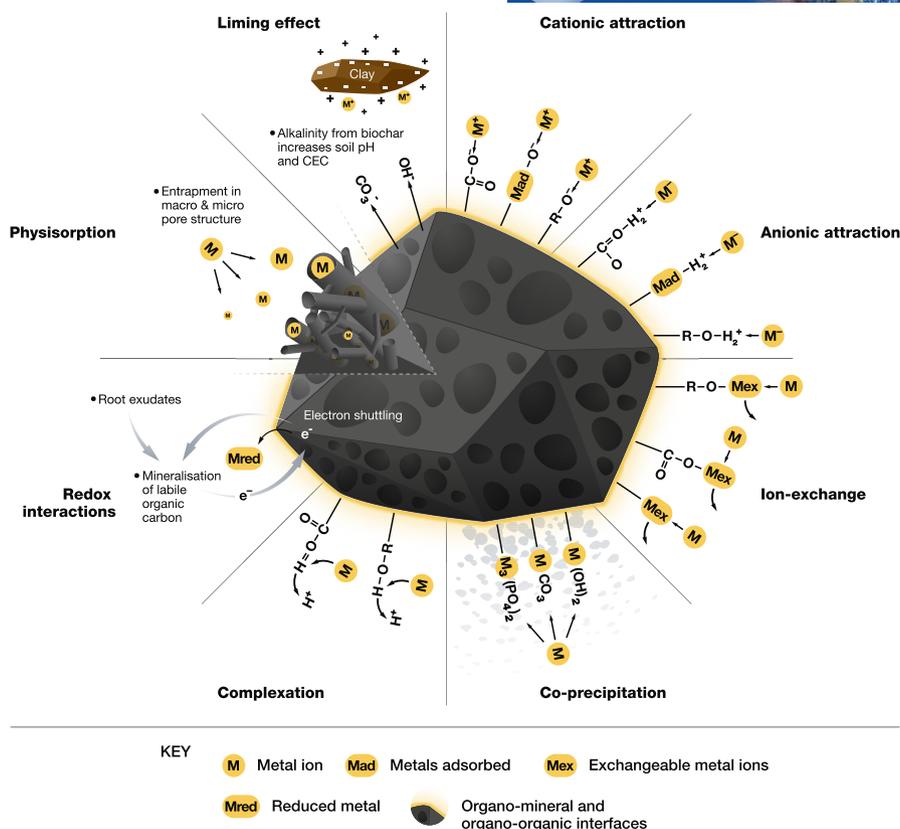


FIGURE 2 Postulated mechanisms of biochar interactions with heavy metals and metalloids (adapted from Ahmad et al., 2014)

in biochar facilitate the formation of insoluble hydrocerussite $Pb_3(CO_3)_2(OH)_2$ (Cao & Harris, 2010; Li et al., 2016). Particles on the surface of biochars consisting of carbon-coated minerals are particularly effective in reducing bioavailability of heavy metals (Kumar & Prasad, 2018). Incorporation into organo-mineral microagglomerates can reduce Cr(VI) to Cr(III) through interaction with reduced Fe, organic compounds, and free radicals (Odinga et al., 2020), including through electron shuttling (Xu et al., 2019), reducing their availability to plants (Kumar, Joseph, et al., 2018; Kumar et al., 2020).

High-temperature willow biochar was found to adsorb heavy metals from sewage sludge through both physisorption and the mechanisms described above (Bogusz et al., 2019). Even feedstocks that contain high contents of heavy metals can reduce the bioavailability of some heavy metals in some soils. For example, sewage sludge biochar decreased the bioaccumulation of As, Cr, Co, Cu, Ni, and Pb, but increased that of Cd and Zn in an acidic paddy soil (Khan et al., 2013).

Biochar can increase the mobility of anionic metalloids such as As (e.g., AsO_4^{3-} , AsO_3^{3-} ; Igalavithana et al., 2017) through a decrease in positively charged sites, which decreases the binding sites for As as soil pH increases (Vithanage et al., 2017). Engineering biochars through adding magnetite nanoparticles can increase AEC and thus adsorb As (Wan et al., 2020).

Plant health

Besides the impacts of biochar on plant growth and development, it has been observed in numerous pathosystems that biochar can elicit systemic resistance in plants against diseases (Frenkel et al., 2017). Biochar in the growing medium can “prime” plants (Ton & Maunch-Mani, 2003) for rapid up-regulation of defense-related genes (Elad et al., 2010; Jaiswal et al., 2014, 2015, 2017, 2020; Jaiswal, Elad, et al., 2018; Kolton et al., 2017; Kumar et al., 2021; Mehari et al., 2015; Meller Harel et al., 2012). Plants in a primed state display faster and stronger activation of cellular defense responses, such as earlier oxidative burst and stronger upregulation of defense genes, upon encountering biotic stresses (Conrath et al., 2006). This effect has been observed also for abiotic environmental pressures such as salt, heat, cold, toxins, and drought (Ton & Maunch-Mani, 2003).

A range of biochar–rhizosphere mechanisms are potentially responsible for these *in planta* responses (Graber et al., 2014), involving biochar's varied direct and indirect influences on the soil/rhizosphere/pathogen/microbiome/plant system. Some of these include: release of Si from biochar (especially straw and rice husk biochars), reported to increase disease resistance and plant growth (Wang, Wang, et al., 2019) by suppression of initial infection and pathogen access to plant tissues; adsorption by biochar of extracellular pathogenic enzymes and toxins (released by soil pathogens

to dissolve and poison roots) lowering their concentrations in the root zone (Jaiswal, Frenkel, et al., 2018); induced systemic acquired resistance through upregulation of genes and pathways associated with plant defense and growth (Jaiswal et al., 2020); and adsorption and deactivation of plant signaling molecules that induce germination of parasitic weed seeds (Eizenberg et al., 2017).

The impact of biochar on plant disease is a function of biochar dose and type (physical/chemical characteristics, as discussed above; Frenkel et al., 2017; Poveda et al., 2021; Rogovska et al., 2017). Generally, no impact is found at low rates ($<2 \text{ Mg ha}^{-1}$), positive impacts are seen at moderate rates ($2\text{--}20 \text{ Mg ha}^{-1}$), and negative impacts at relatively high rates ($>50 \text{ Mg ha}^{-1}$). This response pattern has been observed in studies of plant growth and disease caused by *Rhizoctonia solani* in common beans (Jaiswal et al., 2015) and cucumber (Jaiswal et al., 2014), and in other plant–soil-borne pathogen (Graber et al., 2014) and plant–foliar pathogen (Elad et al., 2011) systems. However, the optimal rate for disease suppression does not always coincide with the optimum rate for growth response. Rates that are beneficial for plant growth in non-diseased systems can result in disease promotion in pathogen-infected systems (Jaiswal et al., 2015).

Few studies have examined *in planta* responses to biochar when faced with environmental pressures. Under sufficient and drought water conditions, *Chenopodium quinoa* and maize both grew significantly better in biochar treatments, which was attributed to improved plant traits (lower proline content and less negative osmotic potential) rather than to increased root zone water content (Ahmed et al., 2018; Kammann et al., 2011). Improved pepper plant productivity in biochar-treated plots in a multi-year trial conducted under extreme environmental pressures (high evaporation demand and vapor pressure deficit, high daytime temperatures (heat stress) at planting and low nighttime temperatures at fruiting, brackish water irrigation) was attributed to biochar-elicited acclimation responses in the plants (Kumar, Elad, et al., 2018). Tests with heat stress and biochar in *Arabidopsis* indicated early microstresses primed the plants to cope better with subsequent acute heat stress. Early microstresses elicited improved energy production and utilization mechanisms, while the acclimation mechanism against the acute heat was related to lower levels of reactive oxygen species. The ability of biochar to induce an early acclimated state to basal microstresses and to prime the plant for coping with subsequent acute stresses was postulated to explain biochar-mediated improvements in plant health, flowering, and growth due to factors other than nutrition, water, or soil structure (Elad et al., 2011).

In addition to *in planta* responses discussed above, biochars buffer pH and poise (equilibrate) Eh (Husson, 2013; Joseph et al., 2015) which can create and maintain conditions in the rhizosphere that support plant growth and resilience

to a range of environmental pressures, such as drought, heat, pathogens and pollutants (Husson et al., 2018). Biochar can rapidly transfer charge (Sun, Levin, et al., 2017; Yu & Kuzyakov, 2021), which could also enhance plants' capacity to cope with oxidative stress (Husson et al., 2018).

In summary, biochar can create conditions in the rhizosphere that increase nutrient supply and uptake; immobilize or deactivate phytotoxic organic and mineral substances; release bioactive compounds that stimulate growth and development; promote beneficial organisms; and inhibit pathogens. Thus, biochar can support plant growth, health, and resilience to disease and environmental stressors.

2.3 | Stage 3: Long-term reactions

Several studies have examined the longer term interactions as biochar “ages” in soil, investigating effects on bulk soil properties and plant growth where biochar has been applied in previous crops, or examining biochar particles extracted from the soil. Disturbance through cultivation, exposure to wetting–drying and freeze–thaw cycles, and ingestion by soil fauna can lead to further fragmentation of biochar particles and oxidation of biochar surfaces exposed through detachment of microagglomerates (Wang et al., 2020).

Two studies identified the formation of porous organo-mineral heterogeneous microagglomerates with mineral phases consisting of Fe, Al, Si oxides, phosphates (Ca/Fe/Al), carbonates (Ca/Mg), and chlorides (K, Na), and dimensions from 1 to 50 nm, bound together by organic compounds and bonded to the biochar surface (Archanjo et al., 2017; Rafiq et al., 2020). Simultaneous occurrence of Fe(II) and Fe(III) present as magnetite and hematite could make N and P more available through redox cycling of Fe (Haider et al., 2020). This could contribute to long-term increase in P availability in response to biochar application, such as identified in the meta-analysis of Glaser and Lehr (2019), who reported enhancement lasting up to 5 years. Aged high-temperature wood biochar particles retain plant-available N as nitrates and ammonium, adsorbed onto the organo-mineral microagglomerates (Haider et al., 2020). The formation of microagglomerates increases the surface area, CEC and AEC, but the pore volume generally decreases compared to the fresh biochar after multiple crop cycles, for example, Dong et al. (2017). Rhizodeposits are protected in soil microaggregates and Fe (oxyhydr)oxides (Jeewani et al., 2020), and a decadal study indicates potential for this mechanism to provide long-term stabilization of newly added plant C (Weng et al., 2017). Biochar particles can also be protected within the soil microaggregates (Figure 3).

The biochar-enriched anthropogenic Terra Preta soils associated with pre-Columbian settlements in the Brazilian Amazon (Steiner et al., 2009) provide evidence of very

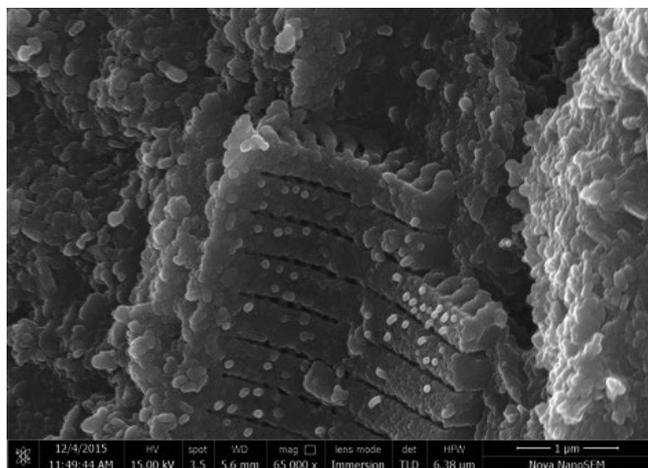


FIGURE 3 Fragment of biochar coated with nanoparticles that have a high concentration of Si, Fe, Al, Ti (see Figure S4) embedded in a soil microaggregate. Nanoparticles are the small spherical and ovoid particles on biochar lattice. Sample of biochar removed from a 9-year field trial of greenwaste biochar (Weng et al., 2017). Mineral nanoparticles on the biochar surface can play a key role in the formation of microaggregates that protect biochar from decomposition. The energy-dispersive X-ray spectroscopy (EDS) spectrum of this image is shown in Figure S4

long-term reactions of biochar in soil. Observations of Terra Preta soils identified that a substantial fraction of the biochar remained in particulate form, protected by Fe and Al oxides (Glaser et al., 2000).

Colloidal aged biochar particles consisting of microagglomerates and fragments of the C matrix may be more mobile in soil than fresh biochar (Wang, Zhang, et al., 2019). These particles can have higher negative charge on the surface compared with fresh biochar due to the higher concentration of C–O functional groups (Wang, Zhang, et al., 2019), further increasing CEC and capacity to adsorb organic molecules.

The bioavailability of heavy metals has been observed to increase or decrease as biochar ages in soil (Wang et al., 2020). For example, the reduction in uptake of Cd and Pb from a highly contaminated soil was sustained over 3 years after a single application of wheat straw biochar (Bian et al., 2014). Potentially, adding a small amount of biochar in a band every year could ensure heavy metals remain immobilized.

In their meta-analysis, Ye et al. (2020) reported an increase in crop yield over multiple years after a single biochar application, where fertilizer was applied. Rafiq et al. (2020) found that moderate rates (2–6 Mg ha⁻¹) of rice husk (high ash) biochar applied with fertilizer gave a residual benefit for pasture yield, lasting at least 3 years, associated with enhanced microbial activity and diversity. Kumar, Elad, et al. (2018) observed increased fruit yield and quality, and resistance to the pathogen causing powdery mildew and the

arthropod pest broad mite, over three seasons in fertilized, irrigated peppers after application of greenwaste and woody biochars. Crop growth on Terra Preta soils is approximately double that on adjacent unamended soils, providing evidence that biochar can increase soil fertility over centuries (Lehmann et al., 2003).

There is a substantial body of literature examining biochar reactions over multiple years based on one-time application of biochar at high rates (e.g., 20–30 Mg ha⁻¹ or 2–3% w/w), often in pots (e.g., Burrell et al., 2016), but there are few studies of biochar or BCF applied at low (commercially viable) rates, as single or repeated applications. Slow release of P from BCF and biochar can increase P-use efficiency in tropical soils over the medium- to long-term (Lustosa Filho et al., 2020), possibly through (i) input with high P biochars such as those made from manure or sewage sludge; and (ii) reduced P sorption due to DOM released from biochar (Schneider & Haderlein, 2016).

In summary, aging through interactions of biochar with soil minerals and microbes generally leads to functionalized surfaces consisting of organo-mineral microagglomerates, which can increase nutrient-holding capacity. Microagglomerates and portions of the C matrix can detach, and colloidal-sized particles can migrate through the soil profile. Aggregation can protect biochar and newly added organic matter, stabilizing new C for long periods in soil. Residual effects of single application of biochar on pH have been recorded, and some residual yield benefits have been observed.

3 | BIOCHAR'S ROLE IN SUPPORTING FOOD SECURITY

Over 1700 studies published between 2010 and 2020 (Web of Science) describe the effects of biochar on plant production. Meta-analyses have found yield responses of annual crops and trees of 10%–42% and identified site and biochar features giving greatest responses (Table 1).

Sandy soils and soils with CEC below 100 mmol_c kg⁻¹ or organic C content below 20 g kg⁻¹ are most responsive (Dai et al., 2020; Ye et al., 2020). Soil pH is consistently identified as a key variable (Dai et al., 2020; Jeffery et al., 2011): Responses were greatest in acidic soils, because of the liming effect of biochar and a concomitant decline in available Al (Van Zwieten, Rose, et al., 2015). Importantly, Ye et al. (2020) identified that yield responses were greater in the third year after a single application, when fertilizer was applied with the biochar. This response most likely reflects the physicochemical and microbial changes that improve soil health as biochar ages (Section 2.3), rather than a simple soil pH response. A meta-analysis by Glaser and Lehr (2019) found availability of P increased on average by a factor of 4.6 in response to biochar application.

They noted that biochar increased P availability by a factor of 5.1 and 2.4 in acidic and neutral soils, respectively, but it had no effect in alkaline soils or at application rates below 10 Mg ha⁻¹ or with biochars produced at HTT < 600 °C (Glaser & Lehr, 2019). The optimal biochar dose differed between studies (Table 1) and is dependent on the biochar characteristics, soil properties, and the constraint being addressed. Biochar may have no effect on yields when low-nutrient biochars are applied without fertilizer, or when biochar is applied to nutrient-rich soils (Ye et al., 2020). Negative effects can result from reduction in soil N and P availability (Nielsen et al., 2014; Prommer et al., 2014) especially at high rates of high temperature biochars (Kammann et al., 2015) through binding mechanisms described in Section 2.2.

A meta-analysis of the impacts of biochar on rice production (Awad et al., 2018) showed a net yield increase of 16%, with greatest response at 11–20 Mg ha⁻¹ and with biochars produced at 400–450 °C. The co-application of biochar with N fertilizer tended to provide the greatest yield increase, supporting previous evidence (Van Zwieten, Kimber, Morris, Chan, et al., 2010) that biochar can increase fertilizer N-use efficiency, and suggesting that biochar addition could maintain crop N uptake at lower doses of fertilizer N. Similarly, in two studies using BCF, N partial factor productivity increased by 37%–74% (Joseph, Graber, et al., 2013; Qian et al., 2014).

Biochars are generally found to increase soil water-holding capacity, which would enhance resilience of agricultural systems to drought, especially under climate change (Edeh et al., 2020) and may further explain the positive effects of biochars in sandy soils especially in arid and semiarid areas. Grass and straw biochars increase water-holding capacity to a greater extent than woody biochars (Burrell et al., 2016; Kroeger et al., 2020). Meta-analyses have shown increases in plant available water content of 33%–45% in coarse-textured soils and 9%–14% in clay soils (Edeh et al., 2020; Omondi et al., 2016; Razzaghi et al., 2020), with greatest response at 30–70 Mg ha⁻¹. Using X-ray μ -tomography, Quin et al. (2014) observed increases in total soil porosity, connectivity of pore space and number of fine pores across soils of different texture, explaining the results of Edeh et al. (2020) and Razzaghi et al. (2020).

The average 27% increase in photosynthetic rate in C₃ plants (but no effect on C₄ plants) observed in the meta-analysis of He et al. (2020) associated with increased stomatal conductance, transpiration rate, and chlorophyll content was attributed to the combined effects of biochar on water availability and N nutrition.

Heavy metal pollution in arable land significantly impacts plant growth and food safety (Luo et al., 2018) especially in developing countries (Hou et al., 2020). Application of biochar to contaminated soils could reduce heavy metal bioavailability via (1) direct interactions between biochar and heavy

metals, and (2) indirect interactions that immobilize heavy metals through modification of soil properties (see Section 2.2.3), and could contribute to the yield benefits of biochar particularly in acid soils, as soil pH is a key property governing the speciation and mobility of heavy metals. Increase in soil CEC following biochar application can also reduce the bioavailability of cationic heavy metals (Mohamed et al., 2017). Biochar application can also alter soil Eh, impacting the speciation, mobility, and bioavailability of anionic heavy metalloids such as As (Yuan et al., 2017).

Heavy metals may be present in biochar produced from feedstocks such as sewage sludge and treated timber. Although the pyrolysis process concentrates most heavy metals, some metals such as Cd and Zn (Dong et al., 2015) and As (Zhang et al., 2020) can be partly volatilized during pyrolysis resulting in lower concentrations than the feedstock.

Application of biochar is a promising approach to mitigate heavy metal contamination; however, the remediation efficacy depends on the type of biochar, biogeochemical properties of soil, plant species, and the specific heavy metal (Albert et al., 2020; Palansooriya et al., 2020). Therefore, selecting the appropriate biochar type to address heavy metal contamination, suited to the soil properties, type of plant, and specific heavy metal, can result in effective remediation while safeguarding food quality.

Improved understanding of the key edaphic properties that constrain plant production and heavy metal uptake, and that can be addressed by biochar, enables design of “bespoke biochars” engineered for specific applications (Crombie et al., 2015) to contribute to food security.

4 | BIOCHAR'S ROLE IN CLIMATE CHANGE MITIGATION

Biochar has been recognized as a negative emissions technology (de Coninck et al., 2018; Cowie et al., 2020), in addition to reducing GHG emissions from soil, as reviewed below. Among carbon dioxide removal strategies, biochar is suggested as a preferred method due to comparatively low cost and large environmental benefits (Smith, 2016).

4.1 | Persistent carbon in biochar

Unlike other forms of biomass that are rapidly decomposed in soil, the majority of C in biochar has a mean residence time in the range of hundreds and thousands of years (Schmidt et al., 2011; Wang et al., 2016). Due to this high persistence, biochar can contribute significantly to long-term C sequestration (Lehmann, 2007). Sequential additions of biochar to soil will continue to build SOC stocks, whereas additions of unpyrolyzed organic matter (plant litter, compost, manure)

will be rapidly mineralized, and will increase SOC stocks only until an equilibrium is reached where inputs equal decomposition rate (Figure 4).

The very slow decomposition of biochar in comparison to unpyrolyzed biomass is attributed to its aromatic structure, which results from chemical transformations of biomass during carbonization. Wood biochars pyrolyzed at temperatures above 450–500°C have a mean residence time of hundreds to a thousand years, compared with decades for manure biochars (Kuzayakov et al., 2014; Kuzayakov & Gavrichkova, 2009; Singh et al., 2012, 2015; Wang et al., 2016; Table 2). Kuzayakov et al. (2009) suggested that mean residence times calculated from incubations (Table 2), which maintain optimal conditions for decomposition, are around 10 times lower than under field conditions (Kuzayakov et al., 2009), although Rasse et al. (2017) found a similar rate of decomposition of *Miscanthus* biochar between laboratory and field conditions over a 90 day incubation period. The kinetics of formation of the fused aromatic C structure depend on the rate of heating, the ratio of lignin to cellulose and hemicellulose, time at the HTT, and mineral content (Budai et al., 2014; Leng & Huang, 2018; Rawal et al., 2016). The initial process of drying and depolymerization is endothermic and takes place between ambient temperatures and approximately 250°C. This is followed by an exothermic phase where most of the volatile gases are released, up to a temperature of approximately 350°C. The largely amorphous structure of biochars pyrolyzed at temperatures in excess of 400–450°C has been found to be persistent. Further heat converts the C matrix to a highly persistent three-dimensional nanographitic structure at around 600°C (McDonald-Wharry et al., 2016). Minerals

present in biochar, especially Si and P, can increase persistence of biochar-C (Xu et al., 2017).

Estimating potential C sequestration through the use of biochar requires prediction of its persistence in soil. Temperature thresholds identified in the transformation processes can indicate persistence. Using hydrogen pyrolysis to assess relative chemical stability, McBeath et al. (2015) estimated, across a wide range of feedstocks, that <20% of the biochar is persistent at pyrolysis temperatures <450°C, with >80% persistent at 600–700°C. These findings are consistent with the structural changes observed by McDonald-Wharry et al. (2016).

While pyrolysis temperature is a convenient measure to obtain predictions for broad trends in persistence, and adequate for national GHG inventories (Ogle et al., 2019), material properties are a more rigorous approach to estimate biochar persistence for project-level GHG accounting and research applications. The elemental ratio of hydrogen to organic C expressed as H/C_{org} has been identified as a simple and reliable parameter for characterizing biochar persistence and recommendations for conservative thresholds have been provided (Budai et al., 2013). These thresholds are being refined as more data become available (Lehmann et al., 2015) and other methods, such as spectral and thermal methods and chemical oxidation, offer additional insights (Leng & Huang, 2018; Li & Chen, 2018).

Biochar properties are the key determinant of its persistence in comparison to mineralization of unpyrolyzed biomass, but edaphic and climatic factors are also influential. As discussed in Section 2.2, the formation of microaggregates through interaction of biochar with minerals and native SOM

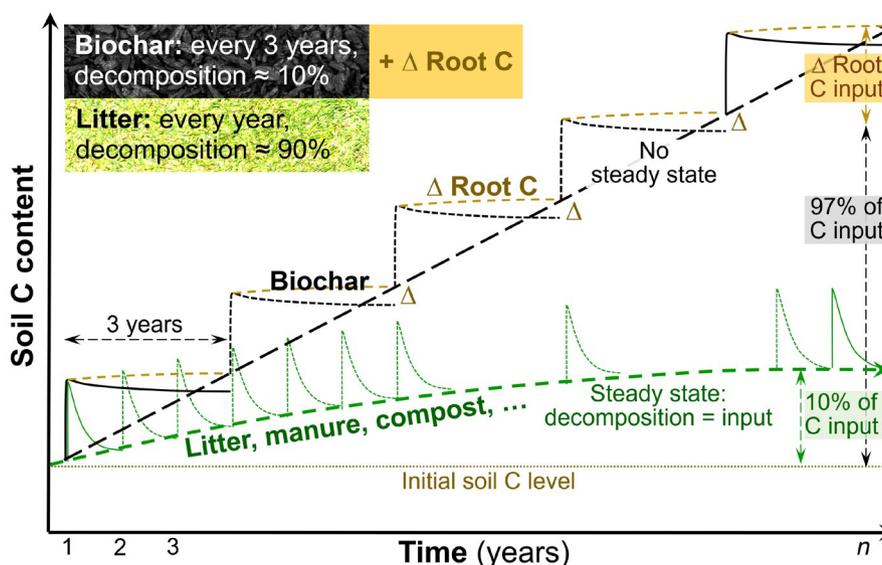


FIGURE 4 Accumulation of soil organic carbon (SOC) stocks with sequential biochar additions, due to (i) the highly persistent carbon in biochar, (ii) biochar-induced negative priming, and (iii) additional C input from plant roots through retention of rhizodeposits (Δ Root C), compared with limited SOC stock increase with addition of unpyrolyzed organic matter. Conceptual example for a scenario where biochar is added every 3 years and decomposes at 3% per year, compared with annual additions of unpyrolyzed biomass, of which 90% decomposes each year

TABLE 2 Mean residence time (MRT) of biochars, limited to studies >150 days duration

| Study (experiment period) | Feedstock | Pyrolysis temperature | | MRT (years) | Soil | Study (experiment period) | Feedstock | Pyrolysis temperature | | MRT (years) |
|-----------------------------------|-------------------------------|-----------------------|------|-------------|--------------------|-----------------------------------|---------------------------|-----------------------|------|-------------|
| | | (°C) | (°C) | | | | | (°C) | (°C) | |
| Maestrini et al. (2014) | Ryegrass | 450 | | 40 | Cambisol without N | Zimmerman (2010) | Oak | 650 | | 5652 |
| (158 days) | Ryegrass | 450 | | 40 | Cambisol with N | (365 days) | Grass | 650 | | 370 |
| Santos et al. (2012) | Pine | 450 | | 605 | Granitic soil | | Cedar | 650 | | 15621 |
| (180 days) | Pine | 450 | | 389 | Andesitic soil | | Bubinga | 650 | | 3937 |
| Nguyen et al. (2014) | Switchgrass | 475 | | 163 | Typic Hapludalf | | Sugar cane | 650 | | 7430 |
| (189 days) | Switchgrass | 475 | | 138 | Aquic Hapludult | Weng et al. (2015) | <i>Eucalyptus saligna</i> | 450 | | 484 |
| | Switchgrass | 475 | | 129 | Lithic Dystrudept | (388 days) | <i>E. saligna</i> | 450 | | 449 |
| | Switchgrass | 475 | | 113 | Ultic Hapludalf | Wu et al. (2016) | Rice straw | 500 | | 857 |
| Naisse et al. (2015) ^a | Maize silage | 1200 | | 105 | Cambisol | (390 days) | Rice straw | 500 | | 2829 |
| (222 days) | Maize silage (weathered) | 1200 | | 211 | Cambisol | | Rice straw | 500 | | 1896 |
| Bai et al. (2013) ^a | <i>Miscanthus × giganteus</i> | 575 | | 28 | Inceptisol | | Rice straw | 500 | | 971 |
| (200 days) | <i>Miscanthus × giganteus</i> | 575 | | 33 | Mollisol | | Rice straw | 500 | | 617 |
| | <i>Miscanthus × giganteus</i> | 575 | | 64 | Inceptisol-Aquept | Herath et al. (2015) ^a | Corn stover | 350 | | 91 |
| Budai et al. (2016) | Corn cob | 369 | | 252 | Inceptisol | (510 days) | Corn stover | 350 | | 91 |
| (364 days) | Corn cob | 416 | | 143 | Inceptisol | | Corn stover | 550 | | 91 |
| | Corn cob | 562 | | 191 | Inceptisol | | Corn stover | 550 | | 91 |
| | Corn cob | 580 | | 138 | Inceptisol | Major et al. (2010) | Old mango tree | 400–600 | | 600 |
| | Corn cob | 796 | | 149 | Inceptisol | (730 days) | | | | |
| | <i>Miscanthus × giganteus</i> | 235 | | 4 | Inceptisol | Fang et al. (2014) ^a | <i>E. saligna</i> | 450 | | 456 |
| | <i>Miscanthus × giganteus</i> | 369 | | 172 | Inceptisol | (730 days) | <i>E. saligna</i> | 450 | | 342 |
| | <i>Miscanthus × giganteus</i> | 385 | | 165 | Inceptisol | | <i>E. saligna</i> | 450 | | 342 |
| | <i>Miscanthus × giganteus</i> | 416 | | 118 | Inceptisol | | <i>E. saligna</i> | 450 | | 342 |
| | <i>Miscanthus × giganteus</i> | 503 | | 125 | Inceptisol | | <i>E. saligna</i> | 550 | | 913 |
| | <i>Miscanthus × giganteus</i> | 600 | | 232 | Inceptisol | | <i>E. saligna</i> | 550 | | 913 |
| | <i>Miscanthus × giganteus</i> | 682 | | 123 | Inceptisol | | <i>E. saligna</i> | 550 | | 685 |

TABLE 2 (Continued)

| Study (experiment period) | Feedstock | Pyrolysis temperature (°C) | Soil | MRT (years) | Study (experiment period) | Feedstock | Pyrolysis temperature (°C) | Soil | MRT (years) |
|-----------------------------------|------------|----------------------------|--------------------|-------------|---------------------------------------|--------------------------|----------------------------|----------|-------------|
| Maestriani, Abiven, et al. (2014) | Pine | 450 | Cambisol without N | 191 | | <i>E. saligna</i> | 550 | Vertisol | 685 |
| (365 days) | Pine | 450 | Cambisol with N | 430 | Zimmerman and Gao (2013) ^a | Grass | 650 | Sand | 104167 |
| Zimmerman (2010) | Pine | 400 | Sand | 1280 | (1173 days) | Oak | 650 | Sand | 588 |
| (365 days) | Oak | 400 | Sand | 1263 | Singh et al. (2012) | <i>E. saligna</i> | 400 | Vertisol | 294 |
| | Grass | 400 | Sand | 793 | (1829 days) | <i>E. saligna</i> leaves | 400 | Vertisol | 270 |
| | Cedar | 400 | Sand | 3967 | | Poultry litter | 400 | Vertisol | 129 |
| | Bubinga | 400 | Sand | 2532 | | Cow manure | 400 | Vertisol | 90 |
| | Sugar cane | 400 | Sand | 2740 | | <i>E. saligna</i> | 550 | Vertisol | 1616 |
| | Pine | 525 | Sand | 2928 | | <i>E. saligna</i> leaves | 550 | Vertisol | 572 |
| | Oak | 525 | Sand | 3223 | | Poultry litter | 550 | Vertisol | 396 |
| | Grass | 525 | Sand | 1218 | | Cow manure | 550 | Vertisol | 313 |
| | Cedar | 525 | Sand | 3465 | | Papermill sludge | 550 | Vertisol | 102 |
| | Sugar cane | 525 | Sand | 1829 | Kuzyakov et al. (2009) (1181 days) | Ryegrass | 400 | Luvisol | 200 |
| | Pine | 650 | Sand | 2284 | Kuzyakov et al. (2014) (3100 days) | Ryegrass | 400 | Luvisol | 402 |

^aWhere not stated by the authors, we calculated MRT as the inverse of the degradation constant k_2 , based on a two-pool exponential model.

can reduce the mineralization of biochar-C; thus, persistence is likely to be greater in soils dominated by minerals that form stable aggregates (kaolinite and sesquioxides), such as Oxisols and Ultisols (Fang et al., 2015; Fungo et al., 2017; Weng et al., 2017). There is some evidence that biochar persistence decreases as ambient temperature increases (Fang et al., 2017). The movement of biochar through the soil profile can increase persistence in some soil types (Singh et al., 2015).

4.2 | Priming effects

Change in the mineralization rate of SOM induced by organic or mineral amendments is known as “priming” (Kuzyakov et al., 2000). Historical addition of pyrogenic organic matter has been shown to slow SOM mineralization and enhance native soil organic C (SOC) stocks (Borchard et al., 2014; Downie et al., 2011; Hernandez-Soriano et al., 2016; Kerré et al., 2016; Liang et al., 2010). The direction of priming can be positive or negative, with an increase or decrease of SOM mineralization, respectively. Priming effects of biochar are reviewed in more detail in Text S3. Meta-analyses show that biochar application commonly induces positive priming initially (for 20 days: Maestrini et al., 2015; 2 years: Ding et al., 2018), followed by negative priming, of 3.8% on average (Wang et al., 2016). Wang et al. (2016) further identified that biochar decreased SOM mineralization by 20% with crop residue biochars, 19% with fast pyrolysis biochars, 19% with low temperature biochars (200–375°C), and 12% with low biochar application rates (0.1%–1% w/w) but increased SOM mineralization by 21% in sandy soils. Ding et al. (2014) found that the magnitude of negative priming increased with increasing pyrolysis temperature, time following biochar application, and soil clay content >50%, but decreased with an increasing C:N ratio of soil.

Mechanisms for biochar-induced positive priming include direct effects from: (1) greater microbial activity and enzyme production fueled by the addition of the easily mineralizable C from biochar (Luo et al., 2013; Singh & Cowie, 2014; Section 2.1), and (2) microbial nutrient mining (e.g., N and P); and indirect effects such as (1) amelioration of acidity by biochar that promotes microbial activities (Luo et al., 2011), (2) amelioration of nutrient constraints (Mukherjee & Zimmerman, 2013), (3) enhanced microbial habitat (Luo et al., 2013; Pokharel et al., 2020) and soil faunal activity, and (4) much better aeration because of increased size and stability of macroaggregates and lower soil bulk density, all leading to increased microbial activities.

Biochar can cause negative priming directly by (1) substrate switching where the easily mineralizable C from biochar may be preferentially consumed by microbes

to temporarily replace the use of SOC (DeCiucies et al., 2018; Kuzyakov et al., 2000) and (2) a dilution effect of substrates where added biochar temporarily reduces the mineralization of the more readily mineralizable C in soil (Whitman et al., 2014) and indirectly from (3) the sorption of organic compounds by biochar (DeCiucies et al., 2018; Kasozi et al., 2010), (4) improved organo-mineral protection and stable aggregation slowing down the mineralization of SOC within the organo-mineral complexes (Fang et al., 2018; Weng et al., 2017, 2018), and (5) inhibition of microbial activity by polyaromatic toxic compounds (Zhang et al., 2018). Biochar amendments reduced the activities of soil enzymes associated with C cycling by 6% (Zhang et al., 2019), improved C-use efficiency (Liu, Zhu, et al., 2019, 2020), increased soil microbial biomass (Li et al., 2020), and lowered the metabolic quotient by 12%–21% (i.e., respiration rate CO₂-C per unit of microbial biomass C) compared with the unamended soils (Zhou, Zhang, et al., 2017), the latter attributed to improved microbial habitats and alleviation of environmental stresses including acid soil constraints. Negative priming is found to result mainly from substrate switching (Ventura et al., 2019) and dilution (DeCiucies et al., 2018) in the short term, with adsorption being more important after several weeks.

Biochar can affect new additions to soil of plant-derived C, and these rhizodeposits can also prime and act as a source of SOC. In a subtropical pasture on a Rhodic Ferralsol, a ¹³C-depleted hardwood biochar (450°C) initiated positive priming up to 0.15 Mg C ha⁻¹ over 62 days, switching to negative priming after 188 days in the presence of plants (Weng et al., 2015). Biochar builds SOC through soil aggregation processes that stabilize new C (i.e., rhizodeposits), by 6%–16% (Ventura et al., 2019; Weng et al., 2015, 2017), as well as by reducing priming caused by plant C input (Whitman et al., 2014). In a 6-year field experiment where woody biochar was applied to corn and bioenergy crops, SOC stocks increased by 14 Mg C ha⁻¹, twice the quantity of C added in the biochar, as a result of negative priming (Blanco-Canqui et al., 2020). Figure 4 illustrates how biochar application can lead to accumulation of SOC stocks through biochar-induced negative priming and enhanced retention of rhizodeposits.

4.3 | Effect on GHG emissions

The complex soil microbial communities that produce and consume N₂O and CH₄ in soil and the interrelated biotic and abiotic processes that take place, make predicting GHG emissions from soil extremely challenging. Microbiological N transformations are the main source of N₂O emissions from soil, with autotrophic nitrification

and heterotrophic denitrification being the main N_2O formation pathways. Biochar can lower denitrification (the reduction of NO_3^- to N_2) by: (i) facilitating the last step of denitrification (the transformation of N_2O to N_2), and (ii) decreasing total denitrification activity (Cayuela et al., 2013; Weldon et al., 2019). Biochar can facilitate the reduction of N_2O to N_2 via: (i) increasing pH in acid soils (Obia et al., 2015) thus enhancing the *nosZ* gene (Harter, Guzman-Bustamante, et al., 2016); (ii) changing the relative abundance and composition of N_2O -reducing microbial communities (Harter, Weigold, et al., 2016); and (iii) facilitating extracellular electron exchange (Chen et al., 2014) or directly donating electrons to denitrifying bacteria (Pascual, Sánchez-Monedero, Cayuela, et al., 2020). The decrease in denitrification may result from decrease in availability of NO_3^- and bioavailable C substrate (Fiorentino et al., 2019; Hagemann, Kammann, et al., 2017; Heaney et al., 2020). Abiotic processes, in particular with biochars containing high Fe and Mn content (see Section 2.2.1), can directly catalyze the reduction of N_2O to N_2 . It has also been shown that N_2O can be transformed to NH_3 , pyridine, or pyrrole compounds on biochar surfaces, thus decreasing N_2O emissions (Quin et al., 2015).

Several meta-analyses have synthesized the results of studies on effects of biochar on soil GHG emissions, and sought to explain the differences between individual studies. Although there are gaps in process understanding, and identification of best management practices, there is solid evidence that biochar can mitigate soil N_2O and CH_4 emissions from soil, at least in the short and medium term (Borchard et al., 2019; Cayuela et al., 2014, 2015; Fan et al., 2017; Jeffery et al., 2016; Liu, Liu, et al., 2019; Liu, Zhang, et al., 2018; Verhoeven et al., 2017).

Early meta-analyses on N_2O emissions showed very high mitigation (around 50% reductions) of N_2O with biochar (Cayuela et al., 2014, 2015). These studies included laboratory experiments performed under controlled conditions, and with very high biochar application rates ($>100 \text{ Mg ha}^{-1}$). A direct correlation between application rate and N_2O decrease was found (Cayuela et al., 2014), with lower N_2O mitigation (average 27%) under more realistic rates equivalent to $10\text{--}20 \text{ Mg ha}^{-1}$. Most experiments included in these meta-analyses were carried out under high moisture conditions favoring denitrification, where biochar is most effective in decreasing N_2O emissions (Cayuela et al., 2013; Weldon et al., 2019).

Later meta-analyses including a larger number of field studies and more realistic biochar application rates found lower average reductions, of 12% (Verhoeven et al., 2017) considering only field studies, and 38% (Borchard et al., 2019) including laboratory and field studies. This contrasts sharply with other (unpyrolyzed) organic amendments. For

example, a meta-analysis on manure application to soil found an average increase of 33% in N_2O emissions compared to synthetic fertilizer (Zhou, Zhu, et al., 2017). Even high C:N amendments that tend to immobilize N in soil have been found to increase N_2O emissions. For instance, Xia et al. (2018) found an average increase of 22% in N_2O emissions when straw was applied. Therefore, although the averaged numbers differ between meta-analyses depending on the criteria for the inclusion of studies and the methodology used, there is strong evidence that biochar amendment reduces (on average) direct N_2O emissions from soil particularly when compared to other organic amendments.

Biochars produced by slow pyrolysis, with high degree of carbonization, high pH, and high surface area, are most effective in suppressing N_2O emissions (Borchard et al., 2019; Cayuela et al., 2015; Weldon et al., 2019). A dose of $10\text{--}20 \text{ Mg ha}^{-1}$ has been found to significantly reduce N_2O emissions (Borchard et al., 2019; Cayuela et al., 2014). The effect of biochar might diminish with time, as biochar ages in soil (Borchard et al., 2019; Fungo et al., 2017; Liu, Zhang, et al., 2018). Nevertheless, the mitigation provided initially can be substantial, and repeated applications may maintain the mitigation benefit.

The impact of biochar on CH_4 fluxes has been widely evaluated in paddy and non-flooded soils. Whereas non-flooded soils mostly act as a sink of atmospheric CH_4 , paddy soils can be a significant source of CH_4 . Several meta-analyses found that, on average, biochar mitigates CH_4 emissions from flooded soils, particularly from acidic soils, but decreases the CH_4 sink of non-flooded soils (Jeffery et al., 2016). Ji et al. (2018) cautioned that the co-application of biochar with nitrogen fertilizers substantially decreased the effectiveness of biochar in reducing soil CH_4 emissions from paddies, however, their meta-analysis also showed that the biochar-induced decrease in CH_4 uptake by non-flooded soils was lessened when N fertilizer was also applied. Further, a recent study demonstrates the relevance of biochar properties to the effect on soil CH_4 uptake rates: biochars with high electrical conductivity and ash concentrations decreased CH_4 sink capacity whereas biochars from woody materials pyrolyzed at high temperatures and with high pore area increased soil CH_4 uptake rates (Pascual et al., 2020). Qian et al. (2014) found a decrease in N_2O and CH_4 emissions from paddy soil when a range of biochar-based BCFs was compared with NPK fertilizers.

4.3.1 | GHG intensity and yield-scaled emissions

To avoid overlooking potential trade-offs with crop yields, studies report GHG intensity (GHG per unit crop yield)

(Mosier et al., 2006) or yield-scaled emissions for N₂O (i.e., N₂O emissions in relation to N uptake of the above-ground crop) (Van Groenigen et al., 2010). Analyses of specific cropping systems show a decrease in GHG intensity with biochar application in vegetable fields (Fan et al., 2017) and in wheat–rice rotation systems (Wu et al., 2019). One of the first studies summarizing results on yield-scaled N₂O emissions was performed by Verhoeven et al. (2017) who found that biochar decreased yield-scaled N₂O emissions across the majority of the studied cropping systems, although a meta-analysis could not be carried out due to the low number of field studies and excessively high variance between studies. Later, Liu, Mao, et al. (2019) were able to incorporate a larger number of studies and showed an overall reduction of GHG intensity by 29% after biochar amendment, with higher reductions in non-flooded soils (−41%) compared to paddy fields (−17%). A meta-analysis focusing on vegetable fields in China also found that biochar application decreased yield-scaled N₂O emissions by an average of 35% (Gu et al., 2020).

4.3.2 | Potential trade-offs between C sequestration and non-CO₂ GHG emissions

In order to evaluate the full net GHG balance of biochar in soil, the fluxes of CH₄ and N₂O and the changes in SOC stocks need to be jointly assessed. Usually, CH₄ and N₂O emissions are expressed in CO₂-equivalents using 100-year global warming potential. In non-flooded soils, the relationship between SOC changes and N₂O emissions usually regulates the net GHG emission, since agricultural soils are often weak CH₄ sinks. One of the greatest difficulties for the comprehensive analysis of the balance between C sequestration and N₂O emission lies in the need for long-term studies to measure changes in SOC reserves (Smith et al., 2020) and the laborious nature of direct measurements of N₂O, which makes long-term N₂O studies (>10 years) very rare.

An increase in SOC is often associated with higher N₂O emissions, which could counteract the mitigation benefits derived from C sequestration (Davies et al., 2020). However, it is precisely in these trade-offs where biochar might have the greatest advantage compared to other soil amendments and other SOC sequestration strategies. Although a comprehensive meta-analysis on these trade-offs has not been published yet, results from separate meta-analyses on C sequestration (Bai et al., 2019) and N₂O emissions (Borchard et al., 2019; Liu, Liu, et al., 2019) point to a strong synergy between C sequestration and mitigation of N₂O emissions with biochar, which is much less evident for other SOC sequestration strategies (Guenet et al., 2021).

5 | BIOCHAR'S ROLE IN THE CIRCULAR ECONOMY

The circular economy concept aims to conserve resources, and minimize inputs and waste. Biochar can support the development of a circular economy at regional and farm scale by improving nutrient recovery and nutrient use efficiency. The economic case for biochar production is strongest for biochar made from residue materials, especially when the residues contain high concentrations of nutrients, such as animal manures and sewage sludge. Concerns that these feedstocks may contain contaminants restrict their beneficial reuse. Fortunately, most organic contaminants are destroyed with high efficiency during pyrolysis, by thermal degradation and volatilization followed by destruction during vapor combustion. This has been shown for PAHs (Zielińska & Oleszczuk, 2015), polychlorinated biphenyls (Bridle et al., 1990), per- and polyfluoroalkyl substances (PFAS; Kundu et al., 2021), microplastics (Ni et al., 2020), antimicrobials (Ross et al., 2016), antibiotics (Tian et al., 2019), antibiotic resistance genes (Kimbell et al., 2018), and hormones (estrogen; Hoffman et al., 2016).

While incineration destroys organic contaminants with similar efficiency to pyrolysis (Baukal et al., 1994), unlike incineration, pyrolysis retains a large portion of the feedstock C (typically around 50%), and most nutrients, in the biochar. In addition, pyrolysis gases can be captured for use as a renewable energy product (see Text S4). Of the main plant nutrients, P and K are fully retained in biochar at typical pyrolysis temperatures (300°–700°) (Bridle & Pritchard, 2004; Buss et al., 2016). Nonetheless, 50%–80% of N can be lost (Hossain et al., 2011; Ye et al., 2020; Yuan et al., 2018) depending on the N content of the feedstock (Torres-Rojas et al., 2020), with greater loss at high pyrolysis temperature. A meta-analysis found N, P, and K concentrations in biochars of 1.0%, 0.4%, and 1.9% (wood-derived biochars), 1.5%, 0.8%, and 4.1% (crop residue biochars) and 2.4%, 2.6%, and 2.5% (manure/sewage sludge biochars), respectively (Ippolito et al., 2020).

Notably, some sewage sludge biochars contain as much as 6%–20% total P (Faria et al., 2018; Roberts et al., 2017; Shepherd et al., 2016; Zhang et al., 2015). However, only a fraction of the total nutrients in biochar is available for plant uptake (in the short-medium term), in the order K>P>N. A meta-analysis found that, on average, the following percentages of the N, P and K present in biochar were bioavailable: 0.5%, 3%, and 9% (wood-derived biochar), 0.4%, 6%, and 22% (crop residue biochar) and 5%, 5%, and 17% (manure/sewage sludge biochar), respectively (Ippolito et al., 2020).

Biochar P availability can be increased by selecting low Ca feedstocks or doping feedstock with K, leading to preferential binding of P with K instead of Ca, Mg, Fe, or Al,

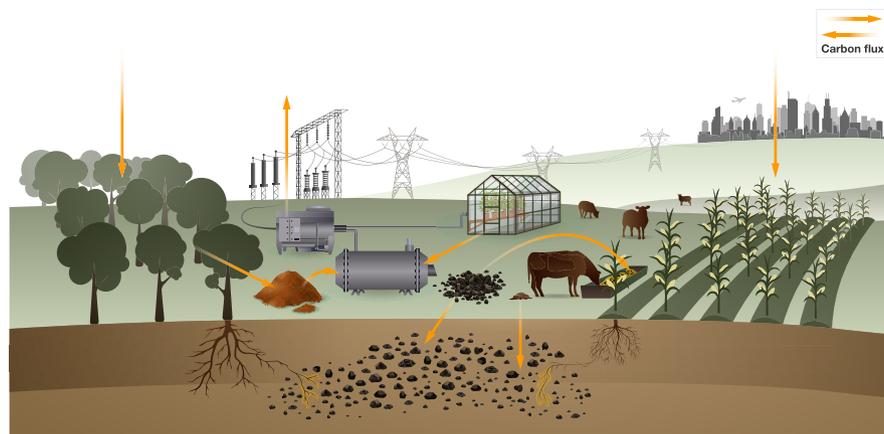


FIGURE 5 Biochar systems utilize organic residues, including forest, crop, and horticultural residues, to produce biochar that is used as a soil amendment directly, and indirectly via feeding to livestock. Pyrolysis gases and process heat, co-products of biochar production, can be used to supply renewable energy

forming highly soluble salts (Buss et al., 2020). Biochars can be optimized to sorb P or N from wastewater and hence be loaded with extra nutrients that are accessible to plants (Mood et al., 2020; Shang et al., 2018; Shepherd et al., 2016, 2017), reducing wastewater P and N concentrations, preventing eutrophication, and returning nutrients to agricultural land.

Controlled release biochar-fertilizer combinations can be produced from low-nutrient biomass mixed with mineral or organic nutrients before pyrolysis and/or organic nutrients after pyrolysis, or by composting to enrich with nutrients (Buss et al., 2019, 2020; Dong et al., 2019; Hagemann, Joseph, et al., 2017; Schmidt et al., 2015) and these can be effective at low application rates when applied in a band near the seed/plant (Qian et al., 2014; Schmidt et al., 2015; Yao et al., 2015; Zheng et al., 2017).

The use of biochar in composting of organic residues such as manures can reduce N losses through volatilization and leaching, reduce GHG emissions, increase C persistence, and reduce availability of heavy metals (Agyarko-Mintah et al., 2017; Akdeniz, 2019; Oldfield et al., 2018; Sanchez-Monedero et al., 2018).

Biochars, including BCFs and biochar used as a compost additive, thus improve nutrient recovery from organic residues, facilitate use of residues in soil amendment, and reduce environmental impacts of waste management. Biochar systems (Figure 5) thereby contribute to building a circular economy.

6 | CONCLUSION AND RECOMMENDATIONS

Soil and plant responses to addition of biochar can be negative, positive, or neutral, depending on many variables, including feedstock and pyrolysis temperature, application

rate and method, and application context (crop, soil type, and environmental and biological stresses). Considering the heterogeneous nature of biochars and the complexity of the physical, biochemical, and microbiological processes underpinning the effects of biochars, reviewed above, it is not surprising that studies report a wide range of responses to biochar application. Results are also strongly influenced by experimental design aspects; studies that do not include plants, or are undertaken in soil-less media, or based on pot trials cannot readily be extrapolated to field situations.

Scientific understanding of the biochar–soil–plant processes and interactions has evolved over the last decade, providing the basis to interpret the divergent results in the literature and identify optimal uses of biochars. The following encapsulates current knowledge, as reviewed in this paper. Biochar catalyzes microbial and abiotic processes in the rhizosphere, decreasing the activation energy for biotic and abiotic reactions, which can increase nutrient mineralization and facilitate nutrient uptake by plants. Higher microbial activities lead to accelerated turnover of organic matter which enhances nutrient supply. Biochar reduces the availability of heavy metals, increases plant resistance to disease, and improves resilience to environmental stressors. The microscale processes on the biochar surface and in the rhizosphere mediate the macro responses of plants to biochar. The catalytic ability of biochar changes as it ages in soil through oxidation and interactions with minerals, microbes, soil fauna, and organic matter.

Significant yield increases occur where site-specific soil constraints, nutrient and water limitations are addressed by appropriate biochar formulations applied at an optimal application rate. Meta-analyses of crop responses to biochar show average yield increases of 10%–42%, with greatest responses in acidic and sandy soils where the biochar has been applied with organic and/or mineral fertilizers. On average, biochars

increase P availability by a factor of 4.6, decrease plant tissue concentration of heavy metals by 17%–39%, build SOC through negative priming by 3.8% (range –21% to +20%), and reduce non-CO₂ GHG emissions from soil by 12%–50%.

To enable widespread adoption, biochar needs to be readily integrated with farming operations, and be economically viable. Formulations that combine biochar with mineral and/or organic fertilizers and minerals are likely to have high nutrient use efficiency and be the most cost-effective. Such formulations are the major focus of commercialization, but they have received limited attention in research studies, and very few field trials have been undertaken.

Knowledge gaps remain regarding biochar–soil–plant interactions in the field over the longer term, including longevity of yield response and reduction of N₂O emissions; the direction, magnitude, and duration of organic matter priming; and long-term effects of repeated applications. Research is needed on processes that influence the capture and release of heavy metals in the long term to determine optimum scheduling of re-application of biochar. Further research on the effects of biochar properties on root membrane potential and microbial nutrient cycling will inform the development of optimal formulations to increase nutrient uptake efficiency.

We recommend that guidelines on selecting and producing biochar formulations to meet specific soil and environmental constraints and increase farm profitability be developed, based on the findings of this review. Biochars can be tailored for specific applications through feedstock selection; by modifying process conditions; through pre- or post-production treatments to adjust pH, increase nutrient level and availability, carbon persistence and adsorptive properties; or co-application with organic or mineral fertilizers. Use of biochar in waste management, such as co-composting of animal manures and pyrolysis of sewage sludge, can capture nutrients and reduce GHG emissions.

This review presents strong evidence that biochar can contribute to climate change mitigation through carbon sequestration and reduction in soil GHG emissions, and that significant benefits to plant production are possible, particularly where site-specific soil constraints and nutrient and water limitations are addressed by appropriate biochar and fertilizer applications. Biochar has the greatest potential to increase crop yields in low-nutrient, high P-fixing acidic soils, common in the tropics and humid subtropics, and in sandy soils, particularly in dryland regions that are likely to be increasingly affected by drought under climate change. Biochar can also mitigate heavy metal pollution, that impacts food production and food safety in many developing countries, and enhance resource use efficiency. Thus, biochar can play a key role in addressing climate change and supporting global food security and the circular economy.

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CONFLICT OF INTEREST

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DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created in this study.

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SUPPORTING INFORMATION

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