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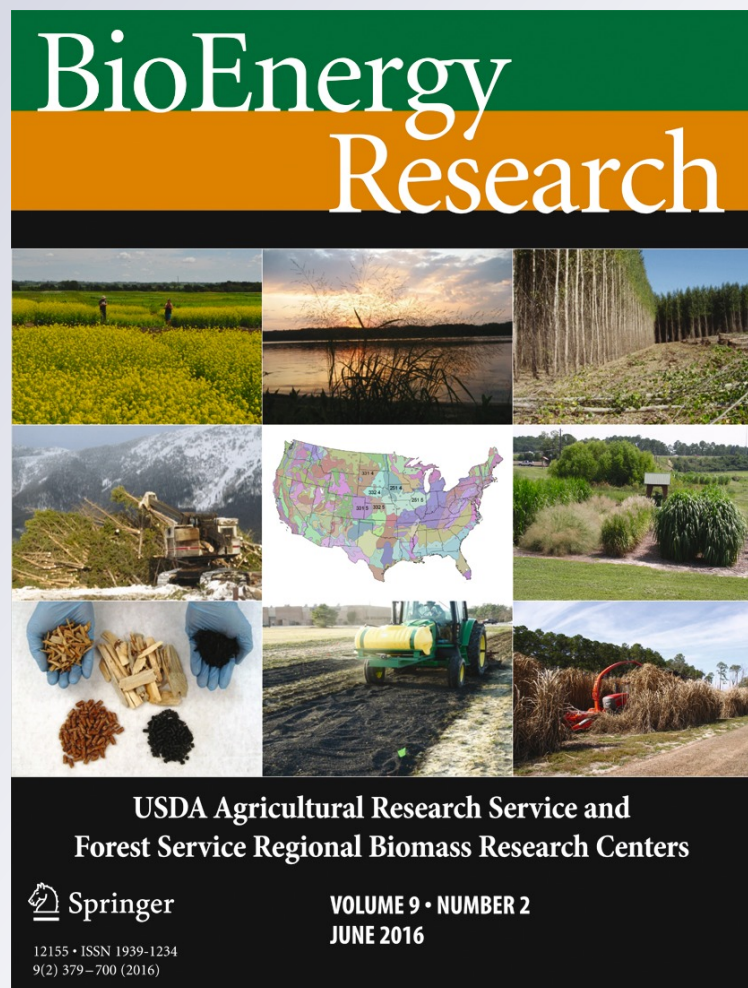
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# Soil Health, Crop Productivity, Microbial Transport, and Mine Spoil Response to Biochars

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**Abstract** Biochars vary widely in pH, surface area, nutrient concentration, porosity, and metal binding capacity due to the assortment of feedstock materials and thermal conversion conditions under which it is formed. The wide variety of chemical and physical characteristics have resulted in biochar being used as an amendment to rebuild soil health, improve crop yields, increase soil water storage, and restore soils/spoils impacted by mining. Meta-analysis of the biochar literature has shown mixed results when using biochar as a soil amendment to improve crop productivity. For example, in one meta-analysis, biochar increased crop yield by approximately 10 %, while in another, approximately 50 % of the studies reported minimal to no crop yield increases. In spite of the mixed crop yield reports, biochars have properties that can improve soil health characteristics, by increasing carbon (C) sequestration and nutrient and water retention. Biochars also have the ability

to bind enteric microbes and enhance metal binding in soils impacted by mining. In this review, we present examples of both effective and ineffective uses of biochar to improve soil health for agricultural functions and reclamation of degraded mine spoils. Biochars are expensive to manufacture and cannot be purged from soil after application, so for efficient use, they should be targeted for specific uses in agricultural and environmental sectors. Thus, we introduce the designer biochar concept as an alternate paradigm stating that biochars should be designed with properties that are tailored to specific soil deficiencies or problems. We then demonstrate how careful selection of biochars can increase their effectiveness as a soil amendment.

**Keywords** Biochar · Microbiology · Mine-impacted spoils · Restoration · Soil health

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## Abbreviations

C	Carbon
N	Nitrogen
SOC	Soil organic carbon
USDA-ARS	United States Department of Agriculture-Agricultural Research Service
US EPA	United States Environmental Protection Agency

## Introduction

Over the past 10 years, the use of biochar as a soil amendment has attracted global attention. In this same time span, hundreds of articles have reported on the potential impact of biochar on soil properties, greenhouse gas production, and crop yields (ISI Web of Knowledge at <http://apps.webooknowledge.com>).

Several recent reviews [1–4] have examined the impact of biochar on soil conditions and crop yield. The consensus of those reviews is that both crop and soil response to biochar are variable but can be linked to the biochar attributes and soil properties. For example, Jeffery et al. [2] conducted a meta-analysis on 17 biochar studies. They reported crop yield variability ranged from –28 to +39 %, with an overall average yield increase of 10 %. A meta-analysis of 114 biochar studies showed similar results, corroborating that the ability of biochar to improve crop yield is highly variable [3]. In a recent greenhouse study, an 80:20 blend of pine chip (*Pinus taeda*) and poultry litter biochar increased above- and below-ground biomass of winter wheat (*Triticum aestivum* L.) by 81 % compared to the untreated control in a highly weathered Ultisol [5]. This result is typical in studies that add biochar to highly weathered soils where biochar improves soil pH and provides nutrients [4]. In contrast, variable improvements in crop grain yields over several growing seasons in Idaho were reported on an Aridisol (i.e., relatively unweathered soils) as compared to those used by Sigua et al. [5] suggesting that the specific biochar being evaluated was not always effective [6]. In another report, Spokas et al. [7] reviewed the biochar literature and found that 30 % of the studies reported no significant differences, and 20 % reported negative yield or growth effects. In summary, the unpredictable and variable crop yield response to biochar application reported in these studies suggest caution toward widespread adoption of biochar technology for agricultural purposes without a better understanding of the characteristics and specific biochar properties as well as the potential response by soils with different inherent properties or management-induced (e.g., mining) problems.

Biochar application to soil can have potential impacts on water quality and for reclamation of mine spoils. For example, Novak et al. [8] reported that biochar produced from poultry litter had a negative impact on shallow ground water quality by releasing significant concentrations of dissolved phosphorus and by increasing movement of fecal bacteria through the soil [9, 10]. On the other hand, biochar produced from pine chips significantly decreased movement of fecal bacteria through fine sand [9]. It has also been demonstrated that biochars have an emerging capability for remediating soils impacted by mining [11, 12]. However, reclamation of mine spoils using biochar is a complicated task since the biochar must be capable of binding heavy metals or reducing toxic substance concentrations, while also improving soil health characteristics and thus promoting a more sustainable plant cover to prevent erosion, leaching, or other unintended, negative environmental consequence.

The diversity in chemical and physical characteristics of different biochars can be capitalized on to promote its multifunctional use in agricultural, industrial, and environmental sectors [13]. The large variety of potential feedstocks and biochar production processes must be understood because

they can influence biochar chemical and physical properties and thus influence selection of an appropriate biochar as a soil amendment, carbon (C) sequestration agent, or remediation trigger. Therefore, our objectives are to (1) review the fundamentals of biochar manufacture and characterization, (2) discuss potential impacts of biochar on soil health characteristics, including crop productivity and soil hydraulics, (3) synthesize recent findings regarding the impact of biochar on microbial pathogen movement, and (4) examine the ability of biochar to reclaim mine-impacted soil which is commonly referred to as spoil.

## Biochar Production and Characterization

### Biochar Manufacture

Pyrolysis is the thermal conversion of organic feedstocks for generation of energy through which the leftover material, commonly referred to as biochar is created. Pyrolysis of biomass feedstocks occurs at temperatures typically ranging between 300 and 700 °C under a low oxygen condition [14]. Gasification is another pyrolysis-like technique for making biochar and subjects feedstocks to gasification reactions at higher temperatures (>700 °C). Many types of feedstocks have been used for biochar production including lignocellulosic material such as corn (*Zea mays*, L), stover, switchgrass (*Panicum virgatum*), nut hulls, and crop processing wastes (e.g., cotton (*Gossypium spp.*) gin trash, seed screenings, etc.) along with various animal manures (e.g., poultry, swine, and dairy). Many other municipal and industrial organic byproducts have also been used for biochar production including municipal, wood, and cardboard waste products.

### Biochar Characterization

Feedstock diversity and variable pyrolysis conditions result in biochars with a wide range of chemical and physical characteristics [15]. The carbonization process that converts organic feedstocks into biochar becomes more intensive as the pyrolysis temperature increases from 300 to 700 °C. In the lower temperature range (300 to 400 °C), there is some loss of organic materials due to volatilization, but some ring and carboxylic acid compounds are retained. As the pyrolysis temperature increases (400 to 500 °C), most of the volatile material is removed as a gas, and the remaining non-volatile solid material undergoes further structural conversion. Some volatile material can re-condense as tar-like compounds and become associated with the biochar matrix [16]. After the loss of volatile material, biochars will possess an amorphous core matrix composed of aromatic and aliphatic compounds that can have attached carbonyl and hydroxyl functional groups [17]. Pyrolysis at temperatures from 500 to 700 °C causes the



amorphous aromatic sheets to stack up and reform as turbostratic crystalline-aromatic sheets [18].

## Biochar Impact on Soil Health and Crop Productivity

### Soil Health

In this review, we define soil health as the capacity of soil to function as a living system, to sustain plant and animal productivity, maintain or enhance water quantity, and promote crop productivity. Biochar has the ability to improve soil health characteristics due to its elemental composition and ability to improve pH, retain water in its pore space, and bind nutrients and metals on its functional groups [19]. As mentioned previously, biochars produced at lower pyrolysis temperatures (350 °C) will retain some organic carbon structures that can be decomposed by soil microbes, but as pyrolysis temperatures increase (>400 °C), the remaining biochar material is predominately a C-enriched material that contains organic structures that resist oxidation and hence can have long residence times in soil [20]. Amending soils with stable forms of biochar increases the size of C pools and long-term C sequestration [21]. Biochars are not totally resistant to decomposition, as they can be slowly oxidized by biotic [22] and abiotic mechanisms [23]. In one recent biochar stability study, Spokas et al. [24] demonstrated that biochars can weather into pieces through hydration reactions that expand the organic sheets and eventually exfoliate them as fragments. Weathering of biochars is an important process because it leads to formation of carbonyl and carboxylic functional groups [20] that can consequently increase biochar cation exchange capacity and thus improve plant nutrient retention [15].

Biochars also contain inorganic ash derived from non-volatile feedstock constituents [19] from residual bedding material mixed with manure feedstocks [25]. As shown in Table 1, biochar produced through gasification of Kentucky bluegrass (*Poa pratensis*) seed waste (KBSW) will generally have a high ash content and alkaline pH value (pH ≈ 10). High ash content causes pH values of biochar to be >9 [26, 27], thus making materials such as alkaline KBSW biochar suitable “designer biochar” for neutralizing acidic soils [28, 29]. Furthermore, both biochars presented in Table 1 contain C and nitrogen (N), as well as plant macro- (e.g., Ca, P, and K) and micronutrients (e.g., Cu and Zn). Of interest to some is the dissimilarity in nutrient composition between KBSW and wood biochar, especially with regard to Ca, K, and P concentrations (Table 1). Higher N, Ca, K, and P concentrations in KBSW biochar suggest that it would be a more suitable designer biochar than wood biochar as a soil fertility improvement agent.

**Table 1** Characteristics of two gasified biochars examined in ARS-Corvallis, Oregon. Biochar from Kentucky bluegrass seed waste (KBSW) was produced using a small-scale updraft gasification unit at temperatures of 650 to 750 °C. Biochar from mixed conifer wood was produced using a small-scale downdraft gasification unit at maximum char temperatures ranging from 1100 to 1400 °C. The wood biochar was produced from a mixed conifer logging slash material consisting of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco), Ponderosa pine (*Pinus ponderosa* C. Lawson), white fir (*Abies concolor* (Gord. & Glend.) Lindl. ex Hildebr.), sugar pine (*Pinus lambertiana* Douglas), and incense cedar (*Calocedrus decurrens* (Torr.) Florin)

Variable	Units	KBSW biochar		Wood biochar	
		Mean	±SD	Mean	±SD
Volatile C	%	16.7	0.6	7	0.3
Fixed C	%	32.7	1.6	77.5	1
Ash	%	50.6	2.1	15.6	0.7
Surface area	m <sup>2</sup> g <sup>-1</sup>	26.1	1.2	423.3	52.5
pH		10.2	0.1	10.9	0.01
EC	mS cm <sup>-1</sup>	2.98	0.1	3.56	0.14
CEC	cmol kg <sup>-1</sup>	43.1	2.1	14.8	4.4
Total C	%	35.5	1.5	78	15.9
TSOC	g kg <sup>-1</sup>	7102	213	3905	117
Total N	%	2.2	0.3	0.79	0.4
TSN	g kg <sup>-1</sup>	410	12	BD	
NH <sub>4</sub> -N	mg kg <sup>-1</sup>	84.2	0.5	5.6	0.2
NO <sub>3</sub> -N	mg kg <sup>-1</sup>	2.5	0.2	19.4	0.8
Total K	mg kg <sup>-1</sup>	50,600	2519	34,787	4092
Bray-K	mg kg <sup>-1</sup>	36,357	1532	21,000	1172
Ca	mg kg <sup>-1</sup>	13,330	770	43,293	5768
Total P	mg kg <sup>-1</sup>	15,320	565	5020	849
Bray-P	mg kg <sup>-1</sup>	935	27	6.3	1
Mg	mg kg <sup>-1</sup>	6342	97	12787	1477
S	mg kg <sup>-1</sup>	4650	580	3463	509
Fe	mg kg <sup>-1</sup>	1125	42	4866	157
Mn	mg kg <sup>-1</sup>	755	17	2783	366
Na	mg kg <sup>-1</sup>	411	6	320	34
Zn	mg kg <sup>-1</sup>	143	2	393	80
Cu	mg kg <sup>-1</sup>	36	3	42	9
Ni	mg kg <sup>-1</sup>	BD		25	8
Al	mg kg <sup>-1</sup>	854	106	1908	411
As	mg kg <sup>-1</sup>	BD		BD	
Cd	mg kg <sup>-1</sup>	BD		BD	

BD below detection

The impact of a hardwood biochar on soil fertility characteristics in a sandy, acidic-Ultisol is shown in Table 2. This hardwood biochar caused significant increases in soil pH, organic C, and plant nutrients such as Ca, K, and Mg concentrations, supporting the aforementioned changes in soil characteristics following biochar application. Raising the pH and supplying Ca, K, and Mg is important because this soil has lost its fertility due to leaching of base cations [30]. Unfortunately, this

**Table 2** Soil fertility characteristics of a Norfolk loamy sand (Ultisol) after laboratory incubation for 120 days with and without hardwood biochar (means between columns with a different letters indicate significant differences at  $p < 0.05$ ) (Novak, 2015; unpublished data)

Properties	Norfolk + 0 biochar	Norfolk + 20 g kg <sup>-1</sup> biochar
pH (H <sub>2</sub> O)	5.6a	6.6b
CEC (cmol kg <sup>-1</sup> )	2.1a	2.3a
Ex. acidity (cmol kg <sup>-1</sup> )	1.2a	0.9a
Total N (kg ha <sup>-1</sup> )	1473a	1545a
Organic C (kg ha <sup>-1</sup> )	11,500a	65,695b
Macronutrients (kg ha <sup>-1</sup> )		
P	70a	57a
K	49a	161b
Ca	288a	440b
Mg	47a	67b
Na	6.7a	7.3a
Micronutrients (kg ha <sup>-1</sup> )		
B	0.11a	0.22a
Cu	0.90a	0.90a
Mn	13.4a	14.9a
Zn	4.8a	3.4a

hardwood-based biochar did not produce significant improvements in other important soil plant nutrient (e.g., P and Cu) concentrations in this highly weathered sandy-textured Ultisol.

### Crop Productivity

In anticipation of improving crop productivity, biochars are commonly applied to soils possessing poor to marginal fertility characteristics [27, 31, 32]. The previously cited meta-analyses have shown divergent results regarding improved crop productivity after applying biochar to soils [3, 7]. Liu et al. [33] reviewed published data from 59 pot experiments and 57 field experiments, concluding that crop productivity was increased by 11 % on average. Uzoma et al. [34] reported the effects of biochar produced from cow manure on corn yield, nutrient uptake, and physicochemical properties when used on a sandy soil. They found that applying 15 or 20 t ha<sup>-1</sup> of biochar significantly increased corn grain yield by 150 or 88 %, respectively, when compare to an untreated control.

On the other hand, some studies have reported no increases in crop yield following biochar application [35–37]. For example, Martinsen et al. [38–2015] reported that biochars created from maize (*Zea mays*, L.) cob or groundnut (*Arachis hypogaea*) did not affect maize yields. Similar results were reported by Jones et al. [39], who used biochar produced from commercial wood chips as a soil amendment. The mixed performance of biochar as an amendment is related to the wide

diversity of physiochemical characteristics that translates into variable reactions in soils [8, 40].

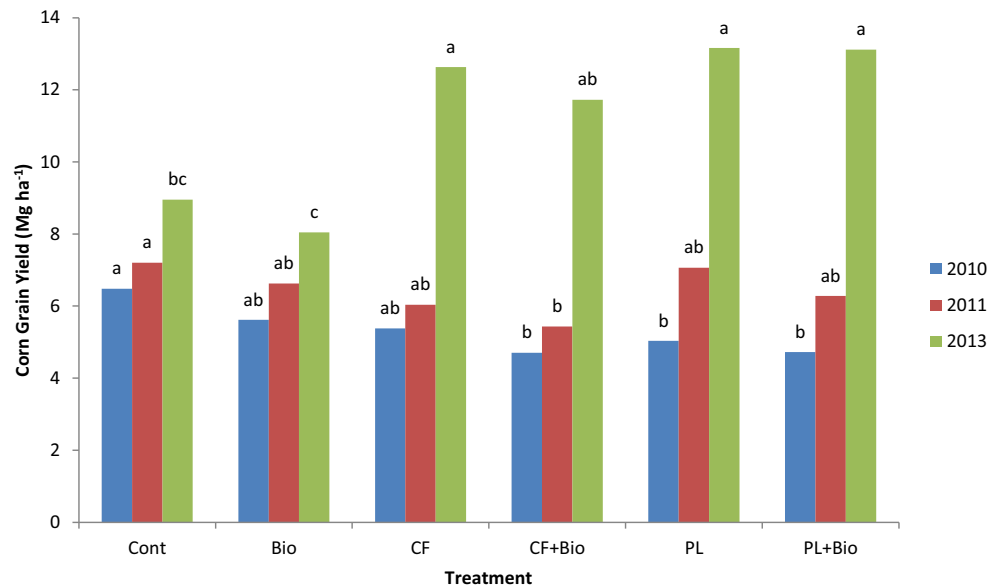
Variable performance of a hardwood biochar was amply demonstrated after its application to a Haplocalcid soil in Idaho [6]. The hardwood biochar was applied to determine if its addition alone, when mixed with fertilizer and when mixed with animal manure would improve soil nutrient cycling resulting in higher corn stover yields. In that study, plots were treated with a one-time application of animal manure (42 Mg ha<sup>-1</sup> dry weight, dw), hardwood biochar (22.4 Mg ha<sup>-1</sup> dw), a blend of the biochar and manure (same rates), and a control (no amendments). Soil tests were collected over a 2-year period to determine changes in soil fertility, total C, total N, and yield of corn silage in Idaho. Lentz and Ippolito [6] reported the only significant soil fertility increases due to biochar were in soil Mn and total organic carbon, while manure-treated soils had significant increases in extractable K, Mn, Cu, Na, and Zn when compared to the untreated control. Biochars affect on silage yield was mixed, producing a slight increase in year one but a 36 % decrease in year two [6]. Further investigations of soil fertility showed that the hardwood biochar was unable to adjust the calcareous soil pH to improve nutrient availability and that it did not significantly improve available P, N, or any important plant cationic nutrients [6].

The same hardwood-based biochar was applied to a Paleudalf soil in Kentucky. Over a 3-year (2010, 2011, and 2013) period, corn grain yields were measured (Fig. 1). The hardwood biochar and the experimental methods were similar to those used in the Idaho experiment, with the exception that poultry manure was applied at 12 to 19 Mg ha<sup>-1</sup> and 224 kg N ha<sup>-1</sup> was applied as liquid urea ammonium nitrate (UAN). Corn grain yields in 2010 and 2011 were impacted by drought and unfavorable rainfall distribution (Fig. 1), so no significant differences were observed among treatments. However, in 2013, the biochar-treated plots produced significantly lower corn grain yield than UAN, poultry litter, and combinations of biochar with UAN or poultry litter. Because the addition of the hardwood biochar with chemical fertilizer and poultry litter did not improve corn grain yield in any of the 3 years (Fig. 1), it was concluded that this specific hardwood biochar did not possess the chemical characteristics capable of improving soil health characteristics of this Paleudalf and thus increase corn productivity.

### Biochar Influence on Soil Water Hydraulics

Water storage and movement within soil (i.e., hydraulics) is an important soil health feature that influences water availability for plants [41], microbial processes [42], and soil nutrient turnover processes [43]. Long ago, farmers recognized the importance of improving soil hydraulics with charcoal to acquire higher crop yields. For example, in 1860, Walden [44]

**Fig. 1** Effects of hardwood biochar (*BIO*), poultry litter (*PL*), chemical fertilizer (*CF*), and biochar + poultry litter (*CF + Bio*) on corn grain yield (data from 2010, 2011, and 2013 growing seasons in Bowling Green, Kentucky; letters after means indicate significant differences at a  $\alpha = 0.5$  among treatments in each year)



reported that the addition of charcoal (i.e., biochar) can improve soil water holding capacities by retaining a “good balance” of moisture around plant roots. Almost 100 years later, Tryon [45] was the first to demonstrate that soil texture was a critical factor controlling the impact of biochar on hydraulic properties. More recently, considerable attention has been given to using biochar to modify soil water hydraulics including water holding capacity and available water content [46–50], as well as soil hydraulic conductivity [51–54]. Laird et al. [47] reported that the addition of 1 to 2 % hardwood biochar to a Midwestern USA Mollisol increased gravity drained water retention by 15 % relative to the untreated control but did not affect soil moisture content measured at soil water potentials of 33 or 1500 kPa (field capacity and wilting point, respectively) [41]. Basso et al. [49] reported similar results ( $\approx 23$  % increase) in gravity-drained water content in a sandy Midwest soil relative to an untreated control. Higher water storage for a sandy soil from the Southeastern USA Coastal Plain was reported by Novak et al. [48] with an additional 1.5 cm of water stored per 15 cm of soil after 2 % ( $w w^{-1}$ ) addition of switchgrass biochar.

Biochar additions to soils have had mixed results with regard to modifying soil hydraulic conductivity ( $K_{sat}$ ) or water infiltration rates. Uzoma et al. [52] and Ouyang et al. [53] reported improvements in  $K_{sat}$  after biochar additions to a silt and sandy loam-textured soil, respectively. In contrast, both Laird et al. [47] and Major et al. [55] reported no significant change in  $K_{sat}$  for biochar applied to loam- and clay-textured soils, respectively. On the other hand, Lim et al. [56] reported that  $K_{sat}$  values declined after additions of 1, 2, and 5 % ( $w w^{-1}$ ) biochar to both a coarse and a fine sand. The decrease was related to the particle size of the biochar. Repeating the experiment using a clay loam-textured soil showed that 1 and 2 % biochar additions universally increased  $K_{sat}$ . To explain

these results, Lim et al. [56] modeled the impact of biochar on  $K_{sat}$  by incorporating soil pedo-transfer functions with the biochar-altered soil texture. Using this model, they showed that soil texture greatly modulates the predicted response on  $K_{sat}$  from biochar additions. Similar results were found by Barnes et al. [54], who showed biochar impacts on  $K_{sat}$  depending on macro- and meso-porosity of the soil. They also found that biochar additions decreased  $K_{sat}$  in sand and organic soils, but increased  $K_{sat}$  in a clay-rich soil.

Water infiltration is another important soil health characteristic because this property regulates water movement into soils vs. movement across the soil surface. Novak et al. [57] measured significant improvement in water infiltration rates after biochar additions to a sandy loam soil. They reported that the biochar-treated soil had significantly higher infiltration rates of 0.157 to 0.219  $mL min^{-1}$  compared with 0.095  $mL min^{-1}$  for an untreated control. For three of the four biochars used in this study, water infiltration rates declined to values similar to the control after four water infiltration simulations. This indicates that these biochars have a limited impact on improving water infiltration and may be a result of the physical clogging of pores by exfoliated biochar fragments [24].

The matric forces of soil controls the quantity of both total and plant available water, and although biochar additions to soils may improve total water retention, plant available water may be limited [58]. Plant available water is not a binary process (i.e., on/off) but rather a continuum that changes constantly due to the diverse capillary forces that are a function of physical pore distribution [59]. Integral water capacity (IWC) and integral energy ( $E_i$ ) are two indices that can be used to assess this altering function of soil water availability [60, 61]. When IWC and integral energy  $E_i$  values were calculated for biochar-amended soils [62], increases in total soil water holding capacity comes at the expense of increasing energy

required to extract the moisture from biochar-amended soil (Table 3). Data in this table also show that increased IWC is primarily in the 14 to 33 kPa fraction, which is gravity-drained water that infiltrates too rapidly to be beneficial for plants. The salient aspect for designing the appropriate biochar for soil water holding improvements is to control where these increases in water holding occur. In this manner, one can target the critical range of plant available soil moisture. As an example, sandy soils do benefit from small particle size additions (<2 mm). Since this size fraction would improve overall plant available water through the increase in pore tortuosity, it will also reduce the saturated conductivity and infiltration rates [56]. For clay-rich soils, the amount of biochar that would need to be added to improve hydraulic properties is too large for practical applications [56].

### Biochar Impact on Pathogen Transport and Microbial Properties

Land application of raw animal and human fecal material is a potential public health risk if humans are exposed to microbial pathogens contained within these materials. One mode of human exposure to these pathogens is through consumption of fecal contaminated groundwater [63, 64]. Transport of microbial pathogens into ground water sources may be significantly reduced by application of biochar [9, 10]. Those researchers evaluated transport of three different *E. coli* isolates through laboratory column that were packed with a fine sandy-textured soil and then amended with poultry litter biochar produced at two different pyrolysis temperatures (350 or

700 °C). Application of the high-temperature poultry litter biochar at 2 % (w w<sup>-1</sup>) did not significantly affect transport behavior of the three *E. coli* isolates whereas a 10 % biochar rate reduced column transport for two of the *E. coli* isolates by ≥99.9 % and reduced transport of the third isolate by 60 %. In contrast, adding the low-temperature biochar to a soil at either rate produced about a twofold increase in bacteria transported for two of the isolates. Transport of the third isolate was unaffected at the 2 % low-temperature biochar rate but was reduced 60 % at the 10 % low-temperature biochar rate. No correlations between changes in microbial transport and changes in soil organic matter content, soil solution ionic strength, pH, and dissolved organic carbon concentration following biochar addition were observed.

In a follow-up study, Abit et al. [65] investigated the role of biochar feedstock (poultry litter and pine chips), pyrolysis temperature (350 and 700 °C), application rate (1 and 2 %), and soil moisture content (50 and 100 %) on the transport of two *E. coli* isolates through a fine sand soil. The authors reported that both high-temperature biochars reduced *E. coli* transport at the 2 % application rate, with substantially greater reductions observed with the pine chip biochar. Application of the low-temperature poultry litter biochar either had no significant effect or increased transport of both *E. coli* isolates—results consistent with those discussed above [10]. Changes in transport behavior following biochar addition were quantitatively similar for both saturated and unsaturated soils, but for all treatments, the effect was more pronounced in partially saturated columns. A strong inverse correlation between soil organic carbon (SOC) and transport of isolates under partially and fully saturated conditions was observed (*r*<sup>2</sup> values ranging

**Table 3** Calculation of integral water capacity (IWC) and integral energy (*E<sub>i</sub>*) for a sequence of 5 and 10 % (w w<sup>-1</sup>) pine chip (*Pinus taeda*) biochar additions to a sandy-textured, highly weathered, Norfolk loamy sand (Ultisol)

Integral water capacity (IWC, cm <sup>3</sup> /cm <sup>3</sup> )									
kPa	5 % biochar addition (size fraction, mm)					10 % biochar addition (w w <sup>-1</sup> )			
	Control	<0.25	0.25–0.50	0.5–1.0	1.0–2.0	<0.25	0.25–0.50	0.50–1.0	1.0–2.0
0–14	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.01
14–33	0.01	0.05	0.05	0.03	0.01	0.05	0.04	0.04	0.08
33–250	0.03	0.05	0.07	0.04	0.04	0.01	0.02	0.04	0.05
250–1200	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.01
1200–1500	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	0.05	0.11	0.16	0.09	0.07	0.07	0.08	0.10	0.15
Integral energy: ( <i>E<sub>i</sub></i> , J kg <sup>-1</sup> )									
0–14	5.83	1.73	1.41	2.45	4.67	0.45	1.52	1.89	0.58
14–33	5.20	9.00	6.77	8.30	4.97	11.13	9.58	7.71	9.02
33–250	35.28	32.0	42.62	32.70	41.3	8.99	23.42	35.7	25.7
250–1200	14.47	19.4	52.74	19.78	26.4	1.22	12.11	31.62	20.2
1200–1500	0.26	0.49	2.36	0.50	0.70	0.01	0.27	1.1	0.64
Total	61.0	62.6	105.9	63.7	78.0	21.8	46.9	78.0	56.2



from  $-0.85$  ( $p=0.07$ ) to  $-0.95$  ( $p=0.015$ )) suggesting that decreases in *E. coli* transport following biochar additions to soil were due, in part, to increased sorption of bacteria to the added biochar. A statistically significant ( $p<0.001$ ) correlation between bacterial sorption and bacterial transport through the columns was also observed, further supporting the hypothesis that sorption-related mechanisms significantly contributed to observed changes in bacterial transport through biochar-amended soils. These results suggest that application of biochar to agricultural fields may affect retention and transport behavior of enteric bacteria through soils, in addition to changing other soil properties previously mentioned.

### Mine-Impacted Spoils and Biochar

There are approximately 500,000 abandoned mines across the USA [66]. Accompanying these abandoned mines are waste piles (tailings) and mine spoils. Mine spoils commonly contain residual metals (e.g., Cd, Cr, Cu, and Zn) or sulfide bearing minerals (e.g., FeS and CuS) that typically undergo hydration, oxidation, and acidification reactions. This causes the spoils to acidify and, in the presence of water, generates acidic mine drainage that can release heavy metals to the environment. The low spoil pH can reduce or eliminate vegetation cover, further enhancing sediment transport and thus off-site heavy metal movement via wind or, water erosion, and leaching. The large number of abandoned mine sites, as well as the extent of mine-impacted landscapes, create a challenge to develop management strategies that promote re-establishment of a vegetative cover and remediation of mine-impacted spoil. Biochar may play an important role in mine land remediation based on its ability to increase pH, soil water retention, nutrient availability, and binding of heavy metals and thus support plant establishment and growth.

Several studies have reviewed the potential ability of biochar to minimize off-site movement of heavy metals and to function as a neutralizing agent for acidified mine spoils [67–69]. These studies reported that biochar can bind heavy metals, ameliorate acidic soils, and improve soil health characteristics. Gwenzi et al. [70] showed that biochar, alone or in combination with compost, was effective in absorbing heavy metals from mine tailings. Additionally, Jain et al. [71] reported that alkaline biochars incorporated into sulfur containing mine waste were effective at neutralizing acidic compounds. Biochars with greater ash contents, such as those produced at high temperatures [72], in the presence of oxygen [73], or from feedstocks with high conversion efficiency, such as from manure, will tend to have higher pH values [25]. This can have important consequences for acidic mine land reclamation, since alkaline biochars may be an effective substitute for lime. As an example, Ippolito (2015; unpublished data) showed that adding increasing amounts of biochar produced

from beetle-killed lodge pole pine (*Pinus contorta* Dougl. Var. *latifolia* Engelm.) to four different acidic mine land soils (from Creede and Leadville, Colorado, and Northern Idaho) significantly increased soil pH (Fig. 2). Concomitantly, significant reductions in bioaccessible heavy metals (i.e., Cd, Cu, Mn, Pb, and Zn) were observed (Table 4). In this same experiment, they observed similar results using biochar produced from switchgrass or tamarisk (*Tamarix spp*) feedstock.

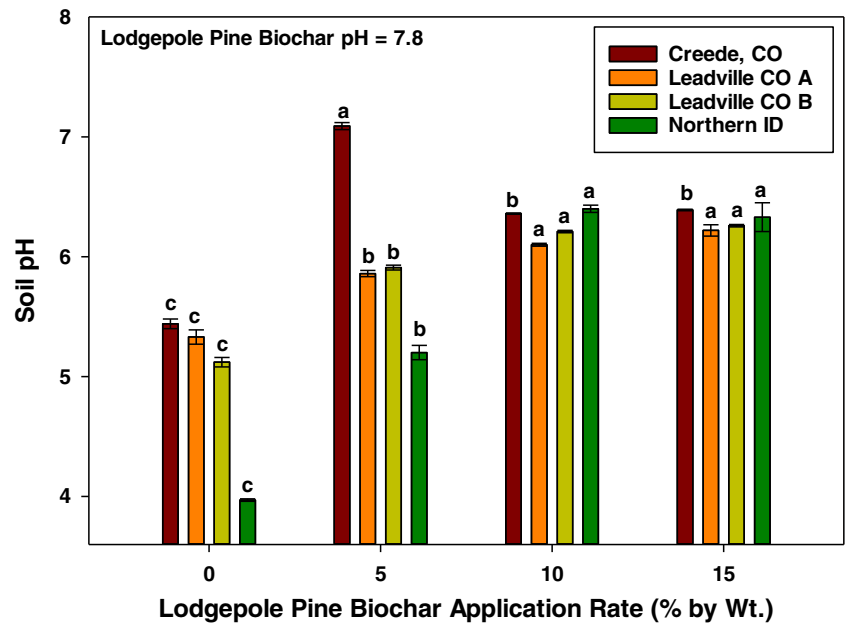
Biochars can also have metal sorption properties when used as a soil amendment [11, 73, 74]. Their ability to bind metals arises from their porosity, surface area, and surface functional groups [75, 76]. Metals will electrostatically bind to the surface functional groups and can be physically held in biochar pore spaces [11]. Additionally, alkaline biochars promote metal precipitation as carbonate, oxide, or hydroxide phases at pH values greater than 7 [75]. Ippolito et al. [75] used extended X-ray absorption fine structure analysis to show that at a solution pH of 6, pecan shell biochar sequestered Cu similar to being bound to organic surface functional groups. As the system pH increased to 9, Cu carbonate and oxide species dominated. Biochars made from manure can have substantial soluble P [27] that can promote the formation of insoluble metal-phosphate mineral phases such as pyromorphite (i.e.,  $Pb_5(PO_4)_3Cl$ ) and reduce Pb bioavailability [77]. In this way, the mobility of Pb with percolating water is reduced, thus lowering the potential of water quality degradation.

Another advantage of using biochar as a tool in mine land remediation is that it is a more stable form of C as compared to other remediation products. Commonly used soil amendments for remediating contaminated mine tailings include biosolids, manures, composts, digestates (i.e., the remains of anaerobic digesters), papermill sludges, yard, and wood wastes [12, 69]. Although these amendments are effective in the short term, each eventually decomposes and thereby reduces their long-term remediation efficacy. On the other hand, black carbon (a biochar-like material formed via wildfires) can have a soil residence time of hundreds to thousands of years [78] and, thus as compared with other amendments, may be a more remediation amendment for mine land reclamation.

### Designing Biochar with Specific Characteristics

In this review, we have drawn attention that biochars are not always an effective amendment at improving soil health characteristics and that crop yield improvements are inconsistent. Nonetheless, biochar is still globally heralded as an effective soil amendment in spite of contradictory results. To make biochar amendments more consistently beneficial, Novak et al. [27, 30] theorized that biochars could be engineered through single or multi-feedstock selection, blending feedstocks, choosing appropriate physical states (e.g., pellets and dust), and modifying pyrolysis temperatures, to produce

**Fig. 2** Effects of biochar produced from lodge pole pine on soil pH values in several mine-impacted soils (significant differences at  $\alpha = 0.05$  between biochar rates for individual soils are denoted by different letters above each bar)



biochar materials that target specific soil health characteristics. The theory was termed “designer biochar” and the concept was vetted through several journal publications [1, 79–82].

Moreover, Sohi et al. [83] expanded the “designer biochar concept” by offering the “systems fit” paradigm for biochar development and utilization. Sohi et al. [83] explained that the

**Table 4** Effect of increasing lodgepole pine (*Pinus contorta*) biochar application rate on 0.01 M CaCl<sub>2</sub>-extractable (i.e., bioaccessible) metals in the Creede, Colorado soil, the Leadville, Colorado A and B soils, and a

soil from Northern Idaho (for comparison within a column and for a specific soil, different letters indicate significant differences at  $\alpha < 0.05$  (Ippolito, 2015; unpublished data))

Lodge pole pine biochar application rate (% by wt.)	Cd	Cu	Mn	Pb	Zn
	mg kg <sup>-1</sup>				
Creede, CO soil					
0	6.38a	0.12	32.4a	8.47a	541a
5	2.22b	ND	1.01b	2.27b	178b
10	1.52b	ND	ND	0.52c	110b
15	2.02b	ND	3.60b	0.36c	149b
Leadville, CO soil A					
0	27.4a	3.21a	485a	ND	2410a
5	7.50b	0.25b	162b	ND	784b
10	4.19b	0.01b	86.8b	ND	432b
15	4.94b	0.01b	108b	ND	510b
Leadville, CO soil B					
0	9.72a	2.73a	163a	0.09	887a
5	2.89b	0.34b	48.0b	ND	295b
10	2.45b	0.02c	41.5b	ND	233b
15	2.87b	0.04c	51.9b	ND	298b
Northern ID soil					
0	2.29a	0.78a	100a	32.0a	146a
5	0.73b	0.06b	14.8c	4.60b	32.1b
10	0.46c	0.01b	6.58d	ND	15.1c
15	0.87b	0.05b	24.8b	0.43c	37.7b

ND non-detectable

“system fit paradigm” causes biochars to be developed through a combination of biochar and non-biochar ingredients. The goal is to fit the biochar into a particular soil-crop system by considering the interaction of relevant waste streams (different feedstock selections), production technology (pyrolysis vs. gasification), and considering specific soil constraints (pH, CEC, etc.). Others have adopted the designer biochar concept and the commercial production of custom-blended biochars [84] has been initiated.

Designer biochars are useful as a soil amendment when they possess physicochemical properties that can target a specific soil improvement [80, 83]. For instance, biochars made from switchgrass using a range of pyrolysis temperatures and material sizes showed the most significant improvement in soil moisture storage in an Ultisol and two Aridisols [49] compared to other biochars. If soil C sequestration and low soil pH are the target variables for improvement, then the appropriate “designer biochar” could be made through high-temperature pyrolysis (700 °C) of pecan (*Carya illinoensis*) or peanut (*Arachis hypogaea*) shells [30]. In areas with high animal manure production and soils containing excessive plant available P concentrations, the manure could be blended and pelletized with lingo-cellulosic feedstocks (i.e., hardwoods, pine shavings, etc.) prior to pyrolysis [80]. Blending the manure and creating pellets is a biochar production strategy to reduce extractable P concentrations, thus causing a rebalancing of soil P contents [80]. On the other hand, for infertile soils that rapidly need SOC, pH, and plant available P improvements, then the unblended animal manure could be pyrolyzed using a mid temperature (~500 °C) setting and the biochar applied as a dust-size material (0.25 mm). These examples show the utility of designing biochars based on feedstock type, blends, and material size to improve a targeted soil limitation. By employing the designer biochar concept, it is our hope that more consistent results with biochars ability to improve soils, remediate mine spoils, and increase crop yields will be obtained.

## Conclusions

Biochars have the capacity to be a useful soil amendment for both agricultural and environmental purposes. While there is not a “one-size-fits-all biochar,” they have the ability to improve soil health characteristics such as raising SOC contents, adjusting soil pH values, and increasing soil nutrient and water retention. Improvement in these salient soil health characteristics in some soils will result in crop yield increases, which is particularly important as soils continue to degrade through anthropogenic activity and by climate change. Biochars also have been used to reduce the movement of microorganisms through soil thereby decreasing the potential for human health risks. Additionally, biochar can be used as a remediation agent

for mine spoils by sequestering metals, raising soil pH, and improving nutrient content on mine-impacted soils.

Several meta-analysis investigations using results from the recent biochar literature has revealed a wide range of soil and crop yield responses—some negative and some positive. Overall, these results indicate that biochar performance is determined by the initial soil fertility level, soil texture, and degree of soil weathering. Negative soil health and crop yield responses are undesirable considering the need to improve crop yields to sustain a growing human population. We suggest that biochars can be made more effective as an amendment if they are designed to have specific chemical and physical properties.

In conclusion, this review shows that biochars can be used in several ways to address problems with soil health, low crop productivity, C sequestration, contaminant movement, and environmental impacts of mine spoils. It remains to be seen what other crop or soil roles will be developed for biochars, but their use in the horticultural, industrial, health, and environmental sector continues to grow [13].

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