The 3R Principles for Applying Biochar to Improve Soil Health

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Abstract: Amending soil with biochar is a promising approach to persistently improve soil health and promote crop growth. The efficacy of soil biochar amendment, however, is soil specific, biochar dependent, and influenced by the biochar application programs. To maximize the benefits of biochar application, this paper proposes the 3R principles for applying biochar to soils: right biochar source, right application rate, and right placement in soil. The quality of biochar as a soil amendment varies significantly with the feedstock and the production conditions. Biochar products capable of everlastingly sustaining soil health are those with high stable organic carbon (OC) content and high water- and nutrient-holding capacities that are manufactured from uncontaminated biomass materials. Acidic, coarse-textured, highly leached soils respond remarkably more to biochar amendment than other types of soils. Soil amendment with particular biochars at as low as 0.1 mass% (equivalent to 2 Mg ha\(^{-1}\)) may enhance the seasonal crop productivity. To achieve the evident, long-term soil health improvement effects, wood- and crop residue-derived biochars should be applied to soil at one time or cumulatively 2–5 mass% and manure-derived biochars at 1–3 mass% soil. Optimal amendment rates of particular biochar soil systems should be prescreened to ensure the pH of newly treated soils is less than 7.5 and the electrical conductivity (EC) below 2.7 dS m\(^{-1}\) (in 1:1 soil/water slurry). To maximize the soil health benefits while minimizing the erosion risk, biochar amendment should be implemented through broadcasting granular biochar in moistened conditions or in compost mixtures to cropland under low-wind weather followed by thorough and uniform incorporation into the 0–15 cm soil layer. Biochars are generally low in plant macronutrients and cannot serve as a major nutrient source (especially N) to plants. Combined chemical fertilization is necessary to realize the synergic beneficial effects of biochar amendment.

Keywords: biochar source; pyrolysis completeness; application rate; placement; soil health

1. Introduction

As a legacy of ancient inhabitants who added biomass-derived char to barren land, Terra Preta (in Portuguese meaning “dark earth”) in the central Amazon basin remains more productive relative to the surrounding highly leached, strongly acidic Oxisols and Ultisols [1–4]. The discovery implicates that biochar is an effective amendment for persistently enhancing and sustaining soil health—“the continued capacity of soil to function as a vital living ecosystem that sustains plants, animals, and humans” [5]. Decades of intensive research have indicated that biochar, “the fine-grained or granular charcoal made from heating vegetative biomass, bones, manure solids, or other plant-derived organic residues in an oxygen-free or oxygen-limited environment and used as a soil amendment for agricultural and environmental purposes,” is capable of improving soil health by ameliorating soil physical, chemical, and biological properties [6–9]. In general, biochar is porous, environmentally recalcitrant (stable), and high in specific surface area (SSA) and cation exchange capacity (CEC) [10–12]. Amendment with biochar reduces the bulk density and increases the water- and nutrient-retention of major agricultural soils [6]. Biochar, however, extends to
a wide range of charcoal products from thermochemical treatments (i.e., pyrolysis and gasification) of diverse biomass materials. Depending on the feedstock source and the production conditions, biochar products may vary significantly in quality characteristics and, consequently, in the capability to enhance soil health. For instance, biochars derived from manures generally contain more nutrients on the dry mass basis than those derived from wood [13–15], while the products manufactured at higher pyrolysis temperature typically possess greater stable C fraction and higher mineral nutrient contents (except for N) than the ones from the same feedstock processed at lower pyrolysis temperature [10,16]. After applied as a soil amendment in crop production and abandoned land reclamation, different biochars exhibited noticeably dissimilar capabilities for improving soil health properties and promoting plant growth [17–19]. The quality variation of differently sourced biochars is a major reason for justifying the inconsistence of reported research results on biochar amendment enhancing soil health and promoting crop growth [6–8].

The effects of biochar amendment on soil health also vary with the soil type and the amendment rate. Biochars normally have a high pH (1:10 w/w water extract) in the range of 8–11 [6,13]. For acidic soils, biochar amendment reduces the soil acidity and subsequently improves the soil health; for alkaline soils, however, addition of biochar with significant liming values may deteriorate the overall soil health by introducing additional alkalinity. Addition of biochar typically increases the water-holding capacity (WHC) of coarse textured soils but influences little or even decreases the WHC of clayey or organic matter-rich soils [20,21]. At different application rates ranging from 0.5 mass% to 10.0 mass%, biochar amendments altered soil physical, chemical, and biological properties to different extents [22–24]. When the application rate was too low or too high (varying with the biochar source and the soil type), the biochar effect on modifying the soil health became either insignificant or even unfavorable [9,25–27], respectively.

The 4R nutrient stewardship guidelines have been extensively followed in fertilizer application to manage soil nutrients for achieving maximal crop productivity and minimal environmental impacts: right fertilizer source, right application time, right application rate, and right placement to crops [28]. If any of the 4Rs is not scientifically determined to be “right”, the entire fertilization program becomes “wrong” toward crop production and natural water production [29]. Similarly, biochar amendment to attain best soil health and crop productivity improvement effects also warrants the scientific selection on the biochar source, application rate, and biochar placement in soil. To date, however, there are no guidelines developed for practitioners to apply biochar for its optimal agricultural and environmental benefits. A common myth among crop producers and the general public is that “biochar is a miraculous material. Once applied with biochar, the soil will be forever fertile and no fertilizers are needed any longer.” Such understanding on biochar and expectations from biochar amendment were constantly negated by the real results, discouraging triers and impacting the extensive adoption of biochar as a soil amendment. This paper is to propose and elucidate the 3R (right source, right rate, and right placement) principles for applying biochar to persistently improve soil health, with an additional aim to provide a better understanding of biochar and biochar application.

2. The Mechanisms for Biochar to Improve Soil Health

The health of a soil in a defined ecosystem describes how well the soil can fulfill its environmental functions: supporting plant growth, regulating water movement, recycling wastes, harboring living organisms, and buffering the atmospheric composition [30]. Soil health is a comprehensive expression of and also determined by the soil composition and properties. An array of soil physical, chemical, and biological properties have been adopted in the soil health assessment system, including soil pH, salinity, sodicity, organic matter content, penetration resistance (hardness), bulk density, structure, aggregate stability, available water capacity, infiltration rate, CEC, erosion rating, root health rating, active carbon content, protein content, respiration rate, presence of earthworms, potentially mineralizable N content, available plant nutrient contents, and toxic element contents [31–33]. Recommended management practices to improve and sustain soil health extend to crop rotation, cover crop planting, conservation tillage, land application of crop residues, manure, and organic composts, agronomic fertilization, liming, and biochar amendment [33,34].
Biochar amendment enhances the overall health of a soil by rectifying its physical, chemical, and biological properties to plant favorable conditions. The environmentally recalcitrant material possesses remarkable water-holding and nutrient-retention capacities, able to help soil conserve water and nutrients [34]. Research has demonstrated that appropriate biochar amendment reduces soil bulk density and penetration resistance, increases soil porosity and hydraulic conductivity, and enhances soil aggregate stability and available water capacity (AWC) [20,35]. Biochar amendment also reduces soil acidity, elevates soil CEC, and improves soil fertility by introducing mineral nutrients and mitigating nutrient leaching losses [36]. Biochar amendment further furnishes degradable organic carbon (OC) to soil organisms and provides more favorable habitats to microbes and, therefore, facilitates soil biological activities [37]. As biochar can persist in natural soils for hundreds of years, the effect of biochar application on soil health improvement is of desirably long-term.

It is noteworthy that biomass residue-derived biochars are typically low in plant nutrients (particularly N) and, therefore, cannot serve as a major nutrient source to take place of chemical fertilizers in modern crop production. For instance, biochars manufactured from waste wood contained <0.3% N and <0.04% P [15]. Crop residue-based biochars (e.g., from peanut hulls, rapeseed straw, wheat straw, corn stover, and switchgrass) showed a total N content <2.7% and a total P content <1.3% [11,16,38,39]. Even manure-derived biochars (e.g., from pig manure solids, cow manure, and poultry litter) contained total N <4.2% and total P <3.2% [10,14,40]. Manure- and animal bones-derived biochars may contain plant nutrients (e.g., P, K, Ca, S, B, Zn, and Cu) at considerable levels [10,41,42] and function as a supplemental nutrient source to crops. The fertilization effect of biochar through releasing the inherent nutrients, however, is temporary, diminishing over time and being invident after one or a few growing seasons. It is the relatively high WHC and nutrient-retention capability of biochar that enable the material to facilitate soil health and crop growth. Soils amended with biochar at significant rates demonstrated noticeable improvements in AWC [43] and reductions in nutrient leaching losses [44,45]. Biomass residue-derived compost possesses comparable or even higher WHC and nutrient-retention capability, yet biochar is more advantageous owning to its high environmental recalcitrance, able to maintain the soil health improvement effect over hundreds of years [4]. It is the everlasting efficacy that entails biochar a preferred soil amendment. Notable improvements in plant growth and crop yield may be observed soon after manure-derived biochars are applied to soils without chemical fertilization [26]. These improvements are primarily a result of the minor nutrients (e.g., P, K, Ca, Mg, and S) inherent in the biochar as ash components. This kind of obvious plant growth-stimulating effect is rather transient, generally disappearing in one growing season [44]. Biochar amendment may decrease the critical agronomic fertilization rates through reducing soil nutrient leaching losses [45,46]. To pursue the high crop productivity in modern agriculture, chemical fertilization remains essential to biochar-amended soils. Furthermore, the long-term soil health improvement effect of biochar amendment can only be achieved when appropriate selections of the biochar source, application rate, and placement in soil are simultaneously practiced.

3. The Right Biochar Source

Nearly all solid biomass residues serve as potential feedstocks for biochar. In research trials, more than fifty types of biomass residues have been tested to produce biochar, covering wood, forest litter, herbaceous debris, crop residues, yard trimmings, animal manures, sewage sludge, fruit and vegetable peels, nutshell, bones, coffee grounds, and cottonseed meal (Table 1). In commercial biochar production, wood and crop residues are the predominant feedstock due to their high availability and handling convenience. Nevertheless, wood from different tree species (e.g., softwood vs. hardwood) and from different parts or growth stages of a tree (e.g., bark, sapwood, and heartwood) varies in density and chemical constitution [47]. Since biomass materials are diverse in lignocellulosic (i.e., lignin, cellulose, and hemicellulose) and mineral element (e.g., N, P, K, S, Ca, Mg, Na, and Si) compositions, conversion of differently-sourced biomass materials to biochar even under the same carbonization conditions results in products dissimilar in physical and chemical characteristics (Table 1). In general,
biochars derived from higher mineral element feedstocks (e.g., animal manures) demonstrate a higher mineral ash content, pH, lime equivalence, and salinity while a lower OC content, SSA, and WHC than those derived from lower mineral element feedstocks (e.g., wood) (Table 1). Wood- and poultry litter-derived biochars prepared under the same 400 °C slow pyrolysis conditions, for instance, consisted of 76.3% and 36.1% OC, respectively and 4.0% and 56.6% ash minerals, respectively [48]. In addition, the pre-treatment of the feedstock in moisture content, particle size, and particle (envelope) density also impacts the product quality through influencing the carbonization process [13].

Carbonization of biomass residues to biochar is mostly realized through pyrolysis and gasification. Processing biomass materials by torrefaction and hydrothermal liquefaction generates black, char-like solids (so-called biocoal and hydrochar, respectively) that should not be viewed as biochar owing to the low stability of the products in natural soils [52–54]. The carbonization conditions as described in 1:5 solid/water extracts; ¶ Mineral ash content; § at 0.2 bar vacuum suction; CEC: cation exchange capacity; SSA: specific surface area; WHC: water-holding capacity; TN: total nitrogen content; TP: total phosphorus content; TK: total potassium content.

Table 1. Yield and quality variations of biochar as a function of the feedstock and production conditions [13,42,49–51].

| Feedstock          | Production Conditions | Yield† | pH‡ | Ash¶ | CEC cmol, kg⁻¹ | SSA m² g⁻¹ | WHC§ g kg⁻¹ | TN g kg⁻¹ | TP g kg⁻¹ | TK g kg⁻¹ |
|--------------------|-----------------------|--------|-----|------|----------------|------------|-------------|-----------|----------|----------|
| Hard wood 400 °C   | 32.7%                 | 7.5    | 32.0 | 7.9  | 15.6           | 1.40       | 2.5         | 0.18      | 3.0      |          |
| Hard wood 500 °C   | 25.8%                 | 8.2    | 42.0 | 7.5  | 26.6           | 1.44       | 3.0         | 0.34      | 3.6      |          |
| Wood               | For fuel charcoal     | 9.2    | 46.0 | 112  | 7.6            | 0.03       | 0.46        |           |          |          |
| Poultry wood 400 °C| 32.0%                 | 9.0    | 19.0 | 144  | 3.0            | 7.8        | 0.44        | 1.4       |          |          |
| Pine chips 400 °C  | 35.0%                 | 7.6    | 7.3  | 2.6  | 0.15           | 1.4        |            |           |          |          |
| Pine chips 500 °C  | 30.0%                 | 8.3    | 5.0  | 2.2  | 0.16           | 1.5        |            |           |          |          |
| Spruce wood and needle mix 400 °C | 36.0% | 6.9    | 35.0 | 73.5 | 1.8            | 10.2       | 0.44        | 3.3       |          |          |
| Greenwaste 450 °C  | 33.0%                 | 9.4    | 107.6| 24.0 | 7.3            | 11.7       |            |           |          |          |
| Switchgrass 500 °C | 29.0%                 | 8.0    | 78.0 | 62.2 | 4.3            | 2.4        |            |           |          |          |
| Rapeseed straw 400 °C | 39.4% | 122.2  |     | 16.0 | 14.3           |            |            |           |          |          |
| Rapeseed straw 600 °C | 32.2% | 138.5  |     | 17.6 | 15.3           |            |            |           |          |          |
| Wheat straw 400 °C | 34.0%                 | 9.1    | 97.0 | 162  | 4.8            | 10.5       | 1.3         | 19.9      |          |          |
| Corn cobs 450 °C   | 26.4%                 | 10.3   | 65.2 | 71.1 | 11.9           | 2.9        | 25.6        |           |          |          |
| Corn cobs 500 °C   | 18.5%                 | 7.8    | <1.0 | 8.5  | 4.4            | 43.4       |            |           |          |          |
| Corn stover 500 °C | 16.8%                 | 7.2    | 3.1  | 14.7 | 12.9           | 23.5       |            |           |          |          |
| Peanut hulls 400 °C| 40.0%                 | 7.9    | 82.0 | 0.52 | 27.0           | 2.6        |            |           |          |          |
| Peanut hulls 500 °C| 50.0%                 | 8.6    | 93.0 | 1.22 | 20.9           | 2.9        |            |           |          |          |
| Rice husks 600 °C  | 39.0%                 | 9.9    | 470.0| 115  | 11.0           | 0.3        | 4.0         |           |          |          |
| Rice straw 380 °C  | 35.0%                 | 9.2    | 360.0| 38.0 | 13.2           | 9.0        | 3.2         | 33.0      |          |          |
| Cotton stalk 600 °C| 28.0%                 | 10.3   | 95.0 | 121  | 48.0           | 4.8        | 28.5        |           |          |          |
| Cottonseed meal 300 °C | 53.8% | 9.1    | 137.0| <1.0 | 0.99           | 89.8       | 22.7        | 29.6      |          |          |
| Cottonseed meal 400 °C | 40.8% | 10.1   | 173.3| <1.0 | 1.14           | 58.2       | 26.3        | 33.5      |          |          |
| Cottonseed meal 500 °C | 35.1% | 10.2   | 193.0| <1.0 | 1.23           | 24.2       | 27.9        | 38.8      |          |          |
| Cottonseed meal 600 °C | 29.4% | 10.3   | 212.7| <1.0 | 1.31           | 5.0        | 31.3        | 42.4      |          |          |
| Poultry litter 300 °C | 60.1% | 9.5    | 478.7| 51.1 | 2.7            | 41.7       | 22.7        | 69.3      |          |          |
| Poultry litter 400 °C | 56.2% | 10.3   | 566.2| 41.7 | 3.9            | 1.01       | 26.3        | 26.3      | 82.2      |          |
| Poultry litter 500 °C | 51.5% | 10.7   | 605.8| 35.8 | 4.8            | 0.99       | 12.1        | 27.9      | 87.9      |          |
| Poultry litter 600 °C | 45.7% | 11.5   | 607.8| 29.2 | 5.8            | 0.95       | 1.2         | 30.5      | 91.5      |          |
| Pig manure solids 420 °C | 40.3% | 9.7    | 345.0| 21.1 | 35.8           |            |            |           |          |          |
| Cow manure 400 °C  | 9.0                  | 703.0  |     | 13.5 | 4.4            |            |            |           |          |          |
| Sewage sludge 300 °C | 67.5% | 9.7    | 468.0| 36.0 | 79.0           | 7.7        |            |           |          |          |
| Sewage sludge 400 °C | 44.2% | 9.7    | 591.0| 33.0 | 198.0          |            |            |           |          |          |

† Percent of the dry feed mass; ¶ in 1:5 solid/water extracts; § Mineral ash content; ¶ at 0.2 bar vacuum suction; CEC: cation exchange capacity; SSA: specific surface area; WHC: water-holding capacity; TN: total nitrogen content; TP: total phosphorus content; TK: total potassium content.
methods have great impacts on the biochar yield and properties. For example, heating at 105 °C helped remove polycyclic aromatic hydrocarbons (PAHs) and other volatile organic hydrophobics remaining in biochar [57] while water washing reduced the soluble salts and organic toxics [57,58]. Cooling biochar right after carbonization using steam as practiced in many commercial biochar plants drastically increases the biochar SSA. At the cost of a slight yield decrease, this post-treatment engenders activated biochar products by simulating the activation process (using oxidizing agents such as steam, O₂ and CO₂) in activated carbon production [59].

The normal carbonization conditions in thermochemical processing of biomass materials by pyrolysis or gasification are listed in Table 2. There are two types of pyrolysis techniques: slow pyrolysis (aiming at biochar production) and fast pyrolysis (aiming at bio-oil generation). Gasification is targeted at harvesting syngas (a mixture of CO and H₂). Treating organic residues by any of the three thermochemical techniques results in three products: char, pyrolysis bio-oil, and syngas, with the relative proportions shifting as a function of the carbonization conditions [60]. Biochar is the main product from slow pyrolysis yet a byproduct from fast pyrolysis or gasification of biomass residues. The peak temperature of slow pyrolysis for producing biochar covers a wide range from 300 to 700 °C, the heating rate (the speed of temperature rising in the center of feedstock particles in response to heat diffusion from the reactor) varies from <1 °C/s to >50 °C/s, and the solid residence time (for the feedstock to undergo pyrolytic decomposition in the reactor) may extend from minutes to days (Table 2). The feedstock characteristics such as particle size, density, moisture content, and mineral ash composition also influence the carbonization process through interfering with the heating rate [61,62]. Dependent on the design of the carbonization system, air may incidentally enter into the reactor and affect the feed pyrolytic decomposition processes [55]. Any changes in the carbonization conditions and the feedstock preparation generate impacts on the yield and quality of the biochar products (Table 1). The optimal carbonization conditions are target product dependent, feedstock specific, and influenced by the design of the reactors (i.e., pyrolyzers and gasifiers). A higher peak temperature generally facilitates pyrolytic decomposition of organic matter, decreasing the yield while increasing the carbon stability of the biochar products [10,48,49]. At a determined peak temperature, adequate solid residence time is required to reach complete pyrolysis, a status at which the pyrolytic decomposition reactions are finished, the resulting biochar is potentially stabilized, and no further volatiles (e.g., smokes) are generated. The adequate solid residence time, however, is determined by the heating rate which is further controlled by the peak pyrolysis temperature and influenced by the feedstock preparation [13,61,62].

Table 2. The carbonization conditions for thermochemically processing biomass residues using pyrolysis and gasification techniques [13,61].

| Carbonization Technique | Pyrolysis | Gasification |
|-------------------------|-----------|--------------|
|                         | Slow Pyrolysis | Fast Pyrolysis |
| Feed particle size      | Chips to logs for batch reactors | <2 mm | <5 mm |
|                         | <10 mm for moving-bed reactors | 300–500 °C for batch reactors | 500–700 °C for moving-bed reactors |
| Peak temperature        | 500–700 °C for moving-bed reactors | 700–1000 °C | 800–1200 °C |
| Heating rate            | <1 °C/s in batch reactors | >200 °C/s | >500 °C/s |
| Solid residence time    | Minutes in batch reactors | Seconds | <3 s |
| O₂ availability         | O₂-free | O₂-free | Controlled air supply |
| Main product            | Charcoal | Bio-oil | Syngas |
| Byproducts              | Bio-oil and syngas | Char and syngas | Char and bio-oil |
| Char yield†             | 30%–40% for batch reactors | 15%–25% | 5%–15% |
|                         | 25%–33% for moving-bed reactors | | |

The International Biochar Initiative (IBI) suggests the following parameters in biochar quality assessment: pH, lime equivalence, EC, mineral ash content, OC content, SSA, H/OC molar ratio (indicating stability), total and available N, P, Ca, Mg, and S contents, particle size distribution,
germination inhibition assay, and contents of toxic elements and organic contaminants [63]. In addition, the stable proportion of OC, the surface acidic functional groups, CEC, and WHC should be directly measured and included in biochar quality evaluation [10]. The nutrient and water retention capabilities of biochar are largely governed by its CEC and SSA (or porosity). To achieve the long-term promoting effect on soil health, more recalcitrant (stable) biochar is preferred. Nevertheless, up to 65% of the OC in biochar products may be unstable, readily mineralizable to 0.056 M acidic dichromate [10,48]. In wood-derived biochars (OC 720–842 g kg\(^{-1}\)) through 300–600 °C complete slow pyrolysis, the stable proportion of OC ranged from 91.8% to 95.1%, slightly increasing as the pyrolysis temperature was elevated (Figure 1). In wheat straw-derived biochars (OC 658–716 g kg\(^{-1}\)) from the same pyrolysis operations, the stable OC proportion was between 60.2% and 93.5%. In poultry litter-derived biochars (OC 325–380 g kg\(^{-1}\)), the stable OC proportion was in the range of 36.8%–86.3% (Figure 1). Without sufficient stable OC, the biochar products would be slowly mineralized once applied to soil, and the long-term effectiveness for sustaining soil health would be compromised. The pH, EC, lime equivalence, mineral ash content, and nutrient contents of biochar determine its temporary capabilities to neutralize soil acidity, modify soil salinity, and supply plant nutrients and, consequently, generate immediate yet transient effects on soil health and plant growth. In pursuit of the long-term soil conditioning effects, biochar products to be used as a soil amendment may be screened based on their stability [OC content × stable [%100-year soil life] carbon proportion; H/OC molar ratio <0.7] indicating the environmental recalcitrance, SSA or porosity implicating the water-holding capacity, and CEC signifying the nutrient-retention capability [10,49,56,64]. Mineral soils typically have a CEC value of 3–20 cmolc kg\(^{-1}\) (>10 cmolc kg\(^{-1}\) implicating little nutrient leaching risk) and a BET-N\(_2\) adsorption SSA value of 1–8 m\(^2\) g\(^{-1}\) [65,66]. Accordingly, a quality biochar product should be high in CEC (e.g., > 20 cmolc kg\(^{-1}\)), SSA (e.g., >10 m\(^2\) g\(^{-1}\)), and the stable proportion of OC (e.g., >45%). It is worth to mention that after applied to the field, biochar gradually increases its CEC and SSA from the originally low levels as result of natural weathering over time [67]. The unstable biochar OC is actually beneficial to soil microbes by serving as a carbon and energy source. The immediately water-extractable portion of the unstable OC, if at a significant content, can be harmful to seed germination and seedling development [57]. Further research is warranted to examine the effects of water extractable biochar OC on soil microorganisms and crop seedlings.

**Figure 1.** The stable proportion of organic carbon (OC) in biochars derived from waste wood (WW), wheat straw (WS), and poultry litter (PL) through complete slow pyrolysis at 300–600 °C peak temperatures. Error bars represent standard deviation of triplicate measurements. The stable OC content was measured in <0.15 mm sample replicates using the dichromate oxidation methods [10].
Biochar is generally alkaline, demonstrating a pH value (in 1:5 solid/water slurries) in the range of 7.5–11.5 (Table 1). The alkalinity is attributed to the base metal (i.e., Na, K, Ca, and Mg) salts of the biochar mineral ash components that also furnish the biochar liming potential. Occasional acidic biochars with pH < 7.0 are likely products from incomplete pyrolysis (e.g., not adequate reaction time) that carry substantial instable OC and harmful organic acids (e.g., formic acid, acetic acid, hydroxybutyric acid, and benzoic acid) [13,60]. Research trials reported mostly negative responses of common crops to pH < 7.0 biochar amendments [68,69]. The presence of carboxylic groups may even entail biochars a negative value of lime equivalence. In a preliminary study using the HCl titration methods [70], we found that the lime equivalent of a pH 10.2 wood-based commercial biochar was -35.0 mg g⁻¹, while for another pH 9.5 wood-based biochar sample it was 118.1 mg g⁻¹. Though the production conditions of these two biochars were unclear, it could be postulated that most organic acids in biochar were not active in natural circumstances (i.e., insoluble in water at room temperature) but their eventual dissolution in water would generate additional acidity. Manure-derived biochars contain significant contents of slowly releasable P, K, Ca, Mg, and S nutrients [10,71], but not do wood-based biochars. During high temperature (e.g., ≥500 °C) pyrolysis, most of the manure N is lost in the pyrolysis vapor, resulting in biochar products fairly low in total N content and N availability [10]. In addition, biochar should be in small granules, as coarser particles are difficult to be evenly incorporated in soil. Commercial biochar products are usually in 0.05–6 mm particles. Field weathering will eventually disintegrate biochar particles to <50 µm (0.05 mm) [72]. In general, wood- and crop residue-derived biochars possess significantly higher contents of stable OC yet lower contents of plant nutrients than manure-derived biochars. For long-term soil health improvement, wood- and crop residue-based granular biochars prepared through complete pyrolysis operations (i.e., with adequate reaction time) and demonstrating a pH level >7.5, a higher CEC value (>20 cmol, kg⁻¹), and a higher SSA value (>10 m² g⁻¹) may be preferentially selected. To amend acidic, low fertility soils (e.g., abandoned mine land soil) where soil acidity reduction is necessary whereas regular fertilization is not affordable while rapid plant establishment is desired, manure-derived biochars generated at low pyrolysis temperature (e.g., <500 °C) and having a pH value >9.0 should be considered (9.0 is the lowest pH value reported for manure-derived biochars, Table 1).

4. The Right Application Rate

In general, biochar amendment enhances soil health and promotes plant growth. The effects, however, may not be evident if the application rate is not significant. Yet, at overly high application rates, negative effects may occur. In accordance with the biochar source and the soil type, appropriate amendment rates should be determined for achieving maximal benefits from amending soil with biochar.

In reported research trials, a wide range of biochar amendment rates was employed, from 0.1 to 15 mass% soil and mostly within 0.5–10 mass% soil and more frequently in 1–5 mass% soil (roughly equivalent to 20 to 100 Mg ha⁻¹ assuming the top 15 cm of field soil at a typical 1.4 g cm⁻³ bulk density is amended with biochar) [6,17,22,45,57,73]. At application rates <1 mass% soil (20 Mg ha⁻¹ or 8 Mg ac⁻¹), the effects of biochar amendment on soil physical properties such as bulk density, hydraulic conductivity, and water-holding capacity may be undetectable after a few months of natural weathering if the biochar is not highly porous to yield a tapped density <0.1 g cm⁻³ [20]. For example, incorporation of a wood-based biochar at 10 Mg ha⁻¹ (~0.5 mass% soil) into the top 15 cm soil of a fallow land [74] or mixing a wheat straw-derived biochar at 10 Mg ha⁻¹ (equivalent to 0.75 mass%) with the top 10 cm soil of a maize field [75] had little influence on the soil bulk density measured 6 months after the biochar application. Even at a 2 mass% amendment rate, a rice husk-derived biochar did not significantly reduce the bulk density of paddy soil pots after 100 d of water flooding [76]. Blending a pecan shell-based biochar at 1 mass% with a loamy sand generated negligible impacts on the penetration resistance of packed soil columns following 70-d laboratory incubation [77]. No significant changes in the available water capacity were detected when sandy soils were amended with biochars at 10 Mg ha⁻¹ [74,78,79]. Most studies demonstrating noticeable improvements of biochar-amended
soils in WHC and AWC used ≥1 mass% amendment rates [35]. Hardie et al. reported that amending the top 10-cm sandy loam soil in an apple orchard with tree greenwaste-derived biochar at 47 Mg ha⁻¹ (equivalent to 3 mass% soil) improved little the soil aggregate stability (measured 30 months after biochar incorporation) [80]. At excessively low application rates, biochar generates little or marginal effect on soil chemical properties and plant growth. For instance, Panaque et al. did not observe any significant changes in soil pH, EC, WHC, and sunflower development when a calcareous soil was amended with pine wood-, paper sludge-, and sewage sludge-derived biochars at 1.5 Mg ha⁻¹ [50]. Regardless of application rates, biochar amendment is transient in neutralizing soil acidity and supplementing plant nutrients. Incorporation of a wood-derived biochar (pH 9.2) in the top 0–5 cm Oxisol (pH 3.9) of maize plots at 8 Mg ha⁻¹ (~1.2 mass%) and 20 Mg ha⁻¹ (~3.0 mass%) increased the soil pH by 0.0 and 0.1 units, respectively, measured 4 years of the biochar application [51]. Amendment with ash-rich biochars (e.g., products derived from manures and many crop residues) at <1 mass% may markedly stimulate the growth of plants in low-fertility soils. The stimulation, however, is primarily a result of the additional mineral nutrients (e.g., K⁺, Ca²⁺, Mg²⁺, PO₄³⁻, and SO₄²⁻) introduced through biochar addition [67]. The effect typically becomes minimal after one or two growing seasons. On the other hand, over application (rates dependent on the biochar source and the soil type) of biochar may inhibit the growth of the first crop owning potentially to the resulting high soil salinity, alkalinity, and soil C:N ratio (limited N availability) [81–83]. Using potting experiments Rondon et al. found that soil amendment with wood-derived biochar at 9 mass% significantly restricted the biomass production and N uptake of the test common bean plants [84].

Many biochar products are strongly alkaline and saline, demonstrating a pH value greater than 10.0 (up to 11.5) and an EC level above 3.5 dS m⁻¹ (up to 31 dS m⁻¹) in 1:5 solid/water extracts. For example, poultry litter-derived biochar manufactured through 600 °C slow pyrolysis showed pH 11.5 and EC 31 dS m⁻¹ (in 1:5 solid/water extracts) [10]. When these types of biochar products are selected, the amendment rate should be controlled to ensure the treated soils have a pH value less than 7.5 and an EC value less than 2.7 dS m⁻¹ (in 1:1 solid/water slurry; equivalent to 4 dS m⁻¹ in saturated soil paste); otherwise the treated soils become alkaline and/or saline, restricting the growth of many crops and decreasing the plant availability of various soil nutrients including P, Fe, Mn, Cu, Zn, and B [30]. Pre-tests may be conducted to determine the maximum allowable amendment rates of individual biochar products in single applications. When a sandy loam soil (pH 6.5 and EC 0.12 dS m⁻¹ in 1:1 solid/water slurry) was amended with a poultry litter-derived biochar (pH 10.3 and EC 26.6 dS m⁻¹ in 1:5 solid/water extracts) at 2 mass%, the pH of the treated soil was elevated to 7.1 and the EC to 2.8 dS m⁻¹ (in 1:1 solid/water slurry) [44], a threshold condition for the optimal growth of plants sensitive to acidity and salinity. At a 3 mass% amendment rate, the poultry litter-derived biochar inhibited the seedling development of winter wheat growing in the treated soil [26]. To protect the in-season crops, it could be concluded that the soil amendment rate of poultry litter-derived biochar should not exceed 2 mass%.

We conducted greenhouse potting experiments to investigate the source and application rate effects of biochar amendment on crop productivity. Biochars were separately produced from fallen deciduous tree leaves (TL), air-dry corn stover (CS), air-dry wheat straw (WS), and poultry litter (PL) pellets through 400 °C complete slow pyrolysis [10]. The biochars were ground to <2 mm and referred to as TL, CS, WS, and PL biochars, respectively. The pH values of these biochars (in 1:5 w/w solid/water slurry) were 10.4, 10.5, 7.6, and 10.1, respectively; and the EC values (1:5 w/w solid/water extract) were 4.03, 11.54, 0.77, and 23.59 dS m⁻¹, respectively. A Greenwich sandy loam (coarse-loamy, mixed, semiactive, mesic Typic Hapludults) (pH 6.5 and EC 0.12 dS m⁻¹ in 1:1 soil/water slurry) was collected from a local corn field and homogenized to <4 mm. In one trial, the soil was amended with PL biochar at 0, 1, 2, and 3 mass%, respectively, with thorough mixing. The amended soils were adjusted to 18% moisture content (75% of WHC) and packed into plastic pots (18 cm height and 19 cm inner diameter). Additional soil pots receiving chemical fertilization at 100 kg N ha⁻¹ (by incorporating NH₄NO₃ at 0.37 g kg⁻¹ soil) and 25 kg P ha⁻¹ (by adding KH₂PO₄ at 0.14 g kg⁻¹ soil), raw PL amendment at
4.5 g kg\(^{-1}\) soil (equivalent to 3.3 Mg ha\(^{-1}\)) to give 100 kg N ha\(^{-1}\), raw TL amendment at 2 mass%, TL biochar amendment at 2 mass%, and combined TL biochar amendment (2 mass%) and chemical fertilization (100 kg N and 25 kg P ha\(^{-1}\)) were also prepared following the same procedures. The soil pots representing 9 triplicated treatments were placed in a greenhouse. To each pot 10 winter wheat (Triticum aestivum) seeds were sown at 4 cm depth in the soil. The soil moisture content was maintained at 15%–20% by spraying tap water. The seed germination rate was 90%–100% in all the pots, not influenced by the treatments. After growing in the greenhouse for 84 days, the wheat plants were harvested by collecting the above-ground biomass and measured for the dry biomass yield of each pot. The average biomass yield data of the nine treatments were statistically compared using the Fisher's least significance difference (LSD) method. In another trial, similar soil pots were prepared with five distinct treatments: 1) chemical fertilization (Chem NP)—soil was fertilized by thorough incorporation of NH\(_4\)NO\(_3\) at 150 kg N ha\(^{-1}\) and KH\(_2\)PO\(_4\) at 25 kg P ha\(^{-1}\); 2) Raw CS-NP—soil was amended with raw corn stover (<1 mm) at 5 mass% in addition to the chemical fertilization; 3) CS biochar-NP—soil was amended with CS biochar at 5 mass% in addition to the chemical fertilization; 4) Raw WS-NP—soil was amended with raw wheat straw (<1 mm) at 5 mass% in addition to the chemical fertilization; and 5) WS biochar-NP—soil was amended with WS biochar at 5 mass% in addition to the chemical fertilization. Five germinated seeds of spinach (Spinacia oleracea) were planted in each pot at a 3-cm depth from the surface. After 45 days of greenhouse growing, the spinach plants were harvested by cutting at the soil surface. The fresh spinach biomass yield of each soil pot was measured and converted to values in g m\(^{-2}\). The results indicated that amending a sandy loam soil with poultry litter-based biochar at 1–3 mass% significantly promoted the growth and biomass production of winter wheat (Figure 2). At a 3 mass% amendment rate, however, the plant seedling growth was visibly inhibited (likely due to the introduced salinity toxicity). Relative to the control soil without any amendments, TL biochar amendment (at 2 mass%) alone slightly decreased the wheat biomass yield; when combined with chemical fertilization, the TL biochar amendment remarkably promoted the biomass yield (Figure 2). In comparison with the chemical fertilization alone, both Chem NP-combined 5 mass% CS biochar and 5 mass% WS biochar amendments significantly increased the growth and biomass yield of spinach, whereas both Chem NP-combined 5 mass% raw CS and 5 mass% raw WS amendments generated clearly opposite effects (Figure 2). The results indicate that soil amendment with manure-derived biochars at 1–3 mass% evidently promotes plant growth. Soil amendment at 2–5 mass% with low-nutrient biochars like those derived from wood and crop residues requires combined chemical N and P fertilization to achieve the plant growth promoting effects. The synergic effects of biochar amendment in combination with chemical fertilization were validated by other researchers [69,85].

In field trials, a wide range of biochar amendment rates from 5 to 50 Mg ha\(^{-1}\) has been employed, with higher rates yielding generally greater results in enhancing soil health [67,86]. Nevertheless, the market price of commercial biochar products has been unaffordably high (e.g., US$100 per metric ton as the lowest price in 2018), restricting application of this desirable soil amendment at large scale and high rates [87]. Consequently, the low rate of 10 Mg ha\(^{-1}\) (~0.5 mass% assuming thorough incorporation in the top 15 cm soil layer) has been the most common select in field biochar applications [67]. Depending on the biochar source and the soil type, biochar amendment at as low as 0.1 mass% (2 Mg ha\(^{-1}\)) may yield significant effects on plant growth [88]. Our research indicates that to secure the evident, long-term soil health improvement benefits, wood- and crop residue-derived biochars may be applied cumulatively at 2–5 mass% soil (40–100 Mg ha\(^{-1}\)) and manure-derived biochars be applied at 1–3 mass% soil (20–60 Mg ha\(^{-1}\)) to cropland. The practical biochar amendment rates should be further confirmed by soil pH and EC prescreening tests.
5. The Right Placement in Soil

Soil texture, pH, EC, OC content, available nutrient level, and other properties influence the beneficial effects that could be attained through biochar amendment. Meta-analysis of the reported biochar studies illustrates that strongly acidic (e.g., pH <5.5), coarse-textured soils generally respond more in improved overall health and crop productivity to biochar amendment than neutral or alkaline, fine-textured soils [35,67]. For instance, application of biochar at >10 Mg ha⁻¹ was able to enhance the P availability of pH <7.5 agricultural soils but had little influence on that of alkaline (pH>7.5) soils [89]. Therefore, the type of soil should be examined upon biochar amendment. To maximize its benefits, biochar should be applied to acidic (i.e., pH <6.5), strongly leached soils with low OC contents (e.g., <10 g OC kg⁻¹ soil or organic matter content <2%) [6]. To alkaline soils (e.g., pH >7.5), biochar amendment may not be appropriate. If practiced, wood-derived biochars (relatively low in mineral ash content and lime equivalence) should be considered over other sources of biochars.

High-quality biochars are rather recalcitrant in the natural environment and can remain in soil over hundreds of years [4]. The short-term benefits (e.g., acid neutralization and nutrient supply) of biochar amendment may dissipate in one or several growing seasons, but the long-term benefits (e.g., improved water and nutrient retention and soil aggregation) will lastingly persist. At sufficiently high rates, biochar amendment should be a “once-a-life” practice; applying biochar to each crop is clearly not necessary [86]. Consecutive biochar applications may be implemented to bring the cumulative amendment rates to the optimal levels if single applications were carried out at lower rates.

Thorough mixing with soil is the most efficient method for applying biochar to improve the overall soil health. This method has been extensively used in research and field trials. At occasions when soil incorporation is not feasible such as biochar amendment to perennial crops and grassland, surface application by broadcasting, banding, or sidedressing may be practiced. Surface-applied biochar functions mainly as a sterilized physical cover; the soil health improvement benefits are barely realized. Furthermore, biochar on the land surface reduces the land albedo and is subject to severe erosion losses by water and wind [74,86]. Subsurface application of biochar can be performed by tillage following broadcasting, band drilling, trenching, and localized holing [84]. Broadcasting followed by soil incorporation through multi-round conventional tillage is effective to mix the applied biochar with the top 15–20 cm soil, through which the overall soil health of the entire cropland can be enhanced. The vast majority of effective plant roots are in the top 30-cm soil layer, with many crops having the top 15 cm soil as the root zone [90,91]. In field trials, biochar incorporation into the 0–5 cm or 0–10 cm top 15 cm soil as the root zone [90,91]. In field trials, biochar incorporation into the 0–5 cm or 0–10 cm top 15 cm soil as the root zone [90,91]. In field trials, biochar incorporation into the 0–5 cm or 0–10 cm top 15 cm soil as the root zone [90,91]. In field trials, biochar incorporation into the 0–5 cm or 0–10 cm top 15 cm soil as the root zone [90,91].

Figure 2. Biomass production of (A) winter wheat and (B) spinach in a sandy loam amended with biochars derived from different organic residues at varied amendment rates. Data are means of triplicate measurements. Error bars represent standard deviation of triplicate measurements. TL—tree leaf; PL—poultry litter; CS—corn stover; WS—wheat straw; NP—nitrogen and phosphorus fertilization.

| Treatments | Dry Wheat Biomass (g/pot) | Fresh Spinach (g/m²) |
|------------|---------------------------|----------------------|
| Control    | 2.0                       | 800                  |
| Chem NP    | 2.5                       | 850                  |
| Raw TL     | 3.0                       | 900                  |
| TL biochar-NP | 3.5                     | 950                  |
| Raw PL     | 3.5                       | 900                  |
| 1% PL biochar | 4.0                     | 1000                 |
| 2% PL biochar | 4.5                     | 1050                 |
| 3% PL biochar | 5.0                     | 1100                 |
cm soil layer was tested [50,74]. It is apparent that the health improvement effects would be limited to the treated soil layer. Migration of fine biochar particles in the soil profile may occur [50], yet the process is slow and happens only in preferential flow channels. To attain the long-term soil health improvement effects, biochar should be spread evenly over the land surface at the pre-determined rate and immediately incorporated in the crop-root-zone soil by tillage. Even so, relatively uniform distribution of biochar in soil is challenging to achieve, especially for products with a wide particle size distribution (e.g., from <0.05 mm to >10 mm). Processing biochar into <2 mm particles would greatly facilitate the soil mixing effect. Compared with coarser particles, biochar in <2 mm particles is also more effective to enhance soil water retention [92].

Commercial biochar products contain significant portions of fine particles (e.g., <0.5 mm). Fine, dry biochar particles at a low envelope density (e.g., ~0.52 g cm$^{-3}$) are readily shifting in the presence of any tangible air current (wind), forming dust in the air and causing air pollution. Up to 25 mass% of biochar could be lost during field broadcasting application [83]. To reduce the dust formation and the related biochar losses, biochar may be moistened with water or mixed with manure, sludge, and compost prior to field application [93,94]. Dust formation becomes minimal when moistened biochar is applied under low-wind (i.e., <8 km h$^{-1}$) weather conditions.

6. Conclusions

Biochar is a promising soil amendment able to persistently improve soil health and promote crop production. Accordingly, best management programs need to be developed to maximize the benefits of biochar amendment. Amending soil with biochar should follow the 3R principles: right biochar source, right application rate, and right placement in soil. Biochar products vary significantly in composition and quality characteristics with the feedstock type and the production conditions. Biochars, in particular those manufactured from wood debris and crop residues do not contain significant contents of plant nutrients (e.g., N and P) and, therefore, should not be expected to serve as a chemical fertilizer alternative and function as a major nutrient source to crops. The promoting effects of biochar amendment on crop production may not be achieved without combined chemical fertilization. The long-term effects on improving soil health should be highlighted with the most value in biochar application programs. The long-term capability of biochar to enhance soil health through persistently ameliorating soil physical, chemical, and biological properties is largely determined by its environmental recalcitrance and water- and nutrient-holding capacities. Desirable biochar products with sufficiently high recalcitrance (stability) and water- and nutrient-retention abilities are prepared through complete pyrolysis of biomass materials. Given complete pyrolysis for the same feed to experience thorough pyrolytic decomposition in the pyrolysis reactor, biochar products generated at a higher pyrolysis temperature in the range of 300–600 $^\circ$C possess greater stability, alkalinity, and water-holding capacity. In field applications, biochar should be preferentially applied to acidic, highly leached soils. The treated soils should maintain a pH value less than 7.5 and an EC level below 2.7 dS m$^{-1}$ (in 1:1 soil/water slurry). The appropriate application rates (one time or cumulatively) are recommended at 2–5 mass% soil (1% is equivalent to 20 Mg ha$^{-1}$) for wood- and crop residue-derived biochars and at 1–3 mass% soil for manure-derived biochars to achieve evident, long-term soil health improvement. Biochar should be processed to granular particle sizes and moistened to 100% water content (dry mass base) or mixed with compost upon field application. The applied biochar should be immediately incorporated into the root zone (e.g., top 15–20 cm) soil with thorough mixing. Combination with chemical fertilization is necessary to attain the synergic beneficial effects of biochar amendment on crop growth.

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