Review

Biochar Impacts on Soil Physical Properties and Greenhouse Gas Emissions

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Abstract: Biochar, a co-product of a controlled pyrolysis process, can be used as a tool for sequestering C in soil to offset greenhouse gas (GHG) emissions, and as a soil amendment. Whereas the impacts of biochar application on soil chemical properties are widely known, the research information on soil physical properties is scarce. The objectives of this review are to (i) synthesize available data on soil physical properties and GHG emissions, (ii) offer possible mechanisms related to the biochar-amended soil processes, and (iii) identify researchable priorities. Application rates of 1%–2% (w/w) of biochar can significantly improve soil physical quality in terms of bulk density (BD), and water holding capacity (WHC). However, little data are available on surface area (SA), aggregation stability, and penetration resistance (PR) of biochar-amended soil. While biochar amendment can initially accentuate the flux of carbon dioxide (CO_2), the emission of GHGs may be suppressed over time. A 2-phase complexation hypothesis is proposed regarding the mechanisms of the interaction between soil and biochar.

Keywords: biochar; green house gas (GHG) emissions; soil amendment; soil physical properties; soil quality

1. Introduction

Biochar is defined as the carbonaceous product obtained when plant or animal biomass is subjected to heat treatment in an oxygen-limited environment and when applied to soil as an amendment [1].

Biochars made from diverse biomass species (feedstock) are characterized by different morphological and chemical properties but also characteristically differ based on specific pyrolysis conditions (*i.e.*, final pyrolysis temperature or peak temperature, rate of charring or ramp rate, and duration of charring time) [2–6]. In the context of this article, the term biochar refers to all residual products of biomass pyrolysis excluding those that are condensates from the vapor phase. It is produced by incomplete pyrolysis of biomass, or sometimes as a co-product of pyrolysis and thus commonly occurs as a component of soil organic matter (SOM) where slash-and-burn agriculture is widely practiced [7–9], and in soils of the fire-prone ecoregions. In general, biochar may not support microbial activity due to the refractory nature of C and thus, can represent a long-term C sink in soil [10,11]. However, some studies show that a small labile part of biochar is utilized by microbial processes [5].

Some Anthrosols with enhanced fertility, popularly known as *Terra Preta* (TP) or Amazonian Dark Earths (ADE), occur in distinct small to large sites (20–350 ha) [12–14], with a total area of ~50,000 ha in central Amazonia between the rivers Tapajos and Curua-Una [13–15], and elsewhere outside of this region. The TPs are a unique type of soil, and are believed to be created by intense anthropogenic activities such as biomass burning and slash-and-burn agriculture [16] or may have been formed by unintentional anthropic activities occurring over long term habitation such as domestic refuse, compost and waste dumping [13,17] by pre-Columbian Amerindians between 500–6000 B.P. years. The TPs are often associated with archaeological artifacts such as ceramic fragments, potsherds, stone tools, charcoal *etc.* [13,18]. Unlike adjacent yellowish or reddish soils, TPs are characteristically black-colored due to high levels of charred or partially charred residues and the presence of high SOM content [19]. These soils are also high in available plant nutrients, pH, cation exchange capacity (CEC) and water and nutrient holding capacity which support higher levels of agriculture compared to adjacent infertile and highly weathered and acidic soils [16]. Whether these soils were created intentionally, such as for improving agricultural productivity, or as an incidental result of habitation, is still unclear [12,20]. In any case, from the assumptions of TP formations, scientists believe that soil properties could be ameliorated by using biochar as an amendment.

Soil functions depend on three key properties, physical, chemical, and biological, and biochar has been applied as an amendment to test its impacts on soil properties. Whereas, biochar is widely considered as a soil amendment, the focus of the past studies has mostly been limited to the nutrient status of the amended soils including CEC, pH, nutrient content, vegetative growth, and the C sequestration potential of the amended soils. Positive effects of biochar have been reported on soil nutrient status and C sequestration [21], microbial community or soil biota [22], and greenhouse gas (GHG) emissions [23–25] which are related to physical properties of soils [26]. However, there is little published information about effects of biochar on soil physical properties and GHG emissions which are closely linked [27,28]. Moreover, existing reviews on GHG emissions are somewhat conflicting in nature as some indicate reductions in GHGs upon biochar application [29–31], while others report enhancement [25,32]. In other words, if one of the GHGs is suppressed by biochar addition another is either enhanced or not affected. Clearly, there is a knowledge-gap as to how biochar alters soil physical properties and the mechanisms responsible for GHG emissions. Thus, the objectives of this article are to collate and synthesize available information regarding the effect of biochar on soil physical properties, and associated effects on GHG emissions, and to identify, rationalize and prioritize researchable topics related to the use of biochar as a soil amendment.

2. Physical Properties of Biochar

All biochars do not have the same properties since their characteristics are controlled by factors such as feedstock type, pyrolysis conditions (final pyrolysis temperature, rate of heating -slow *versus* fast pyrolysis), and duration of charring [2,4,5,33–35]. Physical properties of biochars, altered by variations in feedstock type and pyrolysis condition, are outlined below.

The impact of biochar as an amendment depends on its properties or attributes. Among key properties are the large surface area (SA) and presence of micropores [4,36–38] which contribute to the adsorptive properties of biochars and potentially alter soil's SA, pore size distribution (PSD), bulk density (BD), water holding capacity (WHC) and penetration resistance (PR). There exists a strong and direct relationship between a biochar's SA and the pore volume as measured using N_2 adsorption and Braunauer-Emmett-Teller (BET) modeling [39,40]. The SA can also be measured by using other molecules such as CO_2 on carbonaceous materials at the micrometer scale [4,40]. In general, an abundance of small to medium-sized pores can enhance the SA of the material. Following the pore size classification used by the International Union of Pure and Applied Chemistry [41,42], understanding and determination of the relative abundance and stability of pores of different sizes (micropores: <2 nm, mesopores: 2–50 nm and macropores: >50 nm) are keys to soil ecosystem functioning. Important among these functions are aeration, hydrology, and provision of habitat for microbes while the finer pores could be involved with molecular adsorption and transport [27].

Biochars do not possess similar SA even when derived from the same feedstock due to differences in production conditions, and more specifically the final combustion temperature. However, the relationship between the peak combustion temperature and surface morphological parameters (*i.e.*, SA, pore diameter and volume) of the resulting biochar is highly complex. In general, SA increases with an increase in peak temperature of biochar production [2,4,36–38,43,44]. Yet, there may be either no simple relationship between these two parameters [45,46], or SA may increase with increase in peak temperature up to a certain critical or threshold and then decrease. It is also observed that biochar made at the lowest peak temperature has the lowest SA (~10 m^2 g^{-1}), that produced at intermediate temperatures (650–850 °C) has the highest SA (~400 m^2 g^{-1}); and that produced at temperature ≥1000 °C has the least SA [47–50].

The mechanisms responsible for increases in SA with an increase in peak temperature or heating rate are not yet well understood. The presence of tar, derived from the cellular structure of the parent biomass, may fill biochar's pores at lower combustion temperatures, lowering the SAs [50]. The tar components are volatilized at higher temperatures (650–750 °C), so pores become accessible. Above that temperature range, the micropore structure of biochars collapses and the SA decreases [49]. Others hypothesize against such a collapse of micropore structure, and propose that micropores could be reopened by CO_2 activation of biochars so that N_2 accessible SA increases from a low of 2 to a very high value of 540 m^2 g^{-1} [51]. The pore structure of biochar may be sealed off at temperatures >750 °C with low temperature ramp rates [48]. For high ramp-rate-produced biochars, the rapid carbonization results in extensive cracking during gas evolution due to internal stresses [48]. In other words, cracking becomes a continuous process at a high heating rate and micropores formed give rise to the high SA even at temperatures >750 °C.

Surfaces of biochar produced from sawgrass (*Cladium jamaicense*) forms glassy bio-oil or tar-type coating, which results in low SA and pore volume as these glassy coatings can easily close off the interfacial pores [52]. Lower temperature biochars contain volatile compounds which can "block" pore spaces resulting in lower SA and this effect is diminished when biochar production temperature is high enough (>650 °C) as the volatile matter is burnt off at higher temperatures [4]. Adsorptive nature related to SA is an important physical property of biochars because of strong environmental influence in the uptake and binding effect of materials from their surroundings. The porous nature and surface chemical properties determine the adsorptive capabilities of biochar. Biochars may adsorb poly aromatic compounds, poly aromatic and poly aliphatic hydrocarbons, other toxic chemicals, metals and elements or pollutants in soils, sediments, aerosols and water bodies [8,53–59]. Thus, it is generally believed that the physical properties of soils amended with biochar can be improved.

An important physical property of biochar is its stability in the environment. However, degradation of at least some components (such as volatile matter or labile OM) of biochar may occur [5,60]. On the other hand, sub-soils are characteristically different due to variations in microbial activity and oxygen content, which affect biochar oxidation and aging. Thus, other factors associated with physical stability of biochar in soil include its mobility into the deeper soil profile. Indeed, biochars can move into the sub-soil over time [61–64] e.g., 100 years [60]. The deep profiles of TP soil of the Amazon show high amounts of BC in the form of biochar [12,16,65] which suggests a high recalcitrant nature of biochar in soil over hundreds of years. The susceptibility of biochars in subsoil to microbial processes may also depend on stability of aggregates formed in a biochar-amended soil. These factors not only enhance the stability of SOM in the deeper profile but also improve availability of water and nutrient to crops and decrease erosion risks. Clearly, stability of biochar is controlled by physical properties of soils.

3. Soil Physical Characteristics Affected by Biochar Amendment

The effects of biochar on soil physical properties depend on several factors, such as biomass or feedstock type, pyrolytic condition, application rate, and environmental condition. Impacts of biochar on SA, porosity or PSD, aggregate stability, BD, WHC and PR of soils are briefly described below.

Surface area and porosity: The SA of soil is an important physical parameter which controls essential functions of soil fertility such as water and nutrient holding capacity, aeration, and microbial activity [32]. Improvement in agronomic productivity of biochar-amended soils may be related to the higher SA of the biochar-soil mixtures. The high SA of biochar provides space for formation of bonds and complexes with cations and anions with metals and elements of soil on its surface which improves the nutrient retention capacity of soil [27,28,66]. While many studies have reported the SA data of biochars pyrolized from different biomass sources under a range of pyrolysis conditions, there are only limited data available on SA of biochar-amended soils. However, incorporation of biochar can enhance specific SA up to 4.8 times that of adjacent soils [66]. A long-term soil column incubation study indicated increases in specific SA of an amended clayey soil from 130 to 150 $m^2 \ g^{-1}$ when biochar derived from mixed hardwoods was applied at rates of 0 to 20 $g \ kg^{-1}$ [67]. In addition to high SA, there might be other associated factors such as total porosity or PSD which can play important roles in altering properties of biochar-amended soil surface. Mesoporosity may also increases significantly at the expense of macropores in waste-derived biochar-amended soil compared to control, with the higher

rate of biochar application having a greater effect [68]. Physical and biological interactions between biochar/soil mixture and microbes could enhance SA of amended soils over time but more research is required to understand the processes. To-date limited data are available to investigate mechanisms underpinning changes in SA and PSD although improvement of SA and porosity of amended soil are indicated (Table 1).

Table 1. Impact of biochar on surface area and porosity of amended soils (Rate of 0 represents control or unamended soil).

Soil type	Biochar type	Study type (Scale)	Rate of biochar application % (g g^{-1})	SA (m^2 g^{-1})	Porosity (%)	Reference
Residue sand	Municipal green waste, 450 °C	Laboratory	0	-	0.46	[68]
			2.6	-	0.48	
			5.2	-	0.51	
Clarion fine loamy	Mixed hardwoods (Oak: *Quercus spp.*, Hickory: *Carya spp.*), 500 °C	Laboratory	0	130	-	[67]
			0.5	133	-	
			1.0	138	-	
			2.0	153	-	
Sandy soil	Jarrah woods (*Eucalyptus marginata*), 600 ° C	Greenhouse	0	1.3	56.1	[69]
			0.45	2.7 [1]	57.6	
			2.27	8.4 [1]	62.1	
Silt loam	Birch (*Betula pendula*), 400 °C	Field	0	-	50.9	[70]
			1.2	-	52.8	

[1] Theoretical estimation, calculated based on the data acquired by personal communication.

Bulk density, aggregation, and penetration resistance: In contrast to SA, there are several reports from both field and lab scale experiments regarding BD of biochar-amended soils. Application of biochar can decrease the BD of soils [67,68,71]. About ~2% (w/w) rate of biochar amendment seems enough to decrease BD of amended soils (Table 2), however, in some instances BD can increase over time due to compaction during column leaching events [72]. An experiment conducted by Mankasingh *et al.* [73] showed that soil BD decreased from 1.66 to 1.53 g cm^{-3}, and another involving biochar-amended soil columns showed significantly lower BD compared to no-biochar controls in a column incubation study [67]. In a 3-year field study, application of biochar amendment decreased the BD of 0–7.5 cm soil layer by 4.5 and 6.0% for 0.23 kg m^{-2} and 0.45 kg m^{-2} application rate, respectively [71]. A decrease in soil BD from biochar application rate of 9.4 (± 2.2%) was observed in another 2-year field study [74]. However, a laboratory study showed that all columns were compacted by gravity and periodical leaching events but the biochar-amended column had a lower rate of compaction compared to the control or manure-amended soil columns [72]. Thus, the decrease in BD of biochar amended soil could be one of the indicators of enhancement of soil structure or aggregation, and aeration, and could be soil-specific. The higher the total porosity (micro- and macro-pores) the higher is soil physical quality because micropores are involved in molecular adsorption and transport while macropores affect aeration and hydrology [27]. Clearly, amending top-soil with biochar can decrease BD, however, there are limited available data to understand if this effect of biochar is significantly relevant in the deeper profile.

Table 2. Impact of biochar application on soil bulk density.

Soil type	Biochar type	Study type (Scale)	Rate of biochar application % (g g^{-1})	Bulk density (g cm^{-3})	Reference
Norfolk loamy sand: E	Pecan (*Carya illinoinensis*) shells, 700 °C	Laboratory	0	1.52	[75]
			2.1	1.45 [1], 1.52 [2]	
Norfolk loamy sand: E and Bt			0	1.34	
			2.1	1.36 [1], 1.34 [2]	
Hydroagric stagnic anthrosol	Wheat (*Triticum spp.*) straw, 350–550 °C	Field	0	0.99, 0.94 [3]	[73]
			1.1	0.96, 0.91 [3]	
			2.2	0.91, 0.86 [3]	
			4.4	0.89, 0.88 [3]	
Residue sand	Municipal green waste, 450 °C	Laboratory	0	1.65	[68]
			2.6	1.55	
			5.2	1.44	
Clarion fine loamy	Mixed hardwoods, 500 °C	Laboratory	0	1.21, 1.34 [4]	[67]
			0.5	1.10, 1.24 [4]	
			1.0	1.08, 1.24 [4]	
			2.0	1.08, 1.24 [4]	
Norfolk loamy sand	Peanut (*Archis hypogaea*) hull, 400 °C	Laboratory	0	1.41 [5], 1.57 [6]	[76]
			2.0	1.38 [5], 1.55 [6]	
	Peanut hull, 500 °C		2.0	1.38 [5], 1.61 [6]	
	Pecan (*Carya illinoensis*) shell, 350 °C		2.0	1.39 [5], 1.51 [6]	
	Pecan shell, 700 °C		2.0	1.49 [5], 1.56 [6]	
	Poultry (*Gallus domesticus*) litter, 350 °C		2.0	1.38 [5], 1.57 [6]	
	Poultry litter, 700 °C		2.0	1.40 [5], 1.63 [6]	
	Switchgrass (*Panicum virgatum*), 250 °C		2.0	1.32 [5], 1.43 [6]	
	Switchgrass, 500 °C		2.0	1.26 [5], 1.50 [6]	

[1] measured after 44 days; [2] measured after 94 days; [3] measured after one year; [4] measured after 15 months; [5] measured after 28 days leaching; [6] measured after 118 days leaching; [7] measured after 28 days leaching; [8] measured after 118 days leaching.

Data are scarce on aggregate stability and PR of biochar-amended soil. Furthermore, whatever little information exists is conflicting. Examples of the few studies which investigated soil aggregation with biochar amendment, all carried out under laboratory or greenhouse settings are shown in Table 3. A low temperature (220 °C) hydrochar made from spent brewer's grains, a residue from beer brewing, responded positively on aggregation of Albic Luvisol when (i) incubated for five months at 20 °C in dark, and (ii) used in a pot study with same hydrochar/soil combination (Table 3). These incubation and greenhouse studies involving plant indicates that hydrochar significantly increased water stable aggregates (WSA) compared to control but the extent of WSA differed because the greenhouse study had 2–5 times higher rate of WSA formation compared to laboratory incubation. These data suggest

that plant roots and mycorrhizal fungi which were absent in the incubation study had an important role in soil aggregation [77]. In contrast, with and without mixing Bt and E horizons with pecan shell (*Carya illinoinensis*), biochar amendment decreased aggregation (Table 3) compared to control [75]. Mixing of biochar from pecan with switchgrass increased aggregation, however, the effect was significantly lower when soil was treated only with biochar and without mixing with switchgrass [78]. This trend indicates that a positive effect on soil aggregate stability requires presence of a substrate (*i.e.*, switchgrass) along with biochar as an amendment. However, the application of biochar at the rate of 1% to an Ultisol had no effect on aggregate stability [79]. Clearly, there exists limited information about how biochar affect aggregation and whether another substrate, plant-roots, mycorrhizal fungi or active-C source might be needed to increase WSA in biochar-amended soils. Nevertheless, the highest concentration of black-C was observed in the finest size fraction (<0.53 μm) of soil aggregates [80] suggesting preferential embedding of black-C particles compared to other organic compounds within aggregates. Piccolo *et al.* [81] found higher aggregation percentage by coal derived humic acid which possesses similar active carbonaceous functional groups such as biochars [82]. Some recent studies indicate that humic acid amendment can improve soil characteristics by buffering pH and chelating micronutrients by increasing acidic ligands such as –COOH or Ph–OH groups [83–85] which are common in various biochars [4,82]. Thus, it could be hypothesized that active functional groups of biochar particles may form complexes over time (*i.e.*, aged) to make up soil aggregates. Although more research on this aspect is a priority theme, however, a hypothetical complex aggregate formation hypothesis is proposed in the fourth section of this article.

Table 3. Impact of biochar on aggregation and penetration resistance.

Soil type	Biochar type	Study type (Scale)	Rate of biochar application % (g g^{-1})	Aggregation (%)	Penetration resistance (MPa)	Reference
Norfolk loamy sand: E	Pecan shells, 700 °C	Laboratory	0	14.3	1.19 [1], 0.80 [2]	[75]
			2.1	12.9	1.27 [1], 0.88 [2]	
Norfolk loamy sand: E and Bt			0	27.3	0.71 [1], 0.76 [2]	
			2.1	20.9	0.88 [1], 0.94 [2]	
Norfolk loamy sand: Ap	Pecan shells, 700 °C	Laboratory	0	9.95, 13.0 *	1.04 [1], 1.1 [2]	[78]
			0.5	9.53, 12.7 *	0.96 [1], 1.15 [2]	
			1.0	10.7, 12.3 *	1.03 [1], 1.02 [2]	
			2.0	9.23, 11.8 *	0.82 [1], 0.87 [2]	
Albic Luvisol	Hydrochar, 220 °C	Laboratory	0	49.8	-	[77]
			5	69.0	-	
			10	65.1	-	
		Greenhouse	0	10.3	-	
			5	20.8	-	
			10	33.8	-	

[1] measured after 44 days; [2] measured after 96 days; * with switchgrass addition.

On the other hand, mixing Norfolk loamy sand E, and E and Bt layers with pecan shell biochars produced at 700 °C increased PR measured after 44 days [75]. However, PR was reduced when measured after 96 days (Table 3). In summary, BD may not change and aggregation percentage may decrease with biochar addition (Tables 2 and 3). Thus, soil compaction would not be alleviated by biochar addition over short time period but may be altered in the long run as aging of biochar changes its properties [2,86,87]. Along with time, soil type is also an important factor because another study reported reduction in PR with application of the same biochar on a different soil type (Norfolk loamy sand Ap) [78]. Clearly, the effect of biochar amendment on soil aggregation and PR requires additional research by including variations in biochar and soil type.

Hydrological properties: Soil hydrological properties (*i.e.*, moisture content, WHC, water retention, hydraulic conductivity, water infiltration rate) are invariably related to SA, porosity, BD and aggregate stability. Several studies have reported alterations in WHC and water retention in biochar-amended soils [67,68,88] with as low as 0.5% (g g^{-1}) biochar application rate sufficient to improve WHC (Table 4). However, the response is biochar and soil-specific. Application of a laboratory-produced biochar from black locust (*Robinia pseudoacacia*) increased the available water capacity (AWC) by 97%, and saturated water content by 56%, but reduced hydraulic conductivity [88]. A long-term column study indicated that biochar-amended Clarion soil retained up to 15% more water, and 13% and 10% more water retention at −100 kPa and −500 kPa soil matric potential, respectively, compared to unamended controls [67]. Piccolo *et al.* [89] demonstrated that coal-derived humic acid substances can increase water retention, AWC and aggregate stability of inherently degraded soils. However, the effect of biochar on water retention also depends on soil texture. Tryon [90] reported that application of biochar increased AWC in sandy soil, no effect in a loamy soil, and decreased moisture content in a clayey soil. Such a response may be attributed to the hydrophobic nature of the charcoal and to alterations in PSD. Because the soil moisture retention may only be improved in coarse-textured soils, a careful choice of biochar/soil combination needs to be taken into consideration [21,90].

Table 4. Impact of biochar on water holding capacity.

Soil type	Biochar type	Study type (Scale)	Rate of biochar application % (g g^{-1})	Water holding capacity (g cm^{-3})	Reference
Residue sand	Municipal green waste, 450 °C	Laboratory	0	0.11	[68]
			2.6	0.16	
			5.2	0.20	
Norfolk loamy sand: Ap	Pecan shells, 700 °C	Laboratory	0	0.64	[78]
			0.5	0.59	
			1.0	0.60	
			2.0	0.66	
Sandy loam	Ponderosa pine (*Pinus ponderosa*), 450 °C	Laboratory	0	11.9	[91]
			0.5	12.4	
			1.0	13.0	
			5.0	18.8	

Table 4. *Cont*.

Soil type	Biochar type	Study type (Scale)	Rate of biochar application % (g g−1)	Water holding capacity (g cm−3)	Reference
Norfolk loamy sand	Peanut hull, 400 °C	Laboratory	0	2.87 [1], 7.68 [2], 8.14 [3], 7.71 [4]	[76]
			2.0	3.97 [1], 8.08 [2], 8.59 [3], 8.22 [4]	
	Peanut hull, 500 °C		2.0	4.26 [1], 8.12 [2], 8.64 [3], 8.47 [4]	
	Pecan shell, 350 °C		2.0	3.30 [1], 7.78 [2], 8.27 [3], 8.03 [4]	
	Pecan shell, 700 °C		2.0	3.61 [1], 8.08 [2], 8.30 [3], 8.03 [4]	
	Poultry litter, 350 °C		2.0	4.56 [1], 8.23 [2], 8.62 [3], 8.31 [4]	
	Poultry litter, 700 °C		2.0	4.51 [1], 8.21 [2], 8.64 [3], 8.26 [4]	
	Switchgrass, 250 °C		2.0	3.37 [1], 7.73 [2], 8.14 [3], 7.70 [4]	
	Switchgrass, 500 °C		2.0	4.29 [1], 8.12 [2], 8.35 [3], 8.12 [4]	
Declo silt loam	Switchgrass, 250 °C		0	5.37 [5], 11.99 [6], 12.44 [7], 12.50 [8]	
			2.0	5.54 [5], 11.99 [6], 12.28 [7], 11.95 [8]	
	Switchgrass, 500 °C		2.0	5.58 [5], 12.10 [6], 12.25 [7], 11.92 [8]	
Warden silt loam	Switchgrass, 250 °C		0	5.10 [5], 12.14 [6], 12.51 [7], 12.26 [8]	
			2.0	5.38 [5], 12.23 [6], 12.29 [7], 12.06 [8]	
	Switchgrass, 500 °C		2.0	5.48 [5], 12.06 [6], 12.11 [7], 11.68 [8]	
Compacted sandy loam	Hardwood, 400 °C	Laboratory	0	1.73	[92]
			1	1.71	
			2	1.73	
			5	1.69	
			10	1.63	
Silt loam	Birch, 400 °C	Field	0	0.49	[70]
			1.2	0.54	

[1] measured after 28 days leaching; [2] measured after 63 days leaching; [3] measured after 90 days leaching; [4] measured after 118 days leaching; [5] measured after 34 days leaching; [6] measured after 62 days leaching; [7] measured after 92 days leaching; [8] measured after 127 days leaching.

4. Greenhouse Gas Emissions from Soil Affected by Biochar Amendment

The GHGs: CO_2, methane (CH_4), and nitrous oxide (N_2O) are the main contributors to radiative forcing in the atmosphere [32,93,94]. Besides various anthropogenic activities (fossil fuel combustion, cement production, industrial procedures), agronomic practices (drainage of wetlands, plowing, land use conversion), rice (*Oryza sativa*) paddy fields, fertilizers, livestock and wetlands are important sources of GHGs such as CH_4 and N_2O [95–101]. Emission of GHGs from biochar-amended soils depends on biomass types, pyrolysis conditions (temperature, duration), soil type, climatic conditions, and soil physical properties [29,32,72,102,103]. Yet, the application of biochar amendments may either have no effect or even increase emissions of GHGs [5,35,102,104,105]. In some cases, application of biochar may initially enhance emission of CO_2. Jones *et al.* [102] argued that the initial C loss during a short-term CO_2 emission is comparatively negligible compared to the amount of C stored within the biochar itself and thus should not overshadow the C sequestration potential of biochar on a long-term basis. Nonetheless, 17%–23% of biochar-C can be mineralized leading to CO_2 emission [72]. Such contradictory results of GHG emissions from lab incubation [29,30,106] *versus* field observations [104] indicate that care should be taken in interpretation and extrapolation of lab incubation data to large field scale [104]. In addition, some of the proposed mechanisms of GHG emissions from soils are also debatable [107,108].

N$_2$O Emissions from biochar-amended soils: Some field and incubation studies have demonstrated a reduction in N_2O emissions from biochar-amended soils [72,74,109]. For example, a field trial with paddy soil (hydroagric Stagnic Anthrosol) amended with biochar from wheat straw (*Triticum sativum*) produced at 350–550 °C indicated that CH_4 emission increased by 31 and 49% while N_2O emission decreased by 50 and 70%, at application rates of 10 and 40 Mg ha^{-1}, respectively [74]. Another study, conducted on a fine loamy Clarion soil amended with biochars produced from oak (*Quercus spp.*) and hickory (*Carya spp.*) at 450–500 °C, demonstrated reduction of N_2O but enhancement of CO_2 emission in a long-term column incubation experiment. In this study, soil BD was weakly correlated with N_2O flux indicating that an increase in soil aeration reduced N_2O emission [72]. However, another soil incubation study with hardwood biochar demonstrated that N_2O emission from amended sandy loam was suppressed up to 98% compared to that of the control, but enhancement of soil aeration by biochar amendment did not contribute to this effect [92]. Although most studies document N_2O reduction from biochar-amended soils, there are also examples where biochar-amended soils stimulated N_2O emissions. For example, an initial N_2O enhancement due to higher labile N content of biochar and microbial activity was observed by Singh *et al.* [106]; however, such a spike eventually decreased over time. Yanai *et al.* [110] observed that addition of 10% (w/w) municipal waste biochar produced at 700 °C to a clay loam soil suppressed N_2O emission by 89% when soil was wetted up to 78% water-filled pore space (WFPS). However, N_2O emission was significantly enhanced by up to 51% when the same soil was re-wetted at 83% WFPS. This phenomenon was attributed to aeration improvements of soil that stimulates N_2O-producing microbial activity.

CO$_2$ and CH$_4$ emissions from biochar-amended soils: In contrast to decreases in N_2O emission in most cases, biochar-amended soils may enhance CO_2 and CH_4 emissions [29,31]. Initial spikes in CO_2 release from biochar-amended soils are caused both by biotic and abiotic processes [5,35,102,111]. Liu *et al.* [112] reported that CH_4 and CO_2 emissions were reduced by 51 and 91%, respectively,

when a paddy soil was amended with bamboo (*Bambuseae spp.*) and rice straw biochar pyrolyzed at 600 °C [112]. Acidic soil amended with biochar suppressed CH_4 by 100% and N_2O by 80% in a greenhouse experiment [29]. In a long-term field study, CH_4 emission was reduced from a tropical acid savanna soil in the eastern Colombian Plains amended with biochar derived from mango tree (*Mangifera indica*) [113]. Spokas *et al.* [30] observed reduced emission of CO_2 from a silt loam soil amended with wood chip biochar compared to un-amended control, at a rate of >20% (w/w). A 100-day incubation study conducted by Spokas and Reicosky [31] demonstrated reductions in emissions of all three GHGs when three different soil types were amended with 16 types of biochars. However, no consistent trends were observed in response to types of soil and amendment [31].

No change in CO_2 or CH_4 emissions: Some studies have documented minimal impacts or no significant differences in the net GHG fluxes under field trials or laboratory incubation studies with biochars [31,104,106,109]. While soil N_2O fluxes decreased by up to 79% in different biochar-treated compared to control plots but no significant differences occurred in CH_4 and CO_2 fluxes [109,114]. A field study in Australia carried out by Scheer *et al.* [104] indicated no significant difference in GHG fluxes from control *versus* treated red Ferrosol-amended with cattle waste biochar produced at 550 °C. Spokas and Reicosky [31] observed that among the 16 biochars used, eight of the biochars had no significant change in CO_2 concentrations in biochar-amended soils compared to controls.. Similarly, Singh *et al.* [106] observed that emission of N_2O from wood and poultry manure biochars-amended Alfisols and Vertisols was suppressed by 73% compared to control, while overall CO_2 emission was not significant by addition of biochar. In addition, Hilscher *et al.* [115] observed that a loam soil amended with biochar derived from pine (*Pinus sylvestris*) wood had no changes in respired CO_2 compared to control but enhanced emission with biochar derived from rye grass (*Lolium perenne*) indicating feedstock dependency on gaseous flux.

Mechanisms affecting GHG fluxes with biochar amendment: The effects on GHG fluxes following application of biochar are often contradictory. Specific mechanisms governing such effects are not clearly understood [92,109]. Specific responses may be related to soil chemical, physical (abiotic) or microbiological (biotic) properties and associated processes [32,102,114].

(a) N_2O flux: The N_2O gaseous flux is complex because both aerobic and anaerobic processes are involved. The mechanisms of N_2O production from unamended soils are governed by three biotic pathways: (i) nitrification [116], (ii) nitrifier denitrification [117], and (iii) denitrification [118]. These pathways are related to soil physical properties such as moisture content, and aeration. The mechanisms of N_2O reduction from biochar-amended soils are attributed to increased soil aeration [110,114], sorption of NH_4^+ or NO_3^- [106,114], or presence of microbial inhibitor compounds such as ethylene [119]. In contrast, a range of pH and higher soil aeration may have no impact on N_2O emission from biochar-amended soils, and reduction in N_2O emission is explained by physical or biological immobilization of NO_3^- [92]. In addition, some studies have documented enhanced N_2O emission with biochar amendment. For example, Yanai *et al.* [110] observed N_2O suppression by 89% from clay loam soil amended with 10% (w/w) municipal waste biochar derived at 700 °C under 78% WFPS but re-wetting soils at 83% WFPS significantly enhanced N_2O emission by up to 51%. This phenomenon was attributed to aeration improvement of soil and stimulation of N_2O-producing activity of microbes or nitrifiers [92,110], however, intermittent wetting is identified as one of the causes enhancing N_2O production from various types of soils [120,121]. Thus, the mechanisms behind the

biochar role in N_2O flux in soil are still unclear, and apparently dependent on properties of both biochar and soil and antecedent conditions [32,70,110,114].

(b) CO₂ flux: Application of biochar can initially increase CO_2 efflux because of: (i) microbial decomposition of 'young' or more labile components of biochar [111], (ii) abiotic release of inorganic C [5,102], and (iii) the 'priming effect' by enhanced decomposition of existing OM or soil humus by biochar addition [102,105]. Thus, initial CO_2 release by biochar addition is due both to (i) mineralization of labile-C added through biochar and (ii) stimulation of microbial activity and thereby higher initial decomposition of SOM by biochar addition is expected. Release of labile soluble C from biochar by the first mechanism is due to increased availability of the medium as microbial substrate. In one study, initial CO_2 released from biochar-amended soils was estimated to be coming equally from microbial breakdown of soluble or labile C as well as from the abiotic release of mineral or carbonate C [102]. This change in CO_2 flux is reported to be affected not by soil physical properties (*i.e.*, BD, porosity, and moisture content) upon biochar addition into the soil [102], but mostly by soil temperature regime and land management [104].

(c) CH₄ flux: Increase in soil aeration and porosity by biochar amendment may decrease production of CH_4 from soil as anoxic conditions created may increase oxidation of CH_4 [32]. The latter depends on both diffusion and methanotrophs activity in soil [122]. Furthermore, the aerobic, well drained soils can be a sink for CH_4 due to the high rate of CH_4 diffusion and subsequent oxidation by methanotrophs [123]. Clearly, two mechanisms: (i) decrease in CH_4 production, and (ii) increase in CH_4 oxidation by methanotrophs may be operational in the soil/biochar system depending on specific conditions [70].

In summary, the emissions of CO_2, CH_4 and N_2O from biochar-amended soil are controlled by soil physical properties such as moisture content, aeration, porosity, OM content and they could both be biotic (microbial response) or abiotic (mineralization or decomposition of SOM). However, the responses are soil/biochar specific, complex and mechanisms are not clear yet.

5. A 2-Phase Complex Formation Hypothesis

Soil physical properties and GHG emissions are affected when amended with biochars (Tables 1–5). The main mechanisms leading to impact on soil physical properties and GHG emissions are briefly discussed below:

Factors affecting biochar impacts on soil quality: Not all biochars are similar in physical and chemical properties [4,5,35,124,125] and soil properties also vary widely [126]. Thus, response of soils to biochar amendment also varies widely depending on a range of factors: (i) rate of biochar application, (ii) biochar type, and (iii) time of application (Tables 1–5). Whereas the BD decreases with increase in rate of biochar application [71,73,74], it is a complex response because of temporal changes in BD of amended soils (Table 2). Increasing column-soil compaction over time due to periodic leaching was reported [72], however, the rate of compaction decreased with increasing biochar application. Proportion of stable aggregation also decreases with increase in rate of biochar application, probably due to higher compaction rate of amended soils over time due to gravitational and periodic leaching effects on incubated soil columns [72]. However, SA, porosity, and WHC can be significantly improved with increased rate of biochar application (Tables 1 and 4). A large variation in the rate of biochar application (Tables 1–5) is a critical factor to understanding the cost-effectiveness

of the biochar materials. Factors during biochar production (feedstock type, temperature, charring time) are important controls which affect GHG fluxes. Soil response to biochar also depends on several soil factors (*i.e.*, WHC, SA, porosity, *etc.*) as the temporal change of soil's WHC as a parabolic response was observed in Norfolk loamy sand and Warden silt loam soils, but not in Declo silt loam (Table 4) [76].

Biochar ages in soil environment after application because of various chemical and biological reactions on biochar/soil interface which alter soil quality over time. While surface oxidation and higher acidity are presumably the main changes during aging [87,127], recent data also indicate (i) possible transformations or conversions of surface functional groups such as increase in phenols and conversion of carboxylic acids to cyclic acid anhydride derivatives and (ii) oxidation and subsequent solubilization or microbial uptake of surface functional groups with increase in carboxyl and carbonyl groups in the bulk structure [82]. Soil exchange capacities may increase over short time during aging as an increase in the CEC of aged biochars compared to fresh ones due to generation of oxygenated surface functional groups by surface oxidation process has previously been reported [66,87,127]. In-depth possible short-term (1–2 years) interactions between biochar, soil pores, plant roots and microbes have recently been reviewed, mostly in terms of soil chemical perspectives combining various pathways such as dissolution/precipitation, adsorption/desorption, acid/base, and redox reactions [128]. To-date, few biochar/soil studies have investigated nanoscale organo-mineral interactions under field conditions [129] where soil mineral phase has been demonstrated to be attached with biochar organic phase by two mechanisms. Various spectroscopic techniques combined with image processing and ultimate analyses (volatile matter, ash content, C, H, N, O) have revealed that two characteristically different biochars (chicken manure and paper-mill sludge) made complexes on biochar and soil mineral edges by (i) oxidation reaction and (ii) adsorption of SOM on biochar surface. It has also been shown that these two biochars perform differently in aggregate formation as chicken manure biochar undergoes oxidation/reduction reactions making higher mineral-aggregates coverage on surface over time using Al, Si, and Fe-oxides, while paper-mill biochar facilitates SOM adsorption on biochar surface through Ca-bonded cation bridge formation [129]. While these data support importance and significance of complexation for soil aggregate formation over time, whether the functional groups involved (–COOH, C–OH, C=O, C–O, C–N) in the reactions are from labile or refractory part of biochar is still unknown. In addition, different biochars may behave differently in soil environment and a range of biochars needs to be tested. However, the biochar amendment strategy must be evaluated for longer field trial and current knowledge still lacks in fundamental understanding of biochar interaction in soil over long-time horizon. Hypothetical complexation between biochar bulk and surface functional groups and soil minerals could be the only way to explain high recalcitrant nature of biochar in soil and sustainability of TP over century. Various mechanisms of sorption of organic compounds on biochar surface were proposed by Joseph *et al.* [128] which were mainly derived from the interactions presented in the hypothetical complex organo-mineral conceptual model by Kleber *et al.* [130]. The interactions proposed by this model are (i) surface hydrophobic or hydrophilic interactions (H-bonding, ligand exchange, cation bridging, specific interactions) between organic functional groups and soil mineral phases, (ii) π-π electron donor-acceptor type (EDA) interaction between sorbed SOM and functional groups, (iii) complexation by multidented organic acids with metal ions in soil [130], of which two

interactions are evident from recent biochar study [129]. While all these hypothetical mechanisms may explain some extent of complex formation, however, the insight of the initial high peak of CO_2 within few weeks of biochar application in soil is still lacking. Based on the available data on soil physical properties and gaseous emissions (Tables 1–5) after biochar application and insight from the previously assumed model [130] and evidence of complexation by recent data [129], a 2-phase complex formation hypothesis of interaction of biochar and soil is proposed below in order to better understand the key processes such as physical interaction, biological activity, gaseous emission, and bonding characteristics between biochar functional groups and soil mineral phase.

2-phase complex formation hypothesis: The soil response to biochar involves complex physical, chemical, and biological interactions (Figure 1). Whereas the physical and chemical interaction of biochar with soil are interrelated and create a faster response, the biological interaction is slower at the onset because of other factors such as moisture content, OM or nutrient source, SA and porosity which are important controls to biological functions. Addition of biochar triggers the physical contact of biochar/soil surface and sets-in-motion the physical-chemical interaction. The SA of biochar comprises of aromatic and aliphatic organic surface functional groups [2,4,131] which create direct and indirect bonds with soil mineral and organic phases. The complex formed between biochar surface and soil organic and mineral phases may stabilize aggregates [129] and form the basis of biological interaction. Most parts of the biochar are microbially stable as C from biochar is protected due to presence of thermodynamically stable (*i.e.*, refractory) cyclic organic compounds [38,131–134]. However, a labile component of biochar (*i.e.*, volatile matter) consisting mainly of aliphatic functional groups [2,4,131] is prone to decomposition by soil microbes [5,35]. This labile volatile matter is also affected by the biochar pyrolysis temperatures [2,4] as lower temperature biochars are comprised of a higher content of volatile matter. Thus two situations may arise upon initial contact of labile part of biochar and soil mineral phase: (i) a considerable part of volatile organics could be consumed by microbes, (ii) labile organic functional groups react quickly to make fast but weak initial complexation, which eventually could be degraded by subsequent microbial interaction. While it is not possible to predict which process would precede over other, quick peak of CO_2 during first few weeks of soil incubation with biochars suggests the initial end-product via microbial interaction [35,115,135,136]. However, some of these labile functional groups still could be left within the microporous structure of biochar as trapped/protected volatile organics [5] and can take part of the subsequent aggregate formation slowly over time. Thus, the labile aliphatic functional groups from the volatile matter of biochars can cause weak and presumably non-specific EDA type interaction, or H-bonding on the soil mineral-biochar surface [130] upon initial biochar addition and can adsorb nutrients and other compounds temporarily within the complex [128,129]. While this initial weak complexation with organic-C has been evident in different biochars, the role of N is less specific as most NH_4^+ or NO_3^--N from biochar is assumed to be either (i) lost by evaporation or dissolution on the aged biochar surfaces over time after application in the soil [129] or, (ii) N is present in most biochars (except animal derived biochars) as heterocyclic or unavailable form (so called 'black-N') [137–140]. Thus, predominantly organic-C from biochar appears to be the main binding agent on soil mineral phase. However, as the microbial process begins, these labile short-duration compounds produced at the biochar and soil surface break down with the short-term release of plant available nutrients and CO_2 as an initial gaseous flux. This phenomenon, may explain the higher fertility of biochar-amended soils in short-term greenhouse studies [21,141,142],

initial release of GHGs from laboratory incubation and field studies [5,35,102,111]. The high amount of SA and distinct pore volumes of biochar surface [2] are potential microbial habitat and accentuate nutrient release upon microbial decomposition and degradation of soil/biochar initial complex. However, the second phase complex formation within the inner core of biochar material consisting of stable cyclic aromatic compounds begins simultaneously through interactions of biochar aromatic organic-C, soil mineral and microbial biomass. The role of aliphatic-C from volatile matter in this stable complex formation is unclear but may be important as lower temperature biochar promoted aggregation with progressively higher rate of amendment application while the similar effect was not apparent for higher temperature biochars without presence of any substrate (*i.e.*, switchgrass) (Table 3). This observation signifies the importance of a labile-C source (either from volatile organics or from any added substrate) for aggregate formation in soil through biochar. Volatile matter can still be protected from microbial decomposition within biochar micropores [5] and may take part in complexation simultaneously. This stable complexation may take place either through specific bonding by biochar surface functional groups and mineral phase of soil, metal-organic cation bridge formation or for some biochar by sorption of SOM on biochar-mineral phase over time as evident by recent study [129]. Thus, stable soil aggregates may be formed through interaction with soil minerals on the higher SA of biochar (Figure 2). The specific bonding of SOM and minerals can retard microbial decomposition of SOM [143], and SOM is physically and chemically protected from microbial attack through formation of stable aggregates [144,145]. Stable aggregates thus formed can also increase recalcitrant nature of biochar-amended soil C over time and reduce the emissions of GHGs [29–31] while slowly releasing the plant available nutrients over time (Figure 2).

Figure 1. Schematic representation of interactions between biochar and soil.

1: Typical agricultural soil composition
2: Hypothetical soil composition after biochar addition
3: Proposed processes involved
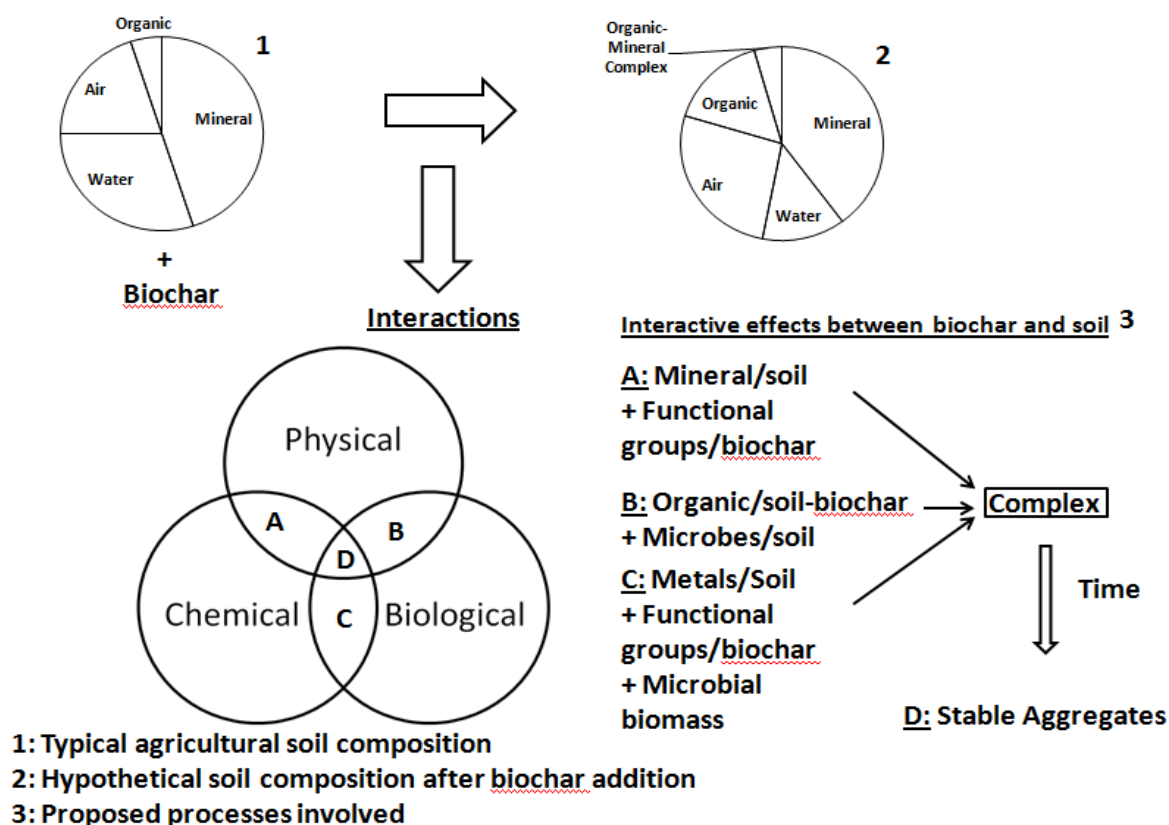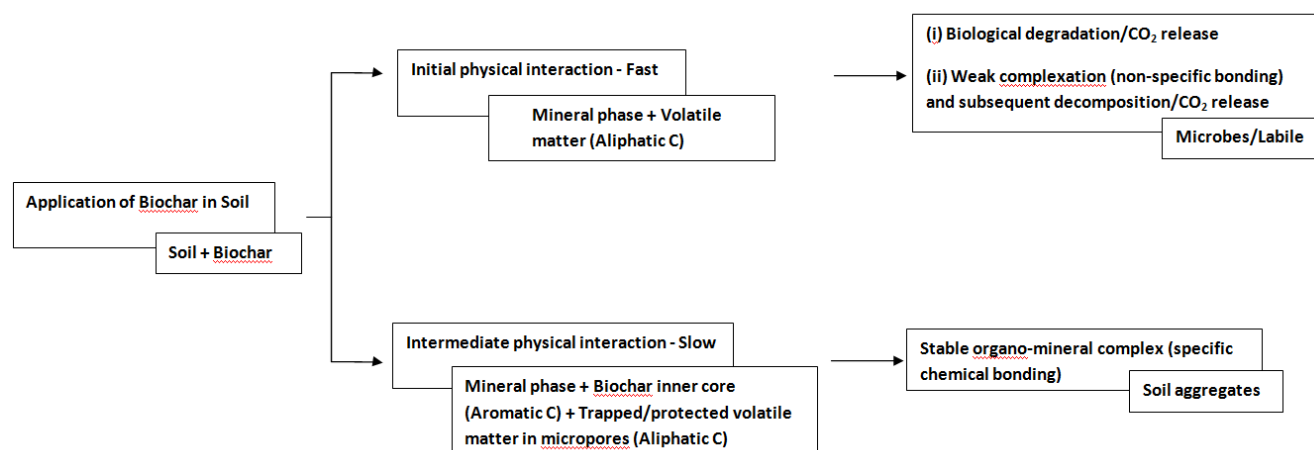
**Figure 2.** Schematic representation of two-phase complex formation.

Table 5. Impact of biochar on greenhouse gas (GHG) emission *.

Soil type	Biochar type	Study type (Scale)	Rate of biochar application % (g g^{-1})	CO$_2$ emission rate (kg ha^{-1} Year^{-1})	CH$_4$ emission rate (kg ha^{-1} Year^{-1})	N$_2$O emission rate (kg ha^{-1} Year^{-1})	References
Hydroagric stagnic anthrosol	Wheat straw (350–550 °C)	Field	0	-	200	2.9	[146]
			0.8	-	330	2.1	
			3.3	-	336	2.3	
Hydroagric stagnic anthrosol	Wheat straw (350–550 °C)	Field	0	9,744 [1], 13,409 [2]	222 [1], 91 [2]	8 [1], 17 [2]	[74]
			0.7	10,380 [1], 11,495 [2]	215 [1], 78 [2]	4 [1], 12 [2]	
			1.3	9,456 [1], 12,174 [2]	560 [1], 140 [2]	3 [1], 9 [2]	
			2.7	9,318 [1], 13,926 [2]	336 [1], 125 [2]	4 [1], 8 [2]	
Red Ferrosol	Cattle feedlot waste (550 °C)	Field	0	21,803	−0.85	4.3	[104]
			1	21,745	−0.79	4.9	
Sandy loam	Oak, cherry (400 °C)	Laboratory	0	260	-	3.6	[92]
			1	405	-	2.7	
			2	404	-	2.7	
			5	319	-	0.9	
			10	239	-	0.1	
Fine loamy Clarion	Mixed hardwood (Oak, Hickory) (450–500 °C)	Laboratory	0	12,634	-	1.4	[72]
			0.005	15,381	-	0.3	
			0.01	18,127	-	0.3	
			0.02	20,325	-	0.2	

* Rates are extrapolated to one year; [1] Measured during the rice cycle in 2009; [2] Measured during the rice cycle in 2010.

6. Research Priorities

A number of research priorities can be identified from this review. There are few data on the effects of biochar on SA, aggregation, porosity, PSD, and PR of biochar-amended soil. Additional research is needed to understand mechanisms of aggregate stability of a biochar-amended soil, especially from field scale experiments for a range of depths and over time. There is also a need to evaluate the effects of biochar pyrolysis conditions (temperature and duration of pyrolysis) on soil physical parameters and GHG emissions. Most studies have been conducted under laboratory settings to measure GHG fluxes with biochar amendment, and few field data are available to validate the incubation studies. There is a strong need to understand the mechanisms of response of biochar to emission of GHGs and to resolve contradictions. The size fractions (coarse *versus* fine) of biochar and depth of incorporation (surface application *versus* subsoil mixing) are also important factors to be addressed. Additionally, aging of biochars changes the properties significantly [2,86,87] which would have subsequent effects on soil over time, and thus time-series field-scale data on soil properties are needed in order to better understand the underlying processes.

The 2-way complex formation hypothesis needs to be validated at a range of scales (*i.e.*, field, greenhouse, and lab incubation), evaluated for diverse soil/biochar combinations for different cropping systems and land use types to determine both positive and negative responses over time. For example, as different biochars make complexes by various mechanisms [129], a range of biochar/soil combinations should be tested. In order to understand first stage of interaction after biochar addition to soil the characterization of functional groups (aliphatic *versus* aromatic) on aged biochar surface and volatile matter content as the proxy of labile-C [4,5] needs to be determined. The amount of organic functional groups determined by Boehm titration [4,5,82] and X-ray photo-electron spectroscopy (XPS) [129] on fresh and aged biochar surfaces needs to be correlated with volatile matter content to evaluate the extent of labile-C involvement during the first phase of interaction as proposed (Figure 2). Additionally, initial spike of CO_2 from biochar amended soils could be monitored by stable isotope technique to assess the source (labile biochar-C *versus* soil-C) of relative proportion of mineralized C. On the other hand, to assess the extent of complexation towards aggregation, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDS) technique can be used to locate stable soil aggregate formation by complexation through either (i) specific bonding of biochar functional groups on soil mineral surface or (ii) adsorption of SOM on biochar and organic-C-metal bridge [129]. Additionally, the extent of di or trivalent metal ions used for metal-organics cation-bridge can be determined by (i) ultimate analyses on fresh and field aged biochar, (ii) elemental analyses on biochar and soil, and (iii) XPS on aged biochar and soil. Thus, various elemental characterization combined with spectroscopic techniques will provide evidences on degree of interactions and clues of the mechanisms involved between biochar and soil over time. Finally, reported high biochar amendment rates [30,110] being not practical, field studies must be conducted at judicious rates and presumably this indicates that some economic assessment of the benefits of biochar is warranted.

7. Conclusions

This review synthesizes available data on physical properties of biochar-amended soils, gains insight of the key processes involved, offers mechanisms of some of the key processes and sets future research priorities. The pyrolysis temperature and charring time of biochar seem to be important factors in order to implement any biochar amendment project. The higher the biochar pyrolysis temperature, higher is the BD, and WHC. However, the relationship is not simple, and time is an important factor. Application rates of 1%–2% (g g^{-1}) biochar can significantly improve soil physical quality in terms of BD, and WHC.

The 2-phase (fast and slow) mechanism of soil/biochar interaction proposed here suggests an explanation of the key processes. It appears that one of the main controls which affect the quality of biochar-amended soils is the pyrolysis temperature. The use of a low-temperature biochar with a higher amount of labile aliphatic functional groups carried by volatile matter can enhance short-term rapid nutrient availability. Yet, the high-temperature biochars can bind soil-C and other nutrients over long run. In addition, higher temperature biochars have higher SA and more micropore volumes than those of lower temperature biochars, which facilitate the second phase stable complex formation. Finally, despite some supporting evidences, the proposed 2-phase complexation hypothesis needs to be evaluated under a range of spatial and temporal scales.

Acknowledgement

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