

This is a repository copy of A review on biochar modulated soil condition improvements and nutrient dynamics concerning crop yields: pathways to climate change mitigation and global food security.

White Rose Research Online URL for this paper: https://eprints.whiterose.ac.uk/144976/

Version: Accepted Version

### Article:

Purakayastha, T.J., Bera, T., Bhaduri, D. et al. (8 more authors) (2019) A review on biochar modulated soil condition improvements and nutrient dynamics concerning crop yields: pathways to climate change mitigation and global food security. Chemosphere, 227. pp. 345-365. ISSN 0045-6535

https://doi.org/10.1016/j.chemosphere.2019.03.170

Article available under the terms of the CC-BY-NC-ND licence (https://creativecommons.org/licenses/by-nc-nd/4.0/).

#### Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: https://creativecommons.org/licenses/

#### Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



# Accepted Manuscript

A review on biochar modulated soil condition improvements and nutrient dynamics concerning crop yields: pathways to climate change mitigation and global food security

T.J. Purakayastha, T. Bera, Debarati Bhaduri, Binoy Sarkar, Sanchita Mandal, Peter Wade, Savita Kumari, Sunanda Biswas, Manoj Menon, H. Pathak, Daniel C.W. Tsang

PII:	S0045-6535(19)30615-0
DOI:	10.1016/j.chemosphere.2019.03.170
Reference:	CHEM 23484
To appear in:	Chemosphere
Received Date:	14 September 2018
Accepted Date:	26 March 2019

Please cite this article as: T.J. Purakayastha, T. Bera, Debarati Bhaduri, Binoy Sarkar, Sanchita Mandal, Peter Wade, Savita Kumari, Sunanda Biswas, Manoj Menon, H. Pathak, Daniel C.W. Tsang, A review on biochar modulated soil condition improvements and nutrient dynamics concerning crop yields: pathways to climate change mitigation and global food security, *Chemosphere* (2019), doi: 10.1016/j.chemosphere.2019.03.170

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



1	A review on biochar modulated soil condition improvements and nutrient dynamics
2	concerning crop yields: pathways to climate change mitigation and global food security
3	
4	T. J. Purakayastha <sup>a*</sup> , T. Bera <sup>b</sup> , Debarati Bhaduri <sup>c</sup> , Binoy Sarkar <sup>d,e</sup> , Sanchita Mandal <sup>e</sup> , Peter
5	Wade <sup>d</sup> , Savita Kumari <sup>a</sup> , Sunanda Biswas <sup>a</sup> , Manoj Menon <sup>f</sup> , H. Pathak <sup>c</sup> , Daniel C.W.Tsang <sup>g</sup>
6	
7	<sup>a</sup> Division of Soil Science and Agricultural Chemistry, ICAR-Indian Agricultural Research
8	Institute, New Delhi 110012, India
9	<sup>b</sup> Soil and Water Sciences Department, University of Florida, Gainesville, FL 32611, USA
10	° ICAR-National Rice Research Institute, Cuttack 753006, Odisha, India
11	<sup>d</sup> Leverhulme Centre for Climate Change Mitigation, Department of Animal and Plant Sciences,
12	The University of Sheffield, Western Bank, Sheffield, S10 2TN, UK
13	<sup>e</sup> Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia
14	<sup>f</sup> Department of Geography, The University of Sheffield, Western Bank, Sheffield, S10 2TN,
15	UK
16	<sup>g</sup> Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University,
17	Hung Hom, Kowloon, Hong Kong, China
18	
19	*Corresponding author at: Division of Soil Science and Agricultural Chemistry, ICAR-Indian
20	Agricultural Research Institute, New Delhi 110012, India, E-mail address:
21	tpurakayastha@gmail.com (T. J. Purakayastha)
22	

- 23 Funding information: National Innovations in Climate Resilient Agriculture (NICRA), Indian
- 24 Council of Agricultural Research, New Delhi, India, Grant Code Number: 12-115

Contents 25 1. Introduction 26 2. Methodology 27 Climate change mitigation using biochar 28 3. 4. Carbon and nutrient contents of biochar 29 Interaction of biochar with soils 5. 30 31 5.1.Soil physico-chemical properties 5.5.1. Biochar modifying soil physical environment 32 5.1.2. Biochar modifying soil pH, buffering system, CEC 33 5.2. Soil nutrient dynamics 34 5.2.1. Effect of biochar on nitrogen dynamics 35 5.2.2. Effect of biochar on phosphorus dynamics 36 5.2.3. Effect of biochar on potassium dynamics 37 5.2.4. Effect of biochar on secondary and micronutrient dynamics 38 6. Pyrolysis conditions, stability and nutrient supplying capacity of biochar 39 Biochar as slow-release fertilizers 7. 40 8. Effect of biochar on crop yield 41 Principal component analysis to evaluate biochar's effect on soil properties and crop 42 9. yields 43 10. Conclusions and future research directions 44 45 References

## 46 ABSTRACT

47 The beneficial role of biochar on improvement of soil quality, C sequestration, and enhancing crop yield is widely reported. As such we could not find a compiled source of information 48 linking biochar modulated soil condition improvement and soil nutrient availability on crop 49 yields. The present review paper addresses the above issues by compilation of world literatures 50 51 on biochar and a new dimension is introduced in this review by performing a meta-analysis of published data by using multivariate statistical analysis. Hence this review is a new in its kind 52 and is useful to the broad spectrum of readers. Generally, alkalinity in biochar increases with 53 54 increase in pyrolysis temperature and majority of the biochar is alkaline in nature except a few which are acidic. The N content in many biochar was reported to be more than 4% as well as 55 less than 0.5%. Poultry litter biochar is a rich in P (3.12%) and K (7.40%), while paper mill 56 sludge biochar is highest in Ca content (31.1%) and swine solids biochar in Zn (49810 mg kg<sup>-1</sup>), 57 and Fe (74800 mg kg<sup>-1</sup>) contents. The effect of biochar on enhancing soil pH was highest in 58 Alfisol, Ferrosol and Acrisol. Soil application of biochar could on an average increase (78%), 59 decrease (16%), or show no effect on crop yields under different soil types. Biochar produced at 60 a lower pyrolysis temperature could deliver greater soil nutrient availabilities than that prepared 61 at higher temperature. Principal component analysis (PCA) of available data shows an inverse 62 relationship between pyrolysis temperature and soil pH, and biochar application rate and soil 63 cation exchange capacity. The PCA also suggests that the original soil properties and application 64 rate strongly control crop yield stimulations via biochar amendments. Finally, biochar 65 application shows net soil C gains while also serving for increased plant biomass production 66 that strongly recommends biochar as a useful soil amendment. Therefore, the application of 67

- biochar to soils emerges as a 'win-win strategy' for sustainable waste management, climatechange mitigation and food security.
- 70
- 71
- 72 Keywords: Biochar, Nitrogen, Phosphorus, Potassium, Micronutrients, Crop yields
- 73

### 74 1. Introduction

During the last decade, biochar has gained importance owing to its roles in climate change 75 mitigation and agronomic benefits among global agriculturists, environmental experts and 76 policy makers. The term "biochar" is referred in recent literature emphasizing its use for 77 atmospheric carbon capture and storage, and soil application differentiating from black carbon 78 (Kookana et al., 2011). The European Commission (Verheijen et al., 2010) comprehensively 79 defined biochar as: "charcoal (biomass that has been pyrolyzed in a zero or low oxygen 80 environment) for which, owing to its inherent properties, scientific consensus exists that 81 application to soil at a specific site is expected to sustainably sequester carbon and concurrently 82 improve soil functions (under current and future management), while avoiding short- and long-83 term detrimental effects to the wider environment as well as human and animal health". 84

Biochar is produced by heating organic materials (e.g., plant residues, manures, waste 85 materials) in absence of oxygen or otherwise known as pyrolysis (Lehmann, 2007). During 86 pyrolysis, one-third to half of biomass carbon is converted into biochar. The heat treatment 87 (more often thermochemical treatment) of organic biomass used to produce biochar contributes 88 89 to its large surface area and its characteristic ability to persist in soils with variable biological decay (Lehmann et al., 2006) having half-life ranging from decades (Nguyen et al., 2009) to 90 centuries (Zimmerman, 2010). Conceptually, biochar can serve multifaceted roles in soils (Fig. 91 1). Biochar can act as a soil conditioner or soil amendment to improve the soil quality, enhance 92 plant growth by supplying nutrients, and retain nutrients. In this regard, an obvious positive 93 attribute of biochar is its nutrient value, supplied either directly by providing nutrients to plants 94 95 or indirectly by improving soil environment, with consequent improvement of fertilizer use efficiency. Nutrient composition and availability from biochar depend upon both the nature of 96

97 the feedstock and the pyrolysis conditions (Gaskin et al., 2009; Bera et al., 2017). It helps to reduce nutrient leaching (Parvage et al., 2013), and increases crop production. It also provides 98 other services such as improving soil physical and biological properties (Lehmann andRondon, 99 2005; Mandal et al., 2016a; Purakayastha et al., 2015; Purakayastha et al., 2016; Bera et al., 100 2016; Bera et al., 2019). Moreover, biochar can alter the root morphology of crop plants in 101 terms of favoring the fine root proliferation increasing the specific root length and decreasing 102 both root diameter and root tissue density. The improved root conditions help plants to exploit 103 more soil volume even under nutrient-starved soils directing towards biochar's role in 104 increasing the fertilizer use efficiency (Olmo et al., 2016). It also has the capability to improve 105 water retention properties of soil and enhance the soil's ability to retain nutrients (Rens et al., 106 2018). It could alter various soil properties through changes in pore size distribution, residence 107 time of soil solution and flow paths of nutrients (Major et al., 2009). Overall, biochar can 108 potentially add a holistic dimension for enhancing the soil quality and health which sooner or 109 later is believed to impact crop productivity positively. 110

Biochar application in soil for increasing crop production and other benefits including soil 111 carbon sequestration is increasingly being recognized as a win-win strategy. The impact of 112 biochar on crop productivity is largely influenced by the crop type, soil and biochar properties, 113 which in turn depend on feedstock source and pyrolysis temperature. Several recent reviews 114 have discussed the roles of biochar in climate change mitigation (Cayuela et al., 2013; Lehman 115 et al., 2006, Mandal et al., 2016a; Meyer et al., 2001; Minasny et al., 2017; Purakayastha et al., 116 2015; Purakayastha et al., 2016; Singh et al., 2010), waste management (Ahmad et al., 2014; 117 Devi and Saroha, 2015; Kookana et al., 2011; Mandal et al., 2018a; Mohan et al., 2014), 118 119 agronomic benefits (Alvarej-Camposa, 2018; Atkinson et al., 2010; Clough et al., 2103; Jeffrey

et al., 2010; Kookana et al., 2011; Lehman et al., 2015; Liu et al., 2013; Mandal et al., 2016b;
Spokas et al., 2000; Woolf et al., 2010), soil quality (Agegnehu et al., 2017; Barrow, 2012; Bera
et al., 2016; Huang et al., 2013; Jones et al., 2012; Lehman et al., 2011; Laird et al., 2010a; Sohi
et al., 2010), bioenergy production (Laird et al., 2009; Ro et al., 2010), and remediation of
polluted soils (O'Connor et al., 2018a,b).

The effectiveness and application of biochar heavily relies on the biomass feedstock and the 125 conditions under which it is produced (Tag et al., 2016; Zhang et al., 2017). Traditional biochar 126 derived from wood or agricultural plant residues may have poor sorption capabilities (Yao et al., 127 2012), due to the absence of important electrostatic attractions between biochar and the 128 negatively charged ions like phosphate (Vikrant et al., 2018). Several studies have attempted to 129 enhance sorption capacities of anions by developing modified biochar through various coating 130 procedures. Metal oxide-coated biochar, manufactured by bioaccumulation within the feedstock 131 plant itself, including Mg-enriched tomato plants, has proven very successful (Yao et al., 2013). 132 Similarly, co-precipitating metal oxides on the surface of biochar, post pyrolysis, including 133 magnesium-coated oak wood biochar was an effective adsorbent (Takaya et al., 2016). Iron-134 impregnated orange peel (Chen et al., 2011), corn straw (Liu et al., 2015) and wood chip 135 (Micháleková-Richveisová et al., 2017) biochars have also been used successfully to remove 136 phosphate from aqueous solutions in laboratory experiments. The biochar based adsorbent 137 production methods recommended for improving contaminant removal efficiency include 138 surface modification (Zhu et al., 2018), chemical group embedding (Zhou et al., 2013), metallic 139 hybridization (Li et al., 2016a,b), and nanomaterial decoration (Invang et al., 2014). For 140 example, graphenes (Gs) and carbon nanotubes (CNTs) have been used as nanomaterial 141 142 precursors for the engineered hybrid biochar adsorbent production (Tang et al., 2015).

Compared with the pristine biochar, CNT-biochar and G-decorated biochar composites 143 exhibited superior adsorbent properties, e.g., strong affinities for aromatic hydrocarbon and 144 heavy metal pollutants and large specific surface area (Invang et al., 2014; Sarkar et al., 2018; 145 Zhang et al., 2012). Hybridization of CeO<sub>2</sub>–MoS<sub>2</sub> hybrid magnetic biochar greatly improved Pb 146 (II) and humate removal compared to magnetic biochar, with > 99% Pb(II) and humate removed 147 within 6 h (Li et al., 2019). In a review, it has been reported that soil amendment with biochar 148 may reduce the bioavailability of a wide range of contaminants, including heavy metal(loids), 149 potentially reclaiming contaminated soils for agricultural use (O'Connor et al., 2018a). The 150 results of this review indicate that biochar application can potentially reduce contaminant 151 bioavailability in the field; for instance, a significant decrease (control normalized mean value = 152 0.55) in the Cd enrichment of rice crops was observed. Sulphur-modified rice husk biochar 153 increased the biochar's Hg<sup>2+</sup> adsorptive capacity ( $Q_{max}$ ) by ~73%, to 67.11 mg g<sup>-1</sup> (O'Connor et 154 al., 2018b). 155

However, there is a dearth of recently compiled information on overall impact of biochar 156 properties on crop productivity and soil quality (Liu et al., 2013). There are continuous array of 157 review publications on biochar, but most of them are related to the environment, for example, 158 environmental contamination, water treatment and pollutant remediation. Principally, 159 information on how key parameters, such as biochar feedstock type, pyrolysis temperature, 160 161 application rate to soil, feedback to soil chemical properties (e.g., pH, cation exchange capacity 162 (CEC) and crop yields are largely inconclusive. Hence, a critical synthesis of information about the above is urgently needed. The current review attempts to reveal biochars' nutrient properties 163 and its role in soil nutrient transformation that influence soil quality and crop productivity in the 164 165 present context of global climate change. Therefore, this review examines - (i) biochar nutrient

value in relation to pyrolysis condition and feedstock types, (ii) biochar roles in soil nutrient availability and transformation, (iii) the potential benefits of biochar in sustainable crop production, and (iv) meta-analysis of the up to date published data for evaluating the effect of biochar on soil condition improvements and crop yield. We believe that this compilation is a useful document highlighting the emerging research needs in this area.

#### 171 **2. Methodology**

#### 172 2.1. Literature search method

Google Scholar was searched for keywords like "biochar", "characteristics", "availability of 173 nutrients", AND "yield" within publication titles. Additional articles were found by searching 174 key words for "biochar" AND "crop yield" with various nutrients, e.g., N, P, K, secondary 175 nutrients and micronutrients. Various online journals, e.g., Science of the Total Environment", 176 "Geoderma", "Soil and Tillage Research", "Bioresource Technology", "Advances in 177 Agronomy", "Agriculture, Ecosystems and Environment", "European Journal of Agronomy", 178 "Soil Biology and Biochemistry", "Bilogy and Fertility of Soils", "Applied Soil Ecology" etc. 179 were also directly consulted for relevant papers. Only the relevant publications meeting the 180 objectives of this review paper were selected to form the basis of this review. The literature 181 search resulted in various publications relevant to this review paper, are presented in Table 1, 2, 182 3 and 4. 183

#### 184 *2.2. Data compilation and analysis*

In this review paper, we have collected the information on nutrient contents in biochar prepared from various feedstocks at different pyrolysis temperatures, their effects on physical, physicochemical properties of soils and dynamics of N, P, K, and secondary and micronutrient dynamics in soil. The information on the impact of biochar on crop yields was based on various

soil orders having dissimilar properties like pH (acidic, neutral to alkaline), texture (silty, sandy 189 clay loam, clay loam), CEC etc. In order to classify biochar, we gathered literature on biochar 190 prepared from various feedstocks, e.g., crop residues, manures, wood, and waste materials. 191 Majority of the information was collected from various peer-reviewed journals of international 192 repute. Two principal component analyses (PCA) were performed in this study using data from 193 published literature: one in which the objective variables were changed in soil chemical 194 properties, e.g., pH and CEC, and the other in which the objective variable was changed in crop 195 yield. Since variables were measured in different units, the variable values were all normalised 196 197 by subtracting the mean and dividing by the standard deviation of the variable group, and the PCA was computed using the correlation matrix between the variables. All PCAs were 198 performed using the program PAST version 3.18 (Hammer et al., 2001). 199

200

# 201 **3.** Role of biochar in mitigating climate change

Any compilation on biochar without mentioning its role in mitigating climate change is 202 incomplete. Thus, it is imperative to briefly mention the role of biochar in negating global 203 warming. In doing so, it is notable to mention that the Paris Climate Agreement in 2015 set a 204 target for participating countries that 'hold the increase in the global average temperature to 205 well below 2°C above pre-industrial levels and to pursue efforts to limit the temperature 206 increase to 1.5°C above pre-industrial levels' (IPCC 2015). While conventional greenhouse gas 207 emission mitigation strategies, such as lowering the consumption of fossil fuels, are needed to 208 achieve the goal of the Paris Agreement, simultaneous actions on negative emissions through 209 sustainable carbon dioxide removal (CDR) technologies and engineered enhancement of natural 210 carbon sinks are also urgently required (Gasser et al. 2015; Rogeljet al., 2016). Recent reports 211

suggest that the goal of holding global warming to well below 2°C is extremely unlikely unless 212 the emissions gap is not closed by 2030 (UNEP, 2017). In order to achieve large reductions in 213 greenhouse gas emissions, sequestering carbon in the terrestrial sink is needed (Paustian et al., 214 2016). The global soil has been estimated to hold the largest terrestrial organic carbon pool 215 (~1,500 Pg C to a depth of 1 m; 2,400 Pg C to 2 m depth) (Batjes, 1996). An increase in organic 216 matter inputs to soil, or a decrease in soil organic matter decomposition rates, or the net carbon 217 gaining effect of the both can increase the carbon stock in soil (Paustian et al., 2016). The 218 recently launched '4 per mille Soils for Food Security and Climate' concept also proposes to 219 increase global soil organic matter stocks by 4 per 1000 (or 0.4 %) per year in order to 220 compensate global greenhouse gas emissions due to anthropogenic activities (Minasny et al., 221 2017). In this connection, the application of biochar to soils has been shown to achieve the net 222 carbon gain in soils while also serving for increased plant biomass production by enhancing the 223 nutrient supply to plants and increasing nutrient and water use efficiencies (NUE and WUE) by 224 plants (Kookana et al., 2011; Lehmann et al., 2015; Minasny et al., 2017). Thus, biochar 225 application to soils has been recommended as an important component of the pathway to 226 'climate-smart soil' management practices in modern global agriculture (Paustian et al., 2016). 227

228

## 229 4. Carbon and nutrient contents of biochar

Biochar is enriched with C, and contains a range of plant macro, micro and secondary nutrient elements (Chan and Xu, 2009). The composition of biochar depends upon the nature of feedstock and pyrolysis conditions, and published literature suggests a wide variation in biochar compositions (Table 1). Carbon contents ranged from 81.2% in biochar prepared from bamboo chip (Mandal et al., 2017) to 19.2% in biochar prepared from paper mill sludge (Devi and

Saroha, 2015) (Table 1). Biochar prepared form crop residues and woody materials contained a 235 higher C content than biochar prepared from manure sources. Waste material biochars had a 236 wide range of C contents (19.2-84.0%) indicating their differential initial constituents. During 237 the pyrolysis process, N in residues is converted to recalcitrant forms, and using nuclear 238 magnetic resonance and near-edge X-ray adsorption fine structure spectroscopy, it was found 239 that both C and N became enriched in aromatic and heterocyclic aromatic structures in biochar 240 (Chen et al., 2014). Manure-derived biochar was undoubtedly the richest source of N among all 241 feedstock types of biochar, showing N content as high as 4.45%. Contrarily, biochar prepared 242 from woody materials was scant in N content. Thus, most of the manure derived biochars had 243 lower C/N ratios ranging between 10-30, with few exceptions. Wood-derived biochar had a wider 244 C/N ratio (Atkinson et al., 2010; Rajkovich et al., 2012). The very low N content (0.04%) in 245 canola straw biochar conferred it the highest C/N ratio (160:1). The P content was recorded the 246 highest (5.90) in swine solid biochar, while the lowest (0.017%) in yellow pine chip biochar. On 247 the other hand, the highest (7.40% for poultry litter) and lowest (0.087% for brush) K contents 248 were recorded in manure and waste material derived biochars, respectively (Cantrell et al., 2012; 249 Ro et al., 2010). The paper mill biochar (Devi and Saroha, 2015) and poultry manure biochar 250 (Enders et al., 2012) prepared at 600 °C were reported to be rich sources of Ca (25 and 31%, 251 respectively) and Mg (0.87 and 0.29%, respectively) (Table 1). Data on micronutrient contents in 252 biochar is limited in the literature. Biochar prepared from swine solids contained 74800, 2240, 253 4981, 2446 and 27.4 mg kg<sup>-1</sup> of Fe, Mn, Zn, Cu, and Mo, respectively (Table 1; Cantrell et al., 254 2012). The majority of biochar samples were alkaline in pH with few exceptions such as 255 sugarcane bagasse biochar, yellow pine chip biochar, hazelnut biochar and eucalyptus biochar, 256 257 which were found to be acidic in solution. Increasing the pyrolysis temperature in general

enhances the acid neutralising property of biochar increasing the pH (Bera et. al., 2018). The
alkalinity of biochar was primarily due to the presence of inorganic alkali salts. The organic
COO- and -O- groups that could modify the acid reaction of biochar surface through association
with H<sup>+</sup> ions might also contribute to biochar alkalinity (Al-Wabel et al., 2013).

The pyrolysis temperature significantly influenced the pH, C, and nutrient compositions of 262 biochar. Purakayastha et al. (2016) reported that increase in pyrolysis temperature from 400 °C 263 to 600 °C significantly increased the C content, while it decreased the N content in all biochars 264 except that was produced from rice hull. These findings were in agreement with the other 265 studies which also found higher C contents in plant material based biochars, e.g., canola, 266 soybean (Yuan et al., 2011), peanut hull, pine chips (Gaskin et al., 2008), Eucalyptus saligna 267 wood and leaf (Singh et al., 2010). Contrastingly, Yuan et al. (2011) reported that the C content 268 decreased in corn and peanut biochar with an increasing pyrolysis temperature from 300 °C to 269 500 °C. In general, the C/N ratio increased due to an increase in pyrolysis temperature. For 270 example, the C/N ratio of switch grass biochar increased from 54 to 84 when pyrolysis 271 temperature increased from 400 °C to 600 °C (Purakayastha et al., 2016). In contrast, Novak et 272 al. (2009) reported that the C/N of sugarcane bagasse biochar decreased from 129 to 79 when 273 pyrolysis temperature increased from 250 °C to 500 °C. The slow and fast pyrolysis process 274 275 during heating could also influence the C and N contents, and C/N ratios. Consequently, the C/N ratio of biochar prepared at slow pyrolysis is expected to be greater than that prepared by 276 fast pyrolysis process (Atkinson et al., 2010). For example, Bruun et al. (2012) reported that 277 biochar prepared from wheat straw at slow pyrolysis contained more C (69.6%) than the biochar 278 prepared at fast pyrolysis (49.3%). 279

#### 280 5. Interaction of biochar with soils

#### 281 5.1. Soil physico-chemical properties

### 282 5.1.1. Biochar modifying soil physical environment

283 Biochar amendments were reported to improve soil bulk density, porosity, water retention, and hydraulic conductivity (Abel et al., 2013; Asai et al., 2009; Atkinson et al., 2010; Jeffery et al., 284 2011; Karhu et al., 2011; Laird et al., 2010a). Moreover, biochar application significantly 285 influenced the infiltration capacity in soils (Lehmann et al., 2006; Sohi et al., 2010). Bayabil et 286 al. (2015) reported that incorporation of woody feedstock (Acacia, Croton, and Eucalyptus) 287 charcoals significantly decreased the soil moisture retention at lower tensions (10 and 30 kPa), 288 resulting in an increase in relative hydraulic conductivity at these tensions in a clay soil. Akhtar 289 et al. (2014) found higher water use efficiencies when irrigation was applied through partial root 290 zone drying along with the application of 5% biochars prepared from rice husk or cotton seed 291 mixture, over full irrigation. Addition of 10 Mg ha<sup>-1</sup> biochar in a sandy soil in Finland increased 292 the available water content in the dry period of the year under *Phleumpratense* growth (Saarino 293 et al., 2013). In contrast, water holding capacity of Quincy sand soil of Washington State 294 remained unchanged in a laboratory incubation study with the application of biochars prepared 295 from switch grass, anaerobically digested fiber, softwood bark and wood pellet (Streubel et al., 296 2011). Biochar prepared from black locust (Robinia pseudoacacia) when applied at a dose of 20 297 Mg ha<sup>-1</sup> increased the available water capacity by 97%, saturated water content by 56%, and 298 reduced the hydraulic conductivity with increasing moisture content in a sandy soil (Uzoma et 299 al., 2011a). 300

301 Soil aggregation is considered as another important physical property which determines the 302 stability and support of soil, and biochar showed its beneficial impact on that as well. Soinne et

303 al. (2014) reported that biochar had the potential to improve the aggregate stability in clay soils, and thus repeated biochar additions could reduce the deteriorating effect of tillage on soil 304 aggregates. It could even lead to the improvement of the structural stability of cultivated clay 305 soils (Soinne et al., 2014). A study using synchrotron-based X-ray micro-computed tomography 306 revealed that the increased porosity of macroaggregates in biochar-amended soil was jointly 307 contributed by the inherent porosity in the applied biochar as well as the newly formed pores 308 out of soil-biochar interactions (Yu et al., 2016). The authors also reported that wood chip 309 biochar and waste-water sludge biochar were more efficient in increasing the porosities of the 310 products over straw biochar, and hence showed greater effects on soil macroaggregates (Yu et 311 al., 2016). Thus, biochar could improve the physical properties of difficultly manageable clay 312 and sandy soils by changing their air-water relationships through mechanisms like increased 313 aggregate stability, water infiltration and water holding capacity (Fig. 1). 314

315

## 316 5.1.2. Biochar modifying soil pH, buffering system, CEC

In soil, availability of nutrients for plants is pH dependent. Biochar may alter soil pH, which in 317 turn can change nutrient solubility, thereby modifying the nutrient availability. The impact of 318 biochar addition on soil pH and CEC has been summarized in Table 2. The resultant soil pH 319 values tended to move to the alkaline side when the soil received an increased biochar 320 application rate, and when the biochar was produced at a high temperature (e.g., 700 °C) 321 (Mandal et al., 2016b; 2018). Effect of wood ash or horticultural biochar in modifying soil pH 322 has long been known, and documented by earlier reports (Clarholm, 1994; Glaser et al., 2002; 323 324 Mahmood et al., 2003). Jeffery et al. (2011) found that biochar could increase soil pH by 0.1-2.0 units in a wide range of soils varying in native pH values. An insight perusal of Table 2 325

326 indicated that the magnitude of soil pH change upon biochar addition was inevitably reliant on soil types, biochar properties, and application rates. Chan et al. (2007; 2008) demonstrated that 327 green waste biochar and poultry litter biochar could gradually increase pH by 0.6 to 2.0 units of 328 an acidic Alfisol at successive application rates ranging from 10 to 100 t ha<sup>-1</sup> under radish 329 (Raphanus sativus) cultivation. Similarly, van Zwieten et al. (2010) reported increased soil pH 330 values due to sludge biochar addition in an acidic Ferrosol cropped with wheat, radish, and 331 soybean. The plotting of biochar application rate and per cent changes in soil pH provided an 332 interesting observation in segregating various soil types as impacted biochar applications (Fig. 333 2). The per cent increase in soil pH due to biochar application was the highest (> 50%) in 334 Alfisol with biochar application rates ranging from 25-50 Mg ha<sup>-1</sup>, while the increase was 335 between 4-50% in Alfisol, Anthrosol, Cambisol, Mollisol, Inceptisol and Oxisolis with biochar 336 application rates ranging from 4-72 Mg ha<sup>-1</sup> (Fig. 2). In Planosol, even at very high rate of 337 biochar application (90-100 Mg ha<sup>-1</sup>), the per cent increase in soil pH was only between 22-338 339 33%. Interestingly, in calcareous soils, and some Cambisol and Mollisol, no effect of biochar on soil pH was observed (Fig. 2). Alfisols, Ferrosols and Acrisols are inherently highly acidic in 340 nature, and biochar being alkaline material neutralised the acidity. As there could be variations 341 in active and potential acidity in these soils, the differential impact of biochar on enhancing the 342 soil pH was noticed. Among the biochars, poultry litter biochar being highly alkaline in nature 343  $(pH\approx 10)$  had the highest impact on the pH of acid soils. 344

The associated increase in soil pH with biochar addition would result in a greater availability of primary and secondary nutrients like K, P, Ca, Mg (Asai et al., 2009; Glaser et al., 2002; Major et al., 2010). The other advantage of increased pH due to biochar addition is the reduction of Al toxicity in acidic soils. In an acidic Ferrosol, 10 t ha<sup>-1</sup> biochar addition reduced the ammonium

acetate extractable Al from 1.93 cmol ( $p^+$ ) kg<sup>-1</sup> soil to an undetectable amount (van Zwieten et 349 al. 2010). The liming effect of biochar in acid soils, as described above, not only could improve 350 the mineral nutrient supply for plant growth, but also could alleviate Al stress for better crop 351 production (Liu et al. 2013; Dai et al., 2017). On the contrary, limited information is available 352 on the effects of biochar addition in alkaline soils of arid and semiarid regions. Some studies 353 (Karer et al., 2013; Lentz and Ippolito, 2012; van Zwieten et al., 2010) did not observe a 354 significant change in soil pH due to biochar addition where initial values were ranging between 355 pH 7.4-7.8. Contrarily, Streubel et al. (2011) found 0.1 to 0.9 unit pH increase of an alkaline 356 sandy soil. Similarly, Mandal et al. (2018) reported that when biochars produced from poultry 357 manure, green waste compost and wheat straw at various temperatures (250 - 700 °C) were 358 applied to an alkaline soil (pH 8.01), they could modify the soil pH values by about 0.84 units 359 in both directions ranging from pH 7.37 to 8.23. These discriminating results about pH values, 360 as discussed above, need thorough investigation by conducting biochar application trials in 361 alkaline soils in arid and semiarid regions of the world. 362

The CEC of soils is an essential property in relation to the soil fertility. A higher CEC soil can 363 hold cationic nutrients in greater amounts and for longer time than a lower CEC soil, preventing 364 the nutrients from leaching loss and increasing their availabilities for plant uptake. As shown in 365 Table 2, CEC increased in all cases except one where the soil was a calcarosol (van Zwieten et 366 al. 2010). The higher CEC of biochar-amended soils was ascribed to the dominance of 367 negatively charged surface functional groups, increased specific surface area of the products, 368 adsorption of highly oxidized organic matter on biochar surfaces, and the presence of residual 369 volatile matter in the biochar matrix (Glaser et al., 2003; Lehmann et al., 2005; Liang et al., 370 371 2006). The increase in total negative charge and charge density on soil applied biochar surfaces

372 was reported due to the biotic and abiotic oxidation of organic functional groups in long-term soil application studies (Cheng et al., 2006; Zimmerman, 2010). Yuan et al. (2011a) found a 373 significant increase in soil CEC (15-25%) when canola, rice, soybean and peanut straw biochars 374 (CEC of biochars ranging between 179-279 cmol (p<sup>+</sup>) kg<sup>-1</sup> were added to a low CEC Acrisol. 375 Similar findings were reported by previous authors (Kloss et al., 2014; Liard et al., 2010b; van 376 Zwieten et al., 2010). The increase in CEC could affect the retention of phosphate by biochar 377 through anion exchange reaction. However, DeLuca et al. (2009) reported that biochar 378 application to soil increased plant P availability by lowering the activity of soluble Al and Fe. 379 The CEC of biochar is mainly influenced by the feedstock type, pyrolysis temperature and 380 aging time (Heitkötter et al., 2015; Bera et al., 2017). Likewise, biochars produced from non-381 leguminous straws had a higher CEC than those produced from leguminous straws (Jiang et al., 382 2014). Thus, a critical decision needs to be made concerning biochar feedstock type, pyrolysis 383 temperature, application rate, and biochar age in order to achieve intended soil pH and CEC 384 values suitable for crop production. 385

386

## 387 *5.2. Soil nutrient dynamics*

Fig. 3 shows the mechanisms how biochar potentially can improve the retention of macro- and micronutrients in soils, and consequently may improve their availability to plants. While biochar can interfere with the key carbon and nitrogen cycle processes by interacting with relevant microorganisms, it can also participate in the nutrient cycling processes by physicochemical interactions, such as surface adsorption of various elements (Agegnehu et al., 2017; Bornø et al., 2018; Mandal et al., 2016b; 2018; Xu et al., 2018a).The unique porous characteristics of biochar along with its heterogeneous surface functional groups can take part in

diffusion-controlled adsorption of elements, surface complexation and ligand exchange
reactions, which ultimately control the plant-available nutrient dynamics in soils (Mandal et al.,
2016a:Liu et al., 2013; Nielsen et al., 2018).

In most of the previous studies, total nutrient contents of biochar were reported rather than the 398 plant available nutrient contents (Table 1). However, the entire amounts of nutrients present in 399 biochar are not readily soluble in water. Nutrients in biochar are present either in available or in 400 difficultly accessible forms pertaining to the complex organic and inorganic composition of the 401 material. There is a scarcity of published reports evidencing direct nutrient availability from 402 biochar to crops. The amount of water-soluble nutrients in biochar except K is usually low 403 (Steiner et al., 2010). Bera et al. (2014) reported that water-soluble P, K, Ca and Mg contents in 404 mustard stalk biochar were 13-16%, 65-70%, 14-17% and 23-26% of the individual total 405 nutrient contents, respectively. The remaining amounts of the nutrients existed either as 406 inorganic minerals captivated within the complex organic moiety of C, H, and O, or as an 407 integral component of the organic moiety. Biochar needs to undergo both chemical and 408 microbial decompositions to release these captivated nutrients and subsequently make them 409 available for plant absorption. Gaskin et al. (2010) reported an increased concentration of 410 mineral nutrients (K, Ca and Mg) in maize tissue and soil extracted by Mehlich-1 reagent when 411 peanut hull and pine chip biochar were added to a loamy sand soil in Tifton, Georgia. The 412 impact of peanut hull biochar was more pronounced than pine chip biochar due to the higher 413 contents of K, Ca and Mg in the former, and in the first year of biochar application than the 414 second year (Gaskin et al., 2010). Novak et al. (2009) also found a high concentration of 415 Mehlich-1 extractable P in Norfolk loamy sand soil amended with poultry litter biochar (4 Mg 416 ha<sup>-1</sup>) containing high total P content (3-4.3%). In another study, soil total N, Olsen-P, 417

exchangeable K, Ca and Mg concentrations increased with cow manure biochar application 418 under maize production in Japan (Uzoma et al., 2011). Following a three years' trial at field 419 conditions, Munda et al (2018) also reported the possibility of soil fertility enrichment vis-a-vis 420 improved grain yield of rice crop via rice husk biochar application. These are all indirect 421 evidences of enriched nutrient availabilities resulted from biochar addition to soils. Thus, future 422 research needs to be undertaken involving isotopic tracer techniques to measure the availability 423 of plant nutrients directly from biochar, or by comparing the relative contribution of soil and 424 biochar sources with regards to plant-available nutrients. 425

426

427 5.2.1. Effect of biochar on nitrogen dynamics

Application of biochar significantly influences the mineralization-immobilization turnover of 428 nutrients, which is affected by altering both microbial activities and community structure of 429 soils. Since biochar is a C-rich substrate with a high C/N ratio, upon its application to the soil, 430 microorganisms are triggered to decompose the native soil organic matter (SOM) to acquire N 431 via priming effect (Blagodatskaya and Kuzyakov, 2008). Biochar being rich in surface 432 functional groups, including aromatic moieties, can alter cation and anion exchange capacities 433 of soils, which further influences N retention (Clough et al., 2013; Slavich et al., 2013; Mandal 434 et al., 2018). Thus, maize biochar was reported to accelerate soil N transformations by 435 increasing the net N mineralization (Nelissen et al., 2012, Gundale and DeLuca, 2006), 436 accelerating nitrification (Song et al., 2013), affecting denitrification (Cayuela et al., 2013), 437 reducing ammonia volatilization (Mandal et al., 2016b; 2018), and through adsorption of 438 ammonia and increasing NH<sub>4</sub><sup>+</sup> storage in soils (Clough and Condon, 2010). 439

440 The transformation of N as impacted by various biochar materials are presented in Table 3. When biochar was added to soil, gross N mineralization, recalcitrant nitrogen fraction and labile 441 N fraction were found to be stimulated (Table 3). This increase was higher in the biochar 442 produced at low temperature (350°C) than that produced at high temperature (550°C) (Nelissen 443 et al., 2012). Results showed accelerated soil N cycling following biochar addition, with 444 increased gross N mineralization (185-221%), nitrification (10-69%) and ammonium (NH<sub>4</sub><sup>+</sup>) 445 consumption rates (333-508%) (Nelissen et al., 2012). Most of the mineralized NH<sub>4</sub><sup>+</sup> under 446 biochar treatments came from the recalcitrant N in soil, while in the control soil most 447 mineralized NH<sub>4</sub><sup>+</sup> originated from the labile N (Nelissen et al., 2012). This could be due to the 448 biochar induced incresae of soil porosity/aeration that stimulates the aerobic/heterotrophic 449 microbial population resulting in the degradation of recalcitrant SOM in the presence of biochar 450 451 (Anderson et al., 2011). Pereira et al. (2015) reported that the gross N mineralization increased in response to soil-applied biochar materials with high H/C ratios (i.e., Douglas fir wood 452 pyrolyzed at 410 and 510°C, and hog waste wood pyrolyzed at 600 and 700°C). The 453 enhancement of N mineralization could be favourable for organic farming systems challenged 454 by insufficient N mineralization during plant growth (Pereira et al., 2015). Studies demonstrated 455 that at least 10% of the <sup>15</sup>N added to the soil as <sup>15</sup>N labelled pyrogenic organic material (PyOM) 456 (obtained from Lolium perenne charred for 4 minutes at 350°C) could be utilized by grasses in a 457 Mediterranean agricultural soil within just 72 days of growth (Rosa and Knicker, 2011). This 458 showed a direct evidence that PyOM produced at a low temperature could be easily degraded, 459 and its N would become available to plants (Rosa and Knicker, 2011). 460

461 The plausible effects of biochar on soil biological processes can significantly influence soil N
462 transformations. Such effects can be partially explained by biochar properties. For example,

463 biochar could increase the mineralization of recalcitrant soil organic N (Nelissen et al., 2012). The other important mechanisms include an enhanced abundance of ammonia oxidizing 464 microorganisms (Song et al., 2013), and promotion of denitrification by the transfer of electrons 465 to soil denitrifying microbes (Cayuela et al., 2013). For instance, PyOM derived from rye grass 466 pyrolyzed at 450°C induced a strongly positive priming effect within the first 18 days, and 467 thereafter exhibiting a negative priming effect in a forest Cambisol (Maestrini et al., 2014). The 468 initial increase in organic matter mineralization corresponded to a higher gross N mineralization 469 and NH<sub>4</sub> content in the PyOM-treated soil than in the untreated soil (Maestrini et al., 2014). The 470 effect of biochar on soil denitrification might depend on temperatures at which the product is 471 produced. Compared to the unamended soil, amendment with biochar (produced at 200°C and 472 400°C from oak wood feedstock) significantly increased N<sub>2</sub>O emissions, but biochar produced 473 at a higher temperature (600°C) did not show such effect on N<sub>2</sub>O emissions (Zhang et al., 2015). 474 During the pyrolysis process, N in biomasses get converted to recalcitrant heterocyclic aromatic 475 structures in biochar, and these structural changes may lead to a reduction in C and N 476 mineralization rates (Chen et al., 2014). The mineralized C decreased from 32.7% of the added 477 C of raw biomass to 0.5% in the biochar produced at temperature above 400°C (Chen et al., 478 2014). The N dynamics thus shifted from N mineralization in raw biomass to N immobilization 479 in biochar at charring temperature 500°C (Chen et al., 2014). As such, soil amended with 480 biochar produced at temperatures exceeding 400°C demonstrated a 25% decrease in dry shoot 481 biomass of water soinach (Ipomoea aquatica) compared with unamended soil principally due to 482 N limitation (Chen et al., 2014). Therefore, the C stability of leguminous green manure like 483 Ipomoea sp. could be enhanced by converting the raw material into biochar, but the charring 484 485 process might limit the immediate supply of N. Similarly, corn stalk biochar proved to contain

486 recalcitrant N as indicated by lower decay rate constants (Blum et al., 2013). Application of Nlimited biochar may induce microbial immobilization of available N in the soil (Lehman et al., 487 2006; van Zwieten et al., 2009). Soil and biochar mixtures showed evidence of both soil nutrient 488 sorption by biochar, and biochar nutrient sorption by the soil, depending upon the biochar and 489 soil types (Mukherjee and Zimmerman, 2013; Rens et al., 2018). For example, application of 490 willow (Salix viminalis L.) branch biochar prepared at 470°C significantly decreased the 491 available NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> levels during 30 to 90 days in flinty clay loam soils of United 492 Kingdom indicating a net N immobilization (Prayogo et al., 2014). Availability of resin-493 extractable NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> fractions in soil decreased with the addition of wheat straw biochar 494 and olive-tree pruning biochar (Olmo et al., 2016), and this might be governed by the porous 495 nature, high surface area and ion exchange capacity of biochar that can enhance the sorption of 496  $NH_4^+$  (cation exchange) and  $NO_3^-$  (within biochar pores) (Lehmann et al., 2003; Atkinson et al., 497 2010; Laird et al., 2010a; Prendergast-Miller et al., 2014). The rate of N immobilization was 498 significantly higher in the treatment receiving both litter and 2% biochar. Nitrogen deficiency in 499 larch (Larixgmelinii) cultivation resulted from the application of Japanese larch wood biochar 500 was also reported (Makoto et al., 2011). The application of hard wood biochar, a mix of white 501 ash (Fraxinus americana), oak (Quercus sp.), and beech (Fragus grandifolia) produced by fast 502 pyrolysis at 500-600 °C with either NPK or digested dairy manure had little effect on N 503 dynamics in Warden silt loam soil of Washington state of USA (Bera et al., 2016). 504

Leaching of N from soils is a serious problem, especially in light-textured soils, causing environmental pollution and eutrophication. To limit the leaching loss of N from soil, biochars prepared from a variety of feedstocks and at different pyrolysis environments (duration, temperature, heating rate) have been extensively investigated in the recent past (Petersen, 1978;

509 Lehmann et al., 2003; Jones et al., 2012; Zhu et al., 2012). Yao et al. (2012) reported that sugarcane bagasse, peanut hull, Brazilian pepperwood, and bamboo biochars could adsorb 1-510 12% NH<sub>4</sub><sup>+</sup>-N from aqueous solution, and Brazilian pepperwood gave the most effective biochar 511 for  $NH_4^+$  adsorption among these feedstocks. Asada et al. (2002) found a greater adsorption of 512 ammonia (NH<sub>3</sub>) by bamboo (*Bambusa* sp.) biochar prepared at 500 °C than that prepared at 513 >700 °C. The NH<sub>4</sub><sup>+</sup> adsorption capacities of commercial coconut shell activated carbon prepared 514 at 600°C and 400°C were found to be 2400 and 600 to 1800 mg NH<sub>3</sub> kg<sup>-1</sup> carbon, respectively 515 (Rodrigues et al., 2007). Recently Hea et al. (2018) reported that biochar application to soil with 516 urea increased NH<sub>3</sub> volatilization losses by 14.1% in the first rice season, primarily due to 517 increased pH and concentrations of NH<sub>4</sub><sup>+</sup>-N in the floodwater, and decreased NH<sub>3</sub> losses in the 518 second rice growth season by 6.8%, probably due to its high adsorption capacity for  $NH_4^+$  and 519 increased nitrification. Application of bamboo charcoal (pyrolyzed at 600 °C) to a variety of 520 sandy silt soils showed a cumulative 15% reduction in NH<sub>4</sub><sup>+</sup>-N leaching loss over 70 days (Ding 521 et al., 2010). The adsorption of  $NH_4^+$  on the biochar surfaces was the result of a week van der 522 Waals forces between positively charged NH<sub>4</sub><sup>+</sup> and negatively charged soil or organic matter 523 surfaces (Hale et al., 2013). The adsorbed NH<sub>4</sub><sup>+</sup>-N eventually become available to plants or 524 microbes in the long run reducing the loss of mineral N in soils (Taghizadeh-Toosi et al., 2012a, 525 2012b). 526

The overall impact of biochar on N transformations in soil is also reflected (positive, negative and neutral) in the post-harvest analysis of soil samples for N contents. Poultry litter biochar and wheat straw biochar, when applied at the rate of 1.0–5.0 Mg ha<sup>-1</sup> to an acidic Aeronosol and a neutral Vertisol, they did not affect the post-harvest total soil N (Macdonald et al., 2014). However, application of these biochars at 5 - 10 Mg ha<sup>-1</sup> to an acidic Ferrasol and alkaline

532 Calcisol increased the total soil N content significantly (Macdonald et al., 2014). Similarly, application of rice husk biochar at 41 Mg ha<sup>-1</sup> was found to increase total soil N after the harvest 533 of rice crop in an acidic Glevsols of Philippines (Haefele et al., 2011). The available N content 534 increased in an alkaline sandy loam soil too under the influence of biochar, and the effect was 535 more pronounced for maize stover than wheat straw biochar (Purakayastha et al., 2015). Jones 536 et al. (2012), however, reported that commercially available biochars derived from 537 mechanically chipped trunks and large branches of Fraxinus excelsior L., Fagus sylvatica L. 538 and Quercus robur L. pyrolyzed at 450°C for 48 h did not affect the dissolved organic N 539 (DON), NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup>-N contents in the soil. Similarly, biochar addition showed limited effects 540 on the turnover of soil organic carbon, DON and no long-term effect on N mineralization, NH<sub>3</sub> 541 volatilization, denitrification and NH<sub>4</sub> sorption (Clough et al., 2013). In contrast, biochar made 542 from chicken manure increased the available nutrient contents in soils including N (Chan and 543 Xu, 2009, Chan et al., 2008). Peanut shell biochar (5% w/w) promoted the urease activity in a 544 saline soil over short-term laboratory incubation indicating the role of biochar in soil N 545 dynamics (Bhaduri et al., 2016). 546

Nishio and Okano (1991) reported that biological nitrogen fixation (BNF) at the early stage of 547 alfalfa growth and nodule development stage was 15 and 227% higher, respectively, than the 548 control when biochar (Eucalyptus deglupta, 350 °C) was added to the soil. Several studies 549 indicate that biochar serves as an excellent support material for Rhizobium inoculants (Pandher 550 et al., 1993; Lal and Mishra, 1998). Rondon et al. (2007) reported that the proportion of fixed N 551 by common bean (Phaseolus vulgaris L.) increased from 50% in the control to 72% with 90 g 552 kg<sup>-1</sup> biochar application. While total N derived from the atmosphere (NdfA) significantly 553 increased by 49 and 78% with 30 and 60 g kg<sup>-1</sup> biochar applications to the soil, respectively, 554

NdfA decreased by 30% than the control with 90 g kg<sup>-1</sup> biochar application (Rondon et al., 2007). The primary reason for the higher BNF with biochar additions was the greater B and Mo availability in the amended soil than the unamended control, while a greater K, Ca, and P availability with higher soil pH and lower N availability and Al saturation might have also concurrently occurred (Rondon et al., 2007).

560

## 561 *5.2.3. Effect of biochar on phosphorus dynamics*

Biochar, produced from common crop residues or unconventional tree species, influences P transformation in soils directly or indirectly by three major mechanisms: (1) being a direct source of soluble P and exchangeable P, (2) modifying the soil pH and ameliorating various elements (e.g.,  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) that are responsible for making complex with P, and (3) acting as a source of C and energy for enhancing the microbial activities and P mineralization (DeLuca et al., 2009). Many studies reported the increase of P availability via biochar application to soils (Table 3).

Biochar produced at both low and high temperatures (350°C and 800°C, respectively) resulted 569 in significant changes in the extractable P pool, with a trend of decreasing extractable P with 570 application of high temperature biochar (Gundale and DeLuca, 2006). Increasing pyrolysis 571 temperature also decreased the water soluble P content in rice, wheat, maize and pearlmillet 572 residue biochars due to the formation of difficultly soluble crystalline P minerals (Bera et al., 573 2017). The extractable P not only depends on the pyrolysis temperature, but also on the 574 feedstock. For example, Zhang et al. (2016) studied biochars prepared from 9 different residues, 575 and concluded that the Bladygrass (Imperata cylindrical) biochar had the greatest amount of 576 577 extractable P among all the biochars. Similarly, application of biochar (prepared at 400°C) at the

rate of 8.94 g kg<sup>-1</sup> increased the available P content in a sandy loam alluvial soil (Purakayastha 578 et al., 2015). The application of poultry litter biochar at 20 g kg<sup>-1</sup> increased Mehlich 1 soil 579 extractable P concentration by 20 to 28 folds (Novak et al., 2009). Laird et al. (2010a) reported 580 that biochar prepared from mixed hardwood feedstock (primarily oak (*Ouercus* sp.) and hickory 581 (Carva sp.)) increased Mehlich III extractable P in soils (Laird et al., 2010a). The total P content 582 ranged 16-9500 mg kg<sup>-1</sup> for crop residue biochar, 5-6000 mg kg<sup>-1</sup> for wood biochar, 2950-583 7.40x10<sup>4</sup> mg kg<sup>-1</sup> for manure biochar, and 90-23300 mg kg<sup>-1</sup> for waste material biochar (Table 584 3). Recently, Xu et al. (2018b) reported that wheat straw biochar application significantly 585 increased (positive effects) various P fractions (except for NaHCO<sub>3</sub>-extractable P and residual 586 P) in a Haplic Luvisol. The increased soil microbial activity and reduced soil acidity or 587 increased CEC may be accounted for enhanced P transformation in the soil. The reduced 588 NaHCO<sub>3</sub>-extractable P content may be related to P immobilization with increased soil microbial 589 activity induced by biochar addition because the high C:P ratios of biochar (ranged from 234 to 590 357) suggested a net P immobilization when biochar was incorporated into the soil (Xu et al., 591 2018b). 592

Biochar having high ion exchange capacity might alter P availability by enhancing the anion
exchange capacity or by influencing the activity of cations that interact with P (Liang et al.,
2006). However, the amount and rate of P adsorption on the surface of ferrihydrite decreased
with the presence of biochar (Hao et al., 2011).

597 The changes in soil P dynamics may vary over time in the presence of biochar. Haefelea et al. 598 (2011) reported that the application of carbonized rice husk biochar increased available P in rice 599 growing soil of International Rice Research Institute (IRRI), Philippines, in the first year, while 600 after three years it did not influence the available P content. In the second cropping year,

available P content in the biochar + pyrogallol treated plot was found to increase by 25% over
the control (Lashari et al., 2013). Two years after application of biochar prepared from mixed
hardwood chips (primarily oak (*Quercus* sp.), elm (*Ulmus* sp.) and hickory (*Caryaspp* sp.)) in a
fine loamy Hapludols decreased the extractable P at different incubation periods (Rogovska et
al., 2014).

Application of 8% maize stover biochar (400 °C) substantially increased soil Olsen-P from 3 to 606 46 mg kg<sup>-1</sup> in a Red earth, and from 13 to 137 mg kg<sup>-1</sup> in a Fluvo-aquic soil in China after a 607 short-term incubation (42 days) (Zhai et al., 2015). These increases were accompnied with an 608 subsequent increase in soil microbial biomass P from 1 to 9 mg kg<sup>-1</sup> in the Red earth, and from 609 9 to 21 mg kg<sup>-1</sup> in the Fluvoaquic soil (Zhai et al., 2015). Researchers indicated that the 610 increase was mainly due to the high concentration of P in the ash fraction of the biochar (77% 611 of total biochar P). Biochar's effect on both soil Olsen-P and microbial biomass-P was 612 increased by higher biochar application rates ensuring lower P-sorption capacity. The maximum 613 concentration of water-soluble P was achieved at the rate of 1% wheat residue biochar (w/w) 614 addition to soils with different textural classes, varying the water-soluble P concentrations from 615 11 to 253% (Parvage et al., 2013). At higher application rates, P concentrations decreased, 616 which coincided with an increase of soil pH by 0.3-0.7 units (Parvage et al., 2013). The wheat 617 residue biochar can act as a source of soluble P, and low and high additions of biochar showed 618 different effects on soil solution P concentration due to possible reactions of P with Ca and Mg 619 added with biochar. The addition of fresh Miscanthus or Salix biochar to soil significantly 620 increased soil P contents, but artificially weathered biochars made no such change in sandy 621 loam soil of the Rothamsted Research experimental farm, United Kingdom (Prendergast-Miller 622 623 et al., 2014). The Miscanthus biochar had distinctly larger extractable-P content than the Salix

biochar (Prendergast-Miller et al., 2014). In sandy soil, addition of biochar produced from
mixture of Norway spruce (*Picea abies* (L.) H. Karst) and Scots pine (*Pinus sylvestris* L.) had
low P sorption affinity, and thus did not increase the sorption of P in incubated soils (Sonnie et
al., 2014).

Among different feedstocks, maize biochar showed the highest available P in the soil after one 628 year of incubation followed by rice, pearl millet and wheat biochars (Purakayastha et al., 2015). 629 Rice straw biochar with the higher CEC and the lowest contents of Ca<sup>2+</sup> and Mg<sup>2+</sup> showed the 630 greatest inhibition of phosphate adsorption, and thus, could likely be the best choice as an 631 amendment to mobilize phosphate in variably-charged soils (Jiang et al., 2015). The phosphate 632 adsorption in both control and biochar-amended soils decreased with increasing pH. 633 Incorporation of the biochars increased the pH of the amended soils, thereby further mobilizing 634 phosphate in the soil (Jiang et al., 2015). However, Macdonald et al. (2014) reported that both 635 poultry litter and wheat straw biochars applied at the rate of 5 and 10 Mg ha<sup>-1</sup> did not affect the 636 Olsen's P in an acidic Ferrasol and alkaline Calcisol, but could increase Olsen's P in an acidic 637 aerosol and neutral Vertisol. The interactions between biochar, P fertilizer and P fractionations 638 indicate shifts in potential P availability both as a result of P fertilization and biochar (prepared 639 from green waste at 550 °C) application after harvest of a wheat crop (Farrel et al., 2014). 640 However, in clayey soils, biochar addition increased soil aggregate stability and reduced 641 detachment of colloidal materials, which in turn could be beneficial for erosion control and 642 thereby reducing particulate P losses from agricultural fields. 643

<sup>645</sup> *5.2.4. Effect of biochar on potassium dynamics* 

646 Biochar itself is a huge source of K, and it can directly take part in the retention of K in the soil because of having a high CEC (Table 3). Available K contents in both Ultisol and Oxisol after 647 first and second years' of a wheat crop were invariably greater when biochar prepared from 648 Eucalyptus trees (Eucalyptus camaldulensis L.) by specialized flash carbonization process was 649 applied to soils (Lashari et al., 2013). Two years of mixed hardwood biochar (primarily oak, 650 elm and hickory) application in fine loamy Hapludols had almost doubled the extractable K 651 content over the unamended soil (Rogovska et al., 2014). In the second cropping year, biochar 652 along with pyrogallol application increased the available K content by 78% over the unamended 653 control (Rogovska et al., 2014). Among the macronutrients (N, P, K), the maximum increase in 654 available pool due to biochar application was observed in the case of K. Purakayastha et al. 655 (2015) found that wheat straw biochar being rich in K contributed in increasing the soil 656 available K. Similarly, Laird et al. (2010a) reported that mixed hardwood biochar amendment 657 (oak and hickory) increased the Mehlich III extractable K in soils. 658

In contrast, application of rice husk biochar at the rate of 41 Mg ha<sup>-1</sup> did not affect exchangeable K content in soil after harvest of rice crp in an acidic Gleysols of IRRI, Philippines (Haefele et al., 2011). Nevertheless, evidence showed that excessive application of liming materials including biochar to a coarse-textured low buffering capacity soil might lead to an abrupt increase in soil pH resulting in deficiencies of some plant nutrients (Kamprath, 1971). For example, K deficiency in radish crop due to the application of poultry litter biochar in an acid soil was noticed (Chan et al., 2008).

666

667 5.2.5. Effect of biochar on secondary and micronutrient dynamics

668 Amongst secondary nutrients, S cycle behaves quite similarly as N cycle in the soil (Stevension and Cole, 1999). Therefore, biochar application could potentially influence the S mineralization 669 in soils like it influences the N transformation (Table 3). Since biochar application influences 670 the pH of soils. S mineralization rates were reported to increase following a fire in a pine forest 671 (biomass converted to biochar by the fire) (Binkley et al., 1992). This effect was probably due 672 to the release of soluble  $SO_4^{2-}$  following partial combustion of biomass during the fire or 673 heating event at temperature more than 200 °C (Gray and Dighton, 2006). The maximum 674 leaching of SO<sub>4</sub><sup>2-</sup> occurred after the application of corn biochar pyrolyzed at 450 °C (11 mg kg<sup>-1</sup> 675 at the first leaching, corresponding to 29% of the total S added), while the main mechanisms 676 involved in this process were: the abiotic release of mineral S, and the hydrolysis of ester-S 677 mediated by soil enzymes without any observed relationship with CO<sub>2</sub> evolution (Blum et al., 678 2013). The role of S-forms in the feedstocks (or initial materials) also seemed to drive the S 679 mineralization process (Blum et al., 2013). 680

Extractable Ca contents increased in both Ultisol and Oxisol after first and second year of wheat 681 crops owing to application of biochar prepared from Eucalyptus tree (Eucalyptuscamaldulensis 682 L.) by flash carbonization process (Butnan et al., 2015). However, it showed no impact on 683 extractable soil Mg content when biochar prepared from the same feedstock via traditional kiln 684 or flash carbonization process was applied to the soil (Butnan et al., 2015). Peanut straw biochar 685 pyrolyzed at 400°C showed significantly higher water soluble Ca and Mg contents in an Oxisol 686 than other starw derived biochars, and rice straw biochar showed the lowest values among 687 various crop straw biochars (Jiang et al., 2015). Rogovska et al. (2014) reported that along with 688 soil available K, soil extractable Ca and Mg also increased in a maize (Zea mays L.) crop due to 689 690 two years application of biochar made from mixed hardwood (oak, elm and hickory) at 500-

691 575°C. After biochar application, Ca and Mg limiting Savana Oxisol was higly productive due to 77-320% greater Ca and Mg availability, increasing soil pH and decreasing exchangable 692 acidity (Major et al., 2010). Slow pyrolysis biochar (550°C) failed to show any effect on 693 exchangeable Ca content after harvest of a maize crop when applied at the rate of 15.0 g kg<sup>-1</sup> in 694 a silty Fluvisol, but it became more efficient when the application rate was increased to 100 g 695 kg<sup>-1</sup> (Borchard et al., 2014). However, the exchangeable Mg content in soil was not influenced 696 by biochar application rate (Borchard et al., 2014). Rice husk biochar applied at the rate of 41 697 Mg ha<sup>-1</sup> also did not affect exchangeable Ca and Mg contents after the harvest of rice in an 698 acidic Gleysol in Philippines (Haefele et al., 2011). Thus, increasing Ca and Mg availability in 699 biochar amended soils would be more realistic in highly acidic Oxisol and Ultisol which are 700 inherently defficient in basic cationic nutrients. 701

Among the micronutrients, soil extractable Mn and Fe decreased, while Cu and Zn increased 702 due to the application of a mixed wood biochar (Rogovska et al., 2014). Similarly, Borchard et 703 al. (2012) reported that composted charcoal could potentially improve plant available Cu<sup>2+</sup> in an 704 acidic sandy soil with small organic matter content. Transient effects of biochar on soil pH can 705 overrule the influence of sorption of micronutrient cations on to biochar, resulting in the 706 variable concentrations of trace elements in the soil solution and their availability to plants 707 (Borchard et al., 2012). Biochar prepared from Eucalyptus tree either via traditional kiln process 708 at 350°C or by flash carbonization at 800°C significantly increased the soluble Mn 709 concentration (1.39–4.61 mg  $L^{-1}$ ) in an Oxisol relative to the control (1.12 mg  $L^{-1}$ ), while they 710 decreased the plant tissue Mn concentration (0.08–0.17 g kg<sup>-1</sup>) compared to the control (0.41 g 711 kg<sup>-1</sup>) (Butnan et al., 2015). 712

## 6. Pyrolysis conditions, stability and nutrient supplying capacity of biochar

A handful of experimental studies unanimously revealed that the source of feedstock (either 715 plant or animal origin) and pyrolysis environments (duration, heating rate, operating method 716 and temperature) had been the most crucial factors to determine whether the produced biochar 717 would be suitably applied to regulate nutrient dynamics in soils, apart from its other chemical 718 and structural features. Hence, these would decide the applicability of biochar for enhancing 719 crop growth and yield by moderating the soil environment. It is emphasized that temperature 720 generated during pyrolysis define the physical and structural characteristics of biochar (Clough 721 et al., 2013; Zhao et al., 2018). Only few studies concentrated on the characterization of biochar 722 prepared at different ranges of pyrolysis temperatures as well as feedstock materials, and 723 compared the biochar stability and applicability for agricultural uses (Yang and Sheng, 2012; 724 Crombie et al., 2013; Rahman et al., 2014; Zhao et al., 2018). Pyrolysis temperature was also 725 found to be the most influential parameter for obtaining specific characteristics of rapeseed stem 726 biochar, demonstrating a positive relationship of temperature with pH, microporous structure, 727 surface area, fixed C and ash content, whilst showing a negative relationship with material 728 yield, average pore size, functional groups, volatile matter, O and H mass fractions, and the 729 number and density of functional groups (Zhao et al., 2018). 730

Realising the serious gap of systematically compiled information in published literature about the above, this paper attempted to gather three sets of information after searching across a large number of publications, for: (1) pH and nutrient composition of various biochars produced at different pyrolysis temperatures (Table 1), (2) changes in soil pH and CEC due to application of biochar prepared from various feedstock types, addition rates and pyrolysis temperatures (Table

2), and (3) effects of biochar on nutrient transformations in soil produced at different pyrolysistemperatures (Table 3).

738

#### 739 7. Biochar as slow release fertilizer

Fertilizers play a significant role in agricultural production. After application to soils, fertilizers 740 can be lost due to the natural processes occurring in the soil. There has been an increasing 741 interest in using fertilizers, which can release nutrients in soils at a slower and steadier rate over 742 an extended period. Therefore, the use of slow-release fertilizer is a favourable strategy to 743 reduce gaseous and leaching losses of nutrients, especially the losses of macronutrients (N, P, 744 and K) (Wang et al., 2013). Pyrolytic conversion of biomass into biochar has shown an effective 745 impact on reducing nutrient losses (NH<sub>3</sub> volatilization, N<sub>2</sub>O emission, CO<sub>2</sub> emission, NO<sub>3</sub> 746 leaching, etc.) from soils, and previous studies found that biochar itself contains nutrients, 747 which help to improve plant growth. It was observed in most studies that nutrients release 748 quickly during the initial period of biochar addition to soils. However, if exogenous nutrients 749 (N, P, and K) was adsorbed on biochar, it could act as a slow-release fertilizer for supplying 750 nutrients (N, P, and K) (Zhou et al., 2015). Kim et al. (2014) observed that lignocellulosic 751 biomass-derived biochar contained low plant nutrients but could be impregnated with additional 752 nutrients and subsequently pelletized, and the final product could control the release of nutrients 753 at a slower rate resulting in a reduced nutrient loss. The slow release was attributed to the 754 physical hindrance in releasing and solubilizing the nutrients through reduced pore size instead 755 of forming any slowly soluble chemical composite (Kim et al., 2014). Wen et al. (2017) 756 prepared biochar based slow release fertilizers (BSRFs) through NH<sub>4</sub><sup>+</sup> absorption on biochar 757 758 prepared from cotton stalks. Authors found that the application of BSRFs to soil could
759 significantly improve both the water retention and water holding capacity of soils. The BSRFs were also capable of releasing N fertilizer slowly with extended N-longevity, and were more 760 effective in improving total N use efficiency and facilitated cotton plant growth through 761 reducing N loss and improving N retention (Wen et al., 2017). The lowest N-leaching-loss were 762 observed with BSRFs, and the phenomenon was attributed to the fact that BSRFs had better 763 slow-release characteristics and water holding capacity than normal biochar (Gonzalez et al., 764 2015; Wen et al., 2017). Yao et al. (2011) also found that the phosphate-laden biochar contained 765 valuable nutrients that could act as a slow release fertilizer to enhance soil fertility and sequester 766 C for a longer time in soil. Moreover, physical activation of biochar materials can also make it a 767 slow release fertilizer. For example, Dünisch et al. (2007) found that the mixing of charcoal 768 with ashes and impregnating wood residues with nutrients such as N, P, and K could produce 769 slow release K and N fertilizers. Studies have shown that biochar based slow-release fertilizers 770 with their effective nutrient retention properties can be widely used in sustainable modern 771 agriculture. However, a full assessment of these biochar based slow-release fertilizers, 772 composites, and pellets as slow nutrients (N, P, and K) release fertilizers are needed, for 773 example, field tests are extremely important before the wide application of these materials in 774 soils for supporting plant growth and development. 775

776

#### 777 8. Effect of biochar on crop yield

Researchers observed that biochar application increased, decreased or had a neutral effect(s) on crop yield(s), depending upon soil types, variation in feedstocks and pyrolysis conditions during biochar preparation (Table 4). In majority of the cases, the yield of various crops was enhanced to the tune of 4 to 144% owing to biochar application, while for few others studies, the yield

782 declined to the extent of 4 to 24%. Some biochars triggered improved growth with increasing pyrolysis temperatures, though opposite trend was also found (Rajkovich et al., 2012). 783 Therefore, pyrolysis temperature remains an important variable to improve biochar performance 784 for crop yield vis-à-vis soil fertility management. Biochars made from food waste and paper 785 mill waste at lower pyrolysis temperature (300-400 °C) resulted in significant growth reduction 786 of corn (Rajkovich et al., 2012). With increasing pyrolysis temperature, however, the adverse 787 effect of biochar produced from the same feedstock nullified (Rajkovich et al., 2012). On an 788 average, biochar produced at 500°C showed a better plant growth than those produced at 300-789 400°C temperature. Biochar made from poultry litter maintained better plant growth over the 790 control irrespective of application rate and pyrolysis temperature (Macdonald et al., 2014). 791 Across all biochar types, average total biomass production of corn (Zea mays L.) was at par for 792 the application rates of 0.2%, 0.5%, and 2%, but reduced to a minimum at the rate of 7% 793 (Rajkovich et al., 2012). Except for the larger application rate (7%), biochar made from corn 794 stover, oak, and pine wood and animal manures exhibited either positive or neutral effect on 795 crop growth, whereas biochar from hazelnut shells did not affect the growth (Enders et al., 796 2012). Studies emphasized that the positive reflection of agronomic performances under biochar 797 application depends both on soil-biochar interaction and the elemental contents of biochar. 798 However, not only the biochar or soil type, crop choices also can determine the response of 799 biochar as van Zwieten et al. (2010) found that wheat biomass increased linearly up to an 800 biochar application rate of 10 t ha<sup>-1</sup>, and decreased with 20 and 50 t ha<sup>-1</sup>, whereas radish growth 801 did not decrease with high rate of biochar in an acid soil of the tropics. Followed by the 802 increasing macro and micronutrients availbility in soil, biochar from mixed hardwood chips 803 804 (oak, elm and hickory) (pyrolysis temperature:  $500 - 575^{\circ}$ C) increased the grain yield of maize

805 by 11 to 55% during the first year (Rogovska et al., 2014), presumably because biochar mitigated adverse effects of allelochemicals released from the decomposing maize residues. 806 However, oat (Avena sativa L.) vield in an acidic sandy loam soil of Denmark showed no 807 significant response to birch wood biochar application, neither for total biomass nor grain yield 808 (Sun et al., 2014). However, on the same occasion, the total biomass of spring barley (Hordeum 809 vulgare) was increased by 11% due to biochar application, though with a non-significant 810 response for grain yield. Maize yield showed a reduction of 22-24% at the single biochar 811 treatment (50 Mg ha<sup>-1</sup>) which was applied in combination with pig slurry at 21 and 42 Mg ha<sup>-1</sup> 812 doses (Sun et al., 2014). In acidic sandy soils, the application of rice hull biochar (2% rate) 813 prepared at 350-400°C increased sugarcane yield in Florida, USA, probably because biochar 814 modulated the nutrient enrichment in the soil (Alvarez-Campos et al., 2018). 815

In an acidic aerosol of Australia, both poultry litter biochar and wheat straw biochar 816 demonstrated non-linear trends of biochar application rates with wheat yields (Macdonald et al., 817 2014). The plant biomass was significantly lower at higher biochar application rates (5 and 10 t 818 ha<sup>-1</sup>), having a prominent impact on shoot production but also evident in grain yield and root 819 biomass (Macdonald et al., 2014). However, in an acidic ferralsol, a different plant response 820 was evident. The magnitude of plant growth stimulation was more visible by applying poultry 821 litter biochar over wheat straw biochar (Macdonald et al., 2014). More biomass (shoot, root and 822 grain) produced under high rate of poultry litter biochar (10 t ha<sup>-1</sup>) as compared to wheat straw 823 biochar (Macdonald et al., 2014). Biochar application to a neutral Vertisol had no impact on the 824 plant growth (Macdonald et al., 2014). Besides acidic soils, biochar also proved beneficial in 825 increasing yield of crops cultivated in alkaline soils. Purakayastha (2010) reported that 826 application of biochar at the rate of 1.9 Mg ha-1 prepared from wheat straw along with the 827

828 recommended doses of NPK (180:80:80 kg ha<sup>-1</sup>) increased the yield of maize in an Inceptisol. Moreover, this treatment was found to be superior for obtaining benefits related to straw 829 reutilization like crop residue incorporation (CRI) and crop residue burning (CRB) in the open 830 field. For both pearl millet and rice, the yields in biochar treatments were at par with those 831 obtained with CRI or CRB treatments (Purakayastha, 2010). In another study, the application of 832 rice straw biochar (prepared at 400 °C) at the rate of 2.25 g kg<sup>-1</sup> (equivalent to 5.0 t ha<sup>-1</sup>) along 833 with 100% NPK increased the rice yield by 24.3% in an Inceptisol, and by 31.3% in an Alfisol 834 (Bera, 2014). The yield and yield attributing characters of lowland rice was also reported to be 835 enhanced by the combined application of rice husk biochar and flyash supplemented with 836 chemical fertilizers (Munda et al., 2016). 837

Fertilizer application along with carbonized rice husk (CRH-biochar) improved the grain yields 838 of rice, but the improvement was not always significant and even showed a decline in yield at 839 Nitisol of Siniloan, Philippines (Haefele et al., 2011). The application of CRH-biochar failed to 840 produce a yield-increasing effect in both anthraquic Gleysols and humic Nitisol in the 841 Philippines (Haefele et al., 2011). Only in a glevic Acrisols, the application of CRH-biochar 842 resulted in a higher yield of rice in all four seasons, although the significant increase was only 843 observed in the third and fourth wet seasons (Haefele et al., 2011). However, Gaskin et al., 844 (2009) found that peanut hull biochar and pine chip biochar failed to show their marks towards 845 crop productivity, and grain yield even decreased for maize crop. 846

Application of 0, 8 and 20 t ha<sup>-1</sup> of biochar to a Colombian savanna Oxisol continuously for four years (2003–2006) under a maize-soybean rotation reported that the maize grain yield did not increase in the very first year, but increased in the 20 Mg ha<sup>-1</sup> plots over the control by 28, 30 and 140%, respectively, in the subsequent years (Major et al., 2010). In that particular

851 experiment, soil pH increased, and exchangeable acidity showed a decreasing trend owing to biochar application. The greater crop yield and nutrient uptake resulted due to more available 852 (77-320%) Ca and Mg in the soil where biochar was applied (Major et al., 2010). Rice yield 853 was increased under biochar treatment in an acidic Anthrosol, and such increase was eventually 854 more (9-28%) in the second cycle than in the first cycle (9-12%) of the crop (Zhang et al., 855 2012). However, this increment could not be correlated with the biochar amendment rates 856 (Zhang et al., 2012). Biochar can also be composted and be applied in soils for enhancing crop 857 productivity. Application of biochar poultry manure compost and pyroligneous solution to a 858 salt-affected soil for consecutive two years showed an ameliorative effect, decreasing the 859 salinity and pH, and subsequently reflected in increased yield of wheat in a tune of 38% 860 (Lashari et al., 2013). 861

Biochar behaved differently to crop growth improvement when applied along with fertilizers. 862 Farrell et al. (2014) reported no significant effect on wheat yield at a low application rate (<1.0 863 Mg ha<sup>-1</sup>) of biochar in highly P-constrained calcareous soil, but a prominent effect of both 864 biochar and fertilizer on P fractionation was observed. Similarly, applying N fertilizer proved 865 beneficial to rice grain yield when 4.0 and 8.0 Mg ha<sup>-1</sup> rates of two commercial biochars 866 prepared from wood feedstocks (e.g., teak (Tectona grandis L.) and rosewood (Pterocarpus 867 *macrocarpus* Kurz)) were applied in a study reported from northern Laos, but at higher dose of 868 biochar (16 Mg ha<sup>-1</sup>) with N-fertilizer no positive yield response was observed (Asai et al., 869 2009) . Higher grain yields in biochar treated plots (4.0 and 8.0 Mg ha<sup>-1</sup>) with N fertilizer 870 resulted due to the combined effects of the improved soil physical properties and the alleviation 871 of biochar induced soil N availability (Asai et al., 2009). Biochar (prepared from 80% varied 872 873 hardwood and 20% varied coniferous wood chips at 750°C) and biochar-compost treatments

874 induced only small, economically irrelevant and mostly non-significant effects vine productivity in a poorly fertile, alkaline, temperate soils of Switzerland (Schmidt et al., 2014). However, 875 vield reduction at a high rate of biochar application (16 Mg ha<sup>-1</sup>) was resonated to N limitation 876 even with N fertilizer application (Asai et al., 2009). Contrary to this observation, Zhang et al., 877 (2012) found maize yield increased by 15.8% and 7.3% without N fertilization, and by 8.8% 878 and 12.1% with N fertilization under biochar amendment at 20 and 40 Mg ha<sup>-1</sup>, respectively, in 879 a calcareous flavor-aquic loamy soil. In an earlier study, Chan et al. (2007) also found the 880 positive interactive effect of biochar (doses at 50 and 100 Mg ha<sup>-1</sup>) with N fertilizer (100 Mg ha<sup>-1</sup>) 881 <sup>1</sup>) on radish yield in a hard setting Alfisol. Improvement in soil physical properties along with 882 pH, organic carbon and content of exchangeable cations were the reasons suggested for the 883 higher radish yield. Recently, Ain et al. (2016) reported that application of biochar prepared 884 from a weed (Parthenium hysterophorus L.) at 370-417 °C temperature to a rice-wheat 885 cropping system could cut down the cost of fertilizer to half although the yield obtained was just 886 as good as with full application of recommended dose of fertilizers. 887

In many instances, biochar behaved as a neutral amendment as far as crop yield enhancement is 888 concerned. The bioavailability of N in a wheat-straw biochar prepared at 400 °C was reported to 889 be very low, and did not increase growth of rice crop or nitrogen use efficiency from fertilizer 890 sources during the first year after application (Xie et al., 2013). Biochar was added to an 891 agricultural field at three different doses (0, 25 and 50 t ha<sup>-1</sup>) and planted with maize (1<sup>st</sup> year) 892 and grass (2<sup>nd</sup> and 3<sup>rd</sup> years) in an acidic sandy loam soil where the biochar addition affected 893 plant performance in the grass crop with significant increase in foliar N (2<sup>nd</sup> year) and above-894 ground biomass (3<sup>rd</sup> year), but biochar treatment behaved neutral towards the maize crop yield 895 896 (Jones et al., 2012). Another study reported that short-term application of biochar amendment

897 had a positive effect on soil quality in rice cultivation across a wide range of climates and soil types in China, though no significant effect of biochar amendment on rice yield was found 898 (Huang et al., 2013). In contrast to biochar amendment, N fertilizer proved less effective for 899 improving soil quality, but more effective for increasing the rice yield (Huang et al., 2013). 900 More interestingly, the same study further hinted that biochar amendment showed an additional 901 benefit on rice yield under N fertilizer application, and there was a close relationship between 902 the effect of biochar amendment on rice yield and agronomic N use efficiency. Another 903 investigation dealing with large volume application of biochar (30 and 60 Mg ha<sup>-1</sup>) on durum 904 wheat in the Mediterranean climate showed positive effects (up to 30%) on biomass production 905 and yield, with no significant differences in the nitrogen content of grains (Vaccari et al., 2011). 906 Moreover, no difference between the two biochar treatments were identified, suggesting that 907 even the very high biochar application rate promoted plant growth with a non-detrimental effect 908 (Vaccari et al., 2011). 909

Biomass production of the N-fixing bean (Phaseolus vulgaris L.) was significantly higher than 910 that of the non-N-fixing isoline across all levels of biochar (Eucalyptus deglupta, 350 °C) 911 additions. Biochar additions significantly increased total biomass production by 39% at a 912 defined biochar dose of 60 g kg<sup>-1</sup>, but decreased biomass at par with the control with a higher 913 biochar dose (90 g kg<sup>-1</sup>). The increase in biomass production by the N-fixing bean was mainly 914 attributed to the greater leaf biomass. Such responses confirmed earlier results with moong bean 915 [Vigna radiata (L.) R. Wilczek], soybean [Glycine max (L.) Merr.], and pea (Pisum sativum L.) 916 (Iswaran et al., 1980), or with cowpea (Vigna unguiculata L.) and rice (Oryza sativa L.) (Nehls, 917 2002; Lehmann et al., 2003). Biochar additions at a rate of 15 t ha<sup>-1</sup> resulted a remarkable 918 919 difference in plant biomass of bean (Phaseolus vulgaris L.) over the control showing an average

of 262% increase in shoot biomass, 164% increase in root biomass, 3575% increase in nodule
biomass, and 2126% increase in N derived from the atmosphere (Güereña et al., 2015).

922

923 9. Principal component analysis to evaluate biochar's effect on soil chemical properties924 and crop yields

925

The soil chemistry variables d\_pH (change in soil pH) and d\_CEC (change in soil CEC) were generated by difference of treatment and control measurements for soil pH and CEC respectively. Mean value substitution was performed on missing CEC values on some of the measurements, resulting in a total number of cases analysed at 48. The variable representing yield change was generated by difference of treatment and control measurements for crop yield, with yield inhibition represented as negative yield, resulting in a total number of cases analysed at 36.

The PCA scatterplot of points for soil chemical properties in the plane of the first two principal 933 component axes is presented in Fig.4a. The total variance explained by the first two principal 934 components was 74.3%. The first principal component, accounting for 39.3% of the variance in 935 the dataset, exhibits loadings dominated by biochar application rate and change in CEC (Table 936 5). The second principal component, accounting for 35% of the variance in the dataset, exhibits 937 loadings dominated by pyrolysis temperature of biochar and pH adjustment of the soil. The 938 latter principal component shows an inverse relationship between [pyrolysis temperature and 939 pH] and [loading rate and CEC]. 940

941 The projections of the variable axes onto the plane of the first two principal components (Fig.942 3a) reveals that all axes exhibit some positive correlation with each other. The highest pairwise

42

943 correlations exist between (i) pyrolysis temperature and pH change in soil, and (ii) between biochar loadings and change in CEC of soil. These observations may be explained by increased 944 temperature of biochar pyrolysis resulting in modifications of the types of chemical functional 945 groups (acidic versus ketonic) on the biochar carbon skeletons, which would modify the basicity 946 of the biochar and thus the resulting pH of the soil which was amended by the biochar (Mandal 947 et al., 2016; 2018). The relationship between loading rate and CEC may be explained by noting 948 that the more oxygen-containing functional groups in a soil, the higher the CEC, thus the greater 949 loading of biochar containing the functional groups the greater the CEC(Schmidt and Noack, 950 2000). The points in Fig. 3 are grouped with respect to soil type, with convex hulls enclosing the 951 groups of points. Points group well with respect to soil type, suggesting that the original 952 chemistry of the soil has a strong component in pH and CEC modification of the soils when 953 amended by biochar. 954

The PCA scatterplot of points for crop yields in the plane of the first two principal component 955 axes is presented in Fig. 4b. In this case, the total variance explained by the first two principal 956 components was 76.8%. The first principal component, accounting for 45.9% of the variance in 957 the data, was dominated by pyrolysis temperature of biochar, but contained appreciable 958 components of application rate and crop yield modification. The second principal component, 959 accounting for 30.9% of the variance in the data, exhibited no appreciable dependence on 960 pyrolysis temperature, and was instead dominated by application rate and yield, which display 961 962 an inverse relationship. This suggests an explanation counter to expectations that greater application rates of biochar result in lower stimulation of crop yield. There was some structure 963 evident in the groupings of points in this analysis by soil type, suggesting that plant yield was 964 965 influenced by soil type also. There was unexplained variance of 23.2% of the dataset that was

neglected from the above analysis. It is likely that the low sample numbers and high diversity
within the samples is such that not much information may be derived from the temperatureapplication rate-yield dataset by PCA.

969

### 970 10. Conclusions and future research directions

Biochar can act as a source of nutrient(s) for plants; it has its distinct, physical, physico-971 chemical and cation exchange properties, which can interact with native soil nutrients and added 972 nutrients in the forms of fertilizer and manures. Therefore, biochar may influence the supply of 973 nutrients to the plants. From the array of published research papers, we discussed in the review, 974 the yield response of crops and nutrient releasing behavior in soil due to biochar application 975 largely depends on the composition of biochar (i.e., feedstock, pyrolysis temperature of biochar 976 preparation) and specific soil type. The majority of biochar is alkaline, except a few like oak 977 and yellow pine chipped biochar, which is acidic. 978

Many studies showed that biochar significantly influences the mineralization/immobilization 979 turnover of N in soil thereby controlling the N availability without any definite conclusion. 980 However, biochar produced from manure sources being rich in N and other essential nutrients 981 and having narrow C: N ratio could be of higher agronomic value. The majority of the studies 982 showed biochar application increased the P and K availability in soil, and the positive effect was 983 achieved at lower pyrolysis temperature over higher pyrolysis temperature. The mechanism 984 through which the positive impacts of biochars on P and K is not clear yet. Therefore, more 985 research efforts are needed to identify the mechanistic pathway by which soil P and K 986 transformations are being impacted. For other secondary nutrients, there was a mixed response 987 988 on their availability due to biochar application.

44

989 Biochar has positive, negative as well as neutral effects on crop productivity. Biochar showed a positive impact on crop productivity when it was applied to acid soil. However, at a higher rate, 990 biochar might decrease the yield of crops and mostly that could be somewhat complemented by 991 application of fertilizers along with biochar. The biochar application has the potential to 992 improve soil quality, but it is highly dependent on inherent soil properties, fertility and fertilizer 993 management history for that specific piece of land. On the other hand, the negative behavior of 994 biochar towards both nutrient availability and crop productivity demands further insight and 995 thus investigations to find out the most probable reasons for such effect. Therefore, before 996 recommending the application of biochar to a soil under specified crop management, the long-997 term study is needed along with the clear understanding of the outcome, out of biochar 998 application. Therefore long-term field scale pilot experiments should be conducted to resolute 999 the following: Impacts of specific biochar properties on crop yield and how these impacts 1000 change across soil types, environmental conditions and agronomic management practices with 1001 judicious choices of the control treatment. Judicious selection of control is utmost necessary to 1002 1003 unify the treatment effects across differential experimental units such as temperate vs. tropical soils; grass land vs. forest soils; or Oxisol vs. Inceptisol, etc. Moreover, the potential of C 1004 sequestration benefit and other soil ecosystem services as provided by biochar should be 1005 considered while recommending for field applications. 1006

1007

#### 1008 Acknowledgements

This review paper has been developed under National Initiative on Climate Resilient
Agriculture (NICRA) (Grant Code No. 12-115) Project of Indian Council of Agricultural
Research.

45

#### 1012

#### 1013 Author contributions

1014 TJP wrote the first draft of the manuscript, with contributions from TB, DB, BS and SM. BS,

1015 and PW undertook data analysis. All authors improved the subsequent drafts and contributed in

1016 the accumulation and addition of appropriate references.

1017

#### 1018 References

1019 Ain, Q.U., Bareena, F.E., Shafiq, M., 2016. Management of the Parthenium hysterophorus

1020 through biochar formation and its application to rice-wheat cultivation in Pakistan. Agric.

1021 Ecosyst. Environ. 235, 265-276.

- Alvarez-Camposa, O., Langa, T.A., Bhadhaa, J.H., McCrayb, J.M., Glazc, B., Darouba, S.H.,
  2018. Biochar and mill ash improve yields of sugarcane on a sand soil in Florida. Agric.
  Ecosyst. Environ. 253, 122-130.
- 1025 Abel, S., Peters, A., Trinks, S., Schonsky, H., Facklam, M., Wessolek, G., 2013. Impact of
- biochar and hydrochar addition on water retention and water repellency of sandy soil.
  Geoderma 202–203, 183–191.
- Agegnehu, G., Srivastava, A.K., Bird, M.I., 2017. The role of biochar and biochar-compost in
   improving soil quality and crop performance: A review. Applied Soil Ecol. 119, 156-170.
- Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M.,
  Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and
  water: A review. Chemosphere 99, 19–23.

1033	Akhtar, S.S., Li, G., Andersen, M.N., Liu, F., 2014. Biochar enhances yield and quality of
1034	tomato under reduced irrigation. Agric. Water Manage. 138, 37-44.

- 1035 Al-Wabel, M.I., Al-Omran, A., El-Naggar, A.H., Nadeem, M., Usman, A.R.A., 2013. Pyrolysis
- 1036 temperature induced changes in characteristics and chemical composition of biochar
- 1037 produced from conocarpus wastes. Bioresource Tech. 131, 374-379.
- Anderson, R.A., Condron, L.M., Clough, T.J., Fiers, M., Stewart, A., Hill, R.A.& Sherlock,
   R.R., 2011. Biochar induced soil microbial community change: implications for
   biogeochemical cycling of carbon, nitrogen and phosphorus. Pedobiologia 54, 309–320.
- Asada, T., Ishihara, S., Yamane, S., Toba, T., Yamada, A., Oikawa, K., 2002. Science of
  bamboo charcoal: study on carbonizing temperature of bamboo charcoal and removal
  capability of harmful gases. J. Health Sci. 48, 473–479.
- Asai, H., Samson, B.K., Haefele, S.M., Songyikhangsuthor, K., Homma, K., Kiyono, Y., Inoue,
  Y., Shiraiwa, T.Horie, T., 2009. Biochar amendment techniques for upland rice
  production in Northern Laos. 1. Soil physical properties, leaf SPAD and grain yield. Field
  Crops Res. 111, 81–84.
- Atkinson, C.J., Fitzgerald, J.D. Hipps, N.A., 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant Soil 337, 1050 1–18.
- Bai, S.H., Reverchon, F., Xu, C.Y., Xu, Z., Blumfield, T.J., Zhao, H., Zwieten, L.V.Wallace,
  H.M., 2015. Wood biochar increases nitrogen retention in field settings mainly through
  abiotic processes. Soil Biol. Biochem. 90, 232–240.

- 1054 Baronti, S., Vaccari, F.P., Miglietta, F., Calzolari, C., Lugato, E., Orlandini, S., Pini, R., Zulian,
- 1055 C., Genesio, L., 2014. Impact of biochar application on plant water relations in *Vitis*1056 *vinifera* (L.). Eur. J. Agron. 53, 38–44.
- Barrow, C.J., 2012. Biochar: potential for countering land degradation and for improving
  agriculture. Applied Geography 34: 21–28.
- Batjes, N.H., 1996. Total carbon and nitrogen in the soils of the world. European J. Soil Sci. 47,
  1060 151–163.

Bayabil, H.K., Stoof, C.R., Lehmann, J.C., Yitaferu, B.Steenhuis, T.S., 2015. Assessing the
potential of biochar and charcoal to improve soil hydraulic properties in the humid
Ethiopian Highlands: The Anjeni watershed. Geoderma 243–244, 115–123.

1064

Bera, T., Purakayastha, T.J., Patra, A.K., 2015. Spectral, chemical and physical characterisation
of mustard stalk biochar as affected by temperature. Clay Res. 33, 36-45.Bera, T.,
Collins, H.P., Alva, A.K., Purakayastha, T.J., Patra, A.K., 2016. Biochar and manure
effluent effects on soil biochemical properties under corn production. Applied Soil Ecol.
71, 360–367.

Bera, T., Purakayastha, T.J., Patra, A.K., Datta, S.C., 2017. Comparative analysis of
 physicochemical, nutrient, and spectral properties of agricultural residue biochars as
 influenced by pyrolysis temperatures. J. Material Cycles Waste Manage. 20, 1115–1127.

48

Bera, T., Vardanyan, L.,Inglett, K.S., Reddy, K.R., O'Connor, G.A., Erickson, J.E., Wilkie,
A.C., 2019. Influence of select bioenergy by-products on soil carbon and microbial

activity: A laboratory study. Science Tot. Environ. 653: 1354-1363.

- Bhaduri, D., Saha, A., Desai, D.Meena, H.N., 2016. Restoration of carbon and microbial
  activity in salt-induced soil by application of peanut shell biochar during short-term
  incubation study. Chemosphere 148, 86–98.
- Binkley, D., Richter, J., David, M.B.Cladwell, B., 1992. Soil chemistry in a loblolly/longleaf
  pine forest with interval burning. Ecol. Appl. 2, 157–164.
- Blagodatskaya, E., Kuzyakov, Y., 2008. Mechanisms of real and apparent priming effects and
  their dependence on soil microbial biomass and community structure: critical review.
  Biol. Fertil. Soils 45, 115–131.
- Blum, S.C., Lehmann, J., Solomon, D., Caires, E.F. Alleoni, L.R.F., 2013. Sulfur forms in
  organic substrates affecting S mineralization in soil. Geoderma 200-201,156–164.
- Borchard, N., Prost, K., Kautz, T., Möller, A. Siemens, J., 2012a. Sorption of copper (II) and
  sulphate to different biochars before and after composting with farmyard manure.
  European J. Soil Sci. 63, 399–409.
- Borchard, N., Ladd, B., Eschemann, S., Hegenberg, M., Maria, B., Amelung, W., 2014. Black
  carbon and soil properties at historical charcoal production sites in Germany. Geoderma,
  232–234, 236–242.

- 1092 Bornø, M.L., Müller-Stöver, D.S., Liu, F., 2018. Contrasting effects of biochar on phosphorus
- dynamics and bioavailability in different soil types. Sci. Total Environ. 627, 963-974.
- 1094 Bruun, E.W., Petersen, C., Strobel, B.W., Hauggaard-Nielsen, H., 2012. Nitrogen and carbon
- leaching in repeacked sandy soil with added fine particulate biochar. Soil Sci. Soc. Am. J.
  76, 1142–1148.
- Butnan, S., Deenik, J.L., Toomsan, B., Antal, M.J., Vityakona, P., 2015. Biochar characteristics
  and application rates affecting corn growth and properties of soils contrasting in texture
  and mineralogy. Geoderma 237–238, 105–116.
- Cantrell, K.B., Hunt, P.G., Uchimiya, M., Novak, J.M.R., K.S., 2012. Impact of pyrolysis
  temperature and manure source on physicochemical characteristics of biochar.
  Bioresource Technol. 107, 419-428.
- Cayuela, M.L., Sanchez-Monedero, M.A., Roig, A., Hanley, K., Enders, A., Lehmann, J., 2013.
  Biochar and denitrification in soils: when, how much and why does biochar reduce N<sub>2</sub>O
  emissions? Scientific Report 3, 1732. <u>http://dx.doi.org/</u> 10.1038/srep01732. Nature
  Publishing Group.
- Chan, K.Y., Xu, Z., 2009. Biochar: nutrient properties and their enrichment. In: Lehmann, J.,
  Joseph, S. (Eds.), Biochar for environmental management: science and technology.
  Earthscan, London, pp. 67–84.
- Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A. Joseph, S., 2007. Agronomic values of
  green waste biochar as a soil amendment. Aust. J. Soil Res. 45, 629–634.

50

1112	Chan, K.Y., Zwieten, V.L., Meszaros, I., Downie, A.Joseph	n, S.	, 2008.	Using	poultry	litter
1113	biochars as soil amendments. Aust. J. Soil Res. 46, 437–4	44.				

- 1114 Chen, Chi-Peng, Cheng, Chih-Hsin, Huang, Yu-Hsuan, Chen, Chien-Ten, Lai, Chao-Ming,
- 1115 Menyailo, Oleg V., Fan, Liang-Jen, YangYaw-Win, 2014. Converting leguminous green
- 1116 manure into biochar: changes in chemical composition and C and N mineralization.
- 1117 Geoderma 232-234, 581–588.
- Cheng, C.H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H., 2006. Oxidation of black
  carbon by biotic and abiotic processes. Org. Geochem. 37: 1477-1488.
- Clarholm, M., 1994. Granulated wood ash and a 'N-free' fertilizer to forest soil: effects on P
  availability. Forest Ecol. Manage. 66, 127–136.
- Clough, T., Condron, L., Kammann, C.,Müller, C., 2013. A review of biochar and soil nitrogen
  dynamics. Agronomy 3, 275–293.
- Clough, T.J., Condron, L.M., 2010. Biochar and the nitrogen cycle: introduction. J. Environ.
  Qual. 39, 1218–1223.
- Crombie, K., Mašek, O., Sohi, S.P., Brownsort, P.Cross, A., 2013. The effect of pyrolysis
  conditions on biochar stability as determined by three methods. GCB Bioenergy 5(2),
  1128 122–131.
- Cui, L.Q., Pan, G.X., Li, L.Q., Yan, J.L., Zhang, A.F., Bian, R.J., Chang, A., 2012. The
  reduction of wheat Cd uptake in contaminated soil via biochar amendment: a two-year
  field experiment. Bioresources 7 (4), 5666-5676.

1132	Dai, Z., Zhang, X., Tang, C., Muhammad, N., Wu, J., Brookes, P.C., Xu, J., 2017. Potential role
1133	of biochars in decreasing soil acidification - A critical review. Sci. Total Environ. 581-
1134	582, 601-611.
1135	DeLuca, T.H., MacKenzie, M.D., Gundale, M.J., 2009. Biochar effects on soil nutrient
1136	transformations. In: Lehman, J., Joseph, S. (Eds.), Biochar for environmental
1137	management, Earthscan, London, UK, pp. 251–270.
1138	Devi, P., Saroha, A.K., 2015. Effect of pyrolysis temperature on polycyclic aromatic
1139	hydrocarbons toxicity and sorption behaviour of biochars prepared by pyrolysis of paper

mill effluent treatment plant sludge. Bioresource Technol. 192, 312–320.

- Ding, Y., Liu, Y., Wu, W., Shi, D., Yang, M., Zhong, Z., 2010. Evaluation of biochar effects on
  nitrogen retention and leaching in multi-layered soil columns. Water Air Soil Pollution
  213 (1), 47–55.
- Dünisch, O., Lima, V.C., Seehann, G., Donath, J., Montoia, V.R., Schwarz, T., 2007. Retention
  properties of wood residues and their potential for soil amelioration. Wood Sci. Technol.
  41(2), 169.
- Enders, A., Hanley, K., Whitman, T., Joseph, S.Lehmann, J., 2012. Characterization of biochars
  to evaluate recalcitrance and agronomic performance. Bioresource Technol. 114, 644–
  653.

1150	Farrell, M., Macdonald, L.M., Butler, G., Chirino-Valle, I., Condron, L.M., 2014.	Biochar and
1151	fertiliser applications influence phosphorus fractionation and wheat yield.	Biol. Fertil.
1152	Soils 50, 169–178.	

- 1153 Gaskin, J.W., Das, K.C., Tassistro, A.S., Sonon, L., Harris, K. Hawkins, B., 2009.
- 1154 Characterization of char for agricultural use in the soils of the southeastern United States.

1155 Amazonian dark earths: Wim Sombroek's Vision 433–443.

- 1156 Gaskin, J.W., Speir, R.A., Harris, K., Das, K.C., Lee, R.D., Morris, L.A., Fisher, D.S., 2010.
- 1157 Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and 1158 yield. Agron. J. 102 (2): 623–633.
- Gaskin, J.W., Steiner, C., Harris, K., Das, K.C., Bibens, B., 2008. Effect of low- temperature
  pyrolysis conditions on biochar for agricultural use. Trans. ASABE 51, 2061–2069.
- Gasser, T., Guivarch, C., Tachiiri, K., Jones, C.D., Ciais, P., 2015. Negative emissions
  physically needed to keep global warming below 2 °C. Nature Commun. 6, 7958.
- Glaser, B., Guggenberger, G., Zech, W. Rulvo, M.L., 2003. Soil organic matter stability in
  Amazonian dark earths. In: Lehman, J., Kern, D., Glaser, B., Woods, W. (Eds.)
  Amazonian Dark Earths: Origin, Properties and Management. Kluwer, Netherlands, pp.
  141–158.
- Glaser, B., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of
  highly weathered soils in the tropics with charcoal: A review. Biol. Fertil. Soils35, 219–
  230.

- 1170 Gonzalez, M.E., Cea, M., Medina, J., Gonzalez, A., Diez, M.C., Cartes, P., Monreal, C., Navia,
- 1171 R., 2015. Evaluation of biodegradable polymers as encapsulating agents for
- the development of a urea controlled-release fertilizer using biochar as support material.
- 1173 Sci. Total Environ. 505, 446-453.
- 1174 Gray, D.M., Dighton, J., 2006. Mineralization of forest litter nutrients by heat and combustion.
- 1175 Soil Biol. Biochem. 38, 1469–1477.
- Güereña, D.T., Lehmann, J., Thies, J.E., Enders, A., Karanja, N., Neufeldt, H., 2015.
  Partitioning the contributions of biochar properties to enhanced biological nitrogen
  fixation in common bean (*Phaseolus vulgaris*). Biol. Fertil. Soils 51, 479–491.
- Gundale, M.J., DeLuca, T.H., 2006. Temperature and substrate influence the chemical
  properties of charcoal in the ponderosa pine/Douglas fir ecosystem. Forest Ecol. Manage.
  231, 86–93.
- Haefelea, S.M., Konboonc, Y., Wongboonc, W., Amarantea, S., Maarifatb, A.A., Pfeiffer, E.M.,
  Knoblauch, C., 2011. Effects and fate of biochar from rice residues in rice-based systems.
  Field Crops Res. 121, 430–440.
- Hale, S.E., Jensen, J., Jakob, L., Oleszczuk, P., Hartnik, T., Henriksen, T., Okkenhaug, G.,
  Martinsen, V., Cornelissen, G., 2013. Short-term effect of the soil amendments activated
  carbon, biochar, and ferric oxyhydroxide on bacteria and invertebrates. Environ. Sci.
  Technol. 47, 8674–8683.
- Hammer, Ø., Harper, D.A.T. P. D. Ryan, 2001. PAST: Paleontological Statistics Software
  Package for Education and Data Analysis. Palaeontologia Electronica 4(1), 9.

1191	Hao, C., Wang, J., Kuang, M., Ming, Fu., Ci En, L., 2011. Enhancing phosphorus availability in
1192	phosphorus-fertilized zones by reducing phosphate adsorbed on ferrihydrite using rice
1193	straw derived biochar. J. Soils Sediments 11 (7), 1135–1141.
1194	Hea, T., Liua, D., Yuana, J., Nic, K., Zamand, M., Luoe, J., Lindseye, S., Dinga, W., 2018. A
1195	two years study on the combined effects of biochar and inhibitors on ammonia
1196	volatilization in an intensively managed rice field. Agric. Ecosyst. Environ. 264, 44-53.
1197	Heitkötter, J. Marschner, B., 2015. Interactive effects of biochar ageing in soils related to

feedstock, pyrolysis temperature, and historic charcoal production. Geoderma 245-246,56-64.

- Hossain, M.K., Strezov, V., Chan, K.Y., Nelson, P.F., 2010. Agronomic properties of
   wastewater sludge biochar and bioavailability of metals in production of cherry tomato
   (*Lycopersicon esculentum*). Chemosphere 78, 1167-1171.
- Huang, M., Yang, L., Qin, H., Jiang, L.Zou, Y., 2013. Quantifying the effect of biochar
  amendment on soil quality and crop productivity in Chinese rice paddies. Field Crops Res.
  154, 172–177.
- Iswaran, V., Jauhri, K, Sen, A., 1980. Effect of charcoal, coal and peat on the yield of moong
  soybean and pea. Soil Biol. Biochem. 12, 191–192.
- Jeffery, S., Martijn Bezemer T., Cornelissen, G., Kuyper, T.W., Lehmann, J., Mommer, L.,
  Sohi, S.P., van de Voorde, T.F.J., Wardle, D.A., van Groenigen, J.W., 2013. The way

- forward in biochar research: targeting trade-offs between the potential wins. GCBBioenergy 7, 1–13.
- 1212 Jeffery, S., Verheijen, F.G.A., van der Velde, M., Bastos, A.C., 2011. A quantitative review of
- 1213 the effects of biochar application to soils on crop productivity using meta-analysis. Agric.
- 1214 Ecosyst. Environ. 144, 175–187.
- Jiang, J., Yuan, M., Xu, R., Bish., D.L., 2015. Mobilization of phosphate in variable-charge
  soils amended with biochars derived from crop straws. Soil Tillage Res. 146, 139–147.
- Jiang, T.Y., Xu, R.K., Gu, T.X. Jiang, J., 2014. Effect of crop-straw derived biochars on Pb (II)
  adsorption in two variable charge soils. J. Integrative Agric. 13, 507–516.
- Jones, D.L., Rousk, J., Edwards-Jones, G., DeLuca, T.H., Murphy, D.V., 2012. Biochar
  mediated changes in soil quality and plant growth in a three year field trial. Soil Biol.
  Biochem. 45, 113–124.
- Kameyama, K., Miyamoto, T., Shiono, T., Shinogi, Y., 2012. Influence of sugarcane bagassederived biochar appalication on nitrate leaching in calcic dark red soil. J. Environ. Qual.
  41 (4), 1131-1137.
- Kamprath, E.J., 1971. Potential detrimental effects from liming highly weathered soils to
   neutrality. Soil Crop Sci. Soc. Florida Proceed. 31, 200–203.
- Karer, J., Wimmer, B., Zehetner, F., Kloss, S., Soja, G., 2013. Biochar application to temperate
  soils: effects on nutrient uptake and crop yield under field conditions. Agric. Food Sci.
  22: 390-403.

1230	Karhu, K., Mattila, T., Bergstr€om, I.,Regina, K., 2011. Biochar addition to agricultural soil
1231	increased CH <sub>4</sub> uptake and water holding capacity e results from a short term pilot field
1232	study. Agric. Ecosyst. Environ.140, 309–313.

- 1233 Khan, S.,C. Chao, M., Waqas, H.P.H., Arp, Zhu, Y.G., 2013. Sewage sludge biochar
- 1234 influenceupon rice (Oryza sativa L) yield, metal bioaccumulation and greenhouse gas
- emissions from acidic paddy soil. Environ. Sci. Technol. 47, 8624–8632.
- 1236 Kim, P., Hensley, D., Labbé, N., 2014. Nutrient release from switchgrass-derived biochar pellets
  1237 embedded with fertilizers. Geoderma 232–234, 341–351.
- Kloss, S., Zehetner, F., Wimmer, B., Buecker, J., Rempt, G., Soja, G., 2014. Biochar
  application to temperate soils: effects on soil fertility and crop growth under greenhouse
  conditions. J. Plant Nutrition Soil Sci. 177, 3–15.
- Kookana, R.S., Sarmah, A.K., van Zwieten, L., Krull, E., Singh, B., 2011. Biochar application
  to soil: agronomic and environmental benefits and unintended consequences. Adv. Agron.
  112, 103–143.
- Laird, D., Fleming, P., Wang, B.Q., Horton, R., Karlen, D., 2010. Biochar impact on nutrient
  leaching from a Midwestern agricultural soil. Geoderma 158, 436–442.
- 1246 Laird, D.A., Brown, R.C., Amonette, J.E., Lehmann, J., 2009. Review of the pyrolysis platform
- 1247 for coproducing bio-oil and biochar. Biofuels Bioproducts Biorefining 3, 547–562.
- Lal, J.K., Mishra, B., 1998. Flyash as a carrier for Rhizobium inoculant. J. Res. 10,191–192.

- 1249 Lashari, M.S., Liu, Y., Li, L., Pan, W., Fu, J., Pan, G., Zheng, J., Zheng, J., Zhang, X., Yu, X.,
- 1250 2013. Effects of amendment of biochar-manure compost in conjunction with pyroligneous
- solution on soil quality and wheat yield of a salt-stressed cropland from Central China
- 1252 Great Plain. Field Crops Res. 144, 113–118.
- Lehmann, J., 2013. Recycle waste for nourishing soils. Nature 504, 33.
- Lehmann, J., 2007. Bio-energy in the black. Frontiers Ecol. Environ. 5, 381–387.
- Lehmann, J., da Silva, J.P., Steiner, C., Nehls, T., Zech, W., Glaser, B., 2003. Nutrient
  availability and leaching in an archaeological anthrosol and a ferralsol of the central
  Amazon Basin: fertilizer, manure and charcoal amendments. Plant Soil 249, 343–357.
- Lehmann, J., da Silva, J.P., Steiner, C., Nehls, T., Zech, W., Glaser, B., 2003. Nutrient
  availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central
  Amazon basin: fertilizer, manure and charcoal amendments. Plant Soil 249, 343–357.
- Lehmann, J., Gaunt, J., Rondon, M., 2006. Biochar sequestration in terrestrial ecosystems– A
  review. Mitigation Adaptation Strategies Global Change 11, 403–427.
- Lehmann, J., Kuzyakov, Y., Pan, G., Ok, Y.S., 2015. Biochars and the plant-soil interface. PlantSoil 395, 1-5.
- Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011.
  Biochar effects on soil biota? A review. Soil Biol. Biochem. 43, 812-1836.

1267	Lehmann, J., Rondon, M., 2005. Biochar soil management on highly-weathered soils in the
1268	humid tropics. In: Uphoff, N. (Ed.), Biological Approaches to Sustainable Soil Systems.
1269	Boca Raton, CRC Press.
1270	Lentz, R.D., Ippolito, J.A., 2012. Biochar and manure affects calcareous soil and corn silage
1271	nutrient concentrations and uptake. J. Environ. Qual. 41, 1033–1043.
1272	Liang, B., Lehman, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O.,
1273	Thies, J., Luizao, F.J., Petersen, J., Neves, E.G., 2006. Black carbon increases cation
1274	exchange capacity in soils. Soil Sci. Soc. Am. J. 70, 1719–1730.
1275	Liu, X., Zhang, A., Ji, C., Joseph, S., Bian, R., Li, L., Pan, G., Paz-Ferreiro, J., 2013. Biochar's
1276	effect on crop productivity and the dependence on experimental conditions-a meta-
1277	analysis of literature data. Plant Soil 373, 583–594.
1278	Macdonald, L.M., Farrel, M., Van Zwieten, L.M., Krull, E.S., 2014. Plant growth responses to
1279	biochar addition: an Australian soils perspective. Biol. Fertil. Soils DOI 10.1007/s00374-

1280 014-0921-z.

- Maestrini, B., Herrmann, A.M., Nannipieri, P., Schmidt, M.W.I., Abiven, S., 2014. Ryegrassderived pyrogenic organic matter changes organic carbon and nitrogen mineralization in a
  temperate forest soil.Soil Biol. Biochem. 69, 291–301.
- Mahmood, S., Finlay, R.D., Fransson, A.M., Wallander, H., 2003. Effects of hardened wood ash
  on microbial activity, plant growth and nutrient uptake by ectomycorrhiza spruce
  seedlings. FEMS Microbiol. Ecol. 43, 121–131.

1287	Major, J., Rondon, M., Molina, D., Riha, S.J., Lehman, J., 2010. Maize yield and nutrition
1288	during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil 333,
1289	117–128.

- Major, J., Steiner, C., Downie, A., Lehmann, J., 2009. Biochar effects on nutrient leaching. In:
  Lehmann, J., Joseph, S. (Eds.), Biochar for environmental management: science and
- technology. Earthscan, London, pp. 271–282.
- Makoto, K., Choi, D., Hashidoko, Y., Koike, T., 2011. The growth of *Larixgmelinii* seedlings as
  affected by charcoal produced at two different temperatures. Biol. Fertil. Soils 47, 467–
  472.
- Mandal, A., Singh, N., Purakayastha, T.J., 2017. Characterization of pesticide sorption
  behaviour of slow pyrolysis biochars as low cost adsorbent for atrazine and imidacloprid
  removal. Sci. Total Environ.577, 376–385.
- Mandal, S., Donner, E., Vasileiadis, S., Skinner, W., Smith, E., Lombi, E., 2018. The effect of
  biochar feedstock, pyrolysis temperature, and application rate on the reduction of
  ammonia volatilisation from biochar-amended soil. Sci. Total Environ. 627, 942-950.
- Mandal, S., Donner, E., Vasileiadis, S., Skinner, W., Smith, E., Lombi, E., 2018. The effect of
  biochar feedstock, pyrolysis temperature, and application rate on the reduction of
  ammonia volatilisation from biochar-amended soil. Sci. Total Environ. 627, 942-950.
- Mandal, S., Sarkar, B., Bolan, N., Novak, J., Ok, Y.S., Van Zwieten, L., Singh, B.P., Kirkham,
  M.B., Choppala, G., Spokas, K., Naidu, R., 2016a. Designing advanced biochar products

- for maximizing greenhouse gas mitigation potential. Critical Reviews Environ. Sci.
  Technol. 46 (17), 1367-1401.
- 1309 Mandal, S., Thangarajan, R., Bolan, N.S., Sarkar, B., Khan, N., Ok, Y.S., Naidu, R., 2016b.
- 1310 Biochar-induced concomitant decrease in ammonia volatilization and increase in nitrogen
- use efficiency by wheat. Chemosphere 142, 120-127.
- Meyer, S., Glaser, B., Quicker, P., 2001. Technical, economical, and climate-related aspects of
  biochar production technologies: A literature review. Environ. Sci. Technol. 45, 9473–
  9483.
- Minasny, B., Malone, B.P., McBratney, A.B., Angers, D.A., Arrouays, D., Chambers, A.,
  Chaplot, V., Chen, Z.-S., Cheng, K., Das, B.S., Field, D.J., Gimona, A., Hedley, C.B.,
  Hong, S.Y., Mandal, B., Marchant, B.P., Martin, M., McConkey, B.G., Mulder, V.L.,
  O'Rourke, S., Richer-de-Forges, A.C., Odeh, I., Padarian, J., Paustian, K., Pan, G.,
  Poggio, L., Savin, I., Stolbovoy, V., Stockmann, U., Sulaeman, Y., Tsui, C.-C., Vågen,
  T.-G., van Wesemael, B.& Winowiecki, L., 2017. Soil carbon 4 per mille. Geoderma 292,
  59-86.
- Mohan, D., Sarswat, A., Ok, Y.S., Pittman, C.U., 2014. Organic and inorganic contaminants
  removal from water with biochar, a renewable, low cost and sustainable adsorbent: A
  critical review. Bioresource Technol. 160,191–202.
- Mukherjee, A., Lal, R., Zimmerman, A.R., 2014. Effects of biochar and other amendments on
  the physical properties and greenhouse gas emissions of an artificially degraded soil.
  Sci. Total Environ.487, 26–36.

- Mukherjee, A., Zimmerman, A.R., 2013. Organic carbon and nutrient release from a range of
  laboratory-produced biochars and biochar–soil mixtures. Geoderma193–194, 122–130.
- 1330 Munda, S., Nayak, A.K., Mishra, P.N., Bhattacharyya, P., Mohanty, S., Kumar, A., Kumar, U.,
- Baig, M.J., Tripathi, R., Shahid, M., Adak, T., 2016. Combined application of rice husk
  biochar and fly ash improved the yield of lowland rice. Soil Res. 54 (4), 451–459.
- Munda, S., Bhaduri, D., Mohanty, S., Chatterjee, D., Tripathi, R., Shahid, M., Kumar, U.,
  Bhattacharyya, P., Kumar, A., Adak, T. and Jangde, H.K., Nayak, A.K., 2018.
  Dynamics of soil organic carbon mineralization and C fractions in paddy soil on
  application of rice husk biochar. Biomass Bioenergy 115, 1-9.
- 1337 Nehls, T., 2002. Fertility improvement of a Terra FirmeOxisol in Central Amazonia by charcoal
  1338 applications. M.Sc. Thesis, University of Bayreuth, Germany.
- Nellisen, V., Rutting, T., Huygens, D., Staelens, J., Ruysschaert, G.,Boeckx, P., 2012. Maize
  biochar accelerate short-term nitrogen dynamics in a loamy sand soil. Soil Biol. Biochem.
  55, 20–27.
- Nielsen, S., Joseph, S., Ye, J., Chia, C., Munroe, P., Zwieten, L.V., Thomas, T., 2018. Cropseason and residual effects of sequentially applied mineral enhanced biochar and N
  fertiliser on crop yield, soil chemistry and microbial communities. Agric. Ecosyst.
  Environ. 255, 52-61.
- Nguyen, B.T, Lehmann J., 2009. Black carbon decomposition under varying water regimes.
  Org. Geochem. 40 (8), 846–853.

- Nishio, M., Okano, S., 1991. Stimulation of the growth of alfalfa and infection of mycorrhizal
  fungi by the application of charcoal. Bull. Natl. Grassl. Res. Inst. 45, 61–71.
- 1350 Novak, J.M., Busscher, W.J., Laird, D.L., Ahmedna, M., Watts, D.W., Niandou, M.A.S., 2009.
- 1351 Impact of biochar amendment on fertility of a south eastern coastal plain soil. Soil Sci.,
- 1352 174, 105–112.
- O'Connor, D., Peng, T., Li, G., Wang, S., Duan, L., Mulder, J., Cornelissen, G., Cheng, Z.,
  Yang, S., Hou, D., 2018a. Sulfur-modified rice husk biochar: a green method for the
  remediation of mercury contaminated soil. Sci. Total Environ. 621, 819–826.
- 1356 O'Connor, D., Peng, T., Zhang, J., Tsang, D.C.W., Alessi, D.S., Shen, Z., Bolan, N.S., Hou, D.,
- 1357 2018b. Biochar application for the remediation of heavy metal polluted land: A review of
  1358 in situ field trials. Sci. Total Environ. 619–620, 815–826.
- Olmo, M., Villar, R., Salazar, P., Alburquerque, J.A., 2016. Changes in soil nutrient availability
  explain biochar's impact on wheat root development. Plant Soil 399 (1-2), 333–343.
- 1361 Pandher, M.S., Gupta, R.P., Bhandal, B.K., Gupta. S.K., 1993. Studies on growth and survival

1362 of Rhizobium isolates in different carriers. Indian J. Ecol. 20,141–146.

- 1363 Parvage, M.M., Ulen, B., Eriksson, J., Strock, J., Kirchmann, H., 2013. Phosphorus availability
- in soils amended with wheat residue char. Biol. Fertil. Soils 49, 245–250.
- Paustian, K., Lehmann, J., Ogle, S., Reay, D., Robertson, G.P., Smith, P., 2016. Climate-smart
  soils. Nature 532, 49-57.

Peng, X., Ye, L.L., Wang, C.H., Zhou, H., Sun, B., 2011. Temperature- and duration-dependent
rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in
southern China. Soil Tillage Res. 112, 159-166.
Pereira, E.I.P., Suddick, E.C., Mansour, I., Mukome, F.N.D., Parikh, S.J., Scow, K., Six, J.,
2015. Biochar alters nitrogen transformations but has minimal effects on nitrous oxide
emissions in an organically managed lettuce mesocosm. Biol. Fertil. Soils 51, 573-582.

- Petersen, H., 1978. Some properties of two high-gradient extractors for soil microarthropods,
  and an attempt to evaluate their extraction efficiency. Natural Jutl 20, 95–122
- 1375 Prayogo, C., Jones, J.E., Baeyens, J., Gary, D., 2014. Impact of biochar on mineralisation of C
- and N from soil and willow litter and its relationship with microbial community biomassand structure Bending. Biol. Fertil. Soils 50, 695–702.
- Prendergast-Miller, M.T., Duvall, M., Sohi, S.P., 2014. Biochar–root interactions are mediated
  by biochar nutrient content and impacts on soil nutrient availability. European J. Soil
  Sci. 65(1), 173–185.
- Purakayastha, T.J., 2010. Effect of biochar on yield of different crops. In: Annual Report,
  Indian Agricultural Research Institute, New Delhi, pp. 55.
- Purakayastha, T.J., Das, K.C., Gaskin, J., Harris, K., Smith, J.L., Kumari, S., 2016. Effect of
  pyrolysis temperatures on stability and priming effects of C3 and C4 biochars applied to
  two different soils. Soil Tillage Res. 155, 107–115.

1386	Purakayastha, T.J., Kumari, S., Pathak, H., 2015. Characterization, stability, and microbia
1387	effects of four biochars produced from crop residues. Geoderma 239 (240), 293-303.

1388 Quilliam, R.S., Marsden, K.A., Gertler, C., Rousk, J., DeLuca, T.H., and Jones, D.L., 2012.

1389 Nutrient dynamics, microbial growth and weed emergence in biochar amended soil are

influenced by time since application and reapplication rate. Agric.Ecosys. Environ. 158,1391 192-199.

Rahman, A.A., Abdullah, N., Sulaiman, F., 2014. Temperature effect on the characterization of
 pyrolysis products from oil palm fronds. Adv. Energy Engineering 2, 14–21.

Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A.R., Lehmann, J., 2012. Corn
growth and nitrogen nutrition after additions of biochars with varying properties to a
temperate soil. Biol. Fertil. Soils 48, 271–284.

Rens, H., Bera, T., Alva, A.K., 2018. Effects of biochar and biosolid on adsorption of nitrogen,
phosphorus, and potassium in two soils. Water Air Soil Poll.
https://doi.org/10.1007/s11270-018-3925-8.

Ro, K.S., Cantrell, K.B., Hunt, P.G., 2010. High-Temperature Pyrolysis of Blended Animal
Manures for Producing Renewable Energy and Value-Added Biochar. Industrial
Engineering Chemistry Res. 49(20), 10125-10131.

1403 Rogelj, J., den Elzen, M., Höhne, N., Fransen, T., Fekete, H., Winkler, H., Schaeffer, R., Sha,

F., Riahi, K., Meinshausen, M., 2016. Paris Agreement climate proposals need a boost to
keep warming well below 2 °C. Nature 534, 631-639.

65

- 1406 Rogovska, N., Laird, D.A., Rathke, S.J.,Karlen, D.L., 2014. Biochar impact on Midwestern
  1407 Mollisols and maize nutrient availability. Geoderma 230–231, 340–347.
- 1408 Rondon, M.A., Lehmann, J., Ramirez, J., Hurtado, M., 2007. Biological nitrogen fixation by
- 1409 common beans (*Phaseolus vulgaris* L.) increases with bio-char additions. Biol. Fertil.
- 1410 Soils 43, 699-708.
- 1411 Rosa, D.L., Knicker, J.M., 2011. Bioavailability of n released from N-rich pyrogenic organic
  1412 matter: an incubation study. Soil Biol. Biochem. 43, 2368–2373.
- Saarnio, S., Heimonen, K.,Kettunen, R., 2013. Biochar addition indirectly affects N<sub>2</sub>O
  emissions via soil moisture and plant N uptake. Soil Biol. Biochem. 58, 99–106.
- Sarkar, B., Mandal, S., Tsang, Y.F., Kumar, P., Kim, K.-H., Ok, Y.S., 2018. Designer carbon
  nanotubes for contaminant removal in water and wastewater: A critical review. Sci.
  Total Environ. 612, 561-581.
- 1418 Schmidt, M.W.I., Noack, A.G., 2000. Black carbon in soils and sediments: Analysis,
- distribution, implications, and current challenges. Global Biogeochem. Cycle 14, 777-793.
- Schmidt, H.P., Kammann, C., Niggli, C., Evangelou, M.W.H., Mackie, K.A., Abiven, S., 2014.
  Biochar and biochar-compost as soil amendments to a vineyard soil: Influences on plant
  growth, nutrient uptake, plant health and grape quality. Agric. Ecosyst. Environ. 191, 117-
- 1423

123.

1424	Singh, B.P., Hatton, B.J., Singh, B., Cowie, A.L., Kathuria, A., 2010. Influence of biochars on
1425	nitrous oxide emission and nitrogen leaching from two contrasting soils. J. Environ. Qual
1426	39, 1224–1235.

- 1427 Slavich, P.G., Sinclair, K., Morris, S.H., Kimber, S.W.L., Downie, A.Van Zwieten, L., 2013.
- 1428 Contrasting effects of manure and green waste biochars on the properties of an acidic 1429 ferralsol and productivity of a subtropical pasture. Plant Soil 366, 213–227.
- 1430 Sohi, S.P., Krull, E., Lopez-Capel, E.Bol, R., 2010. A review of biochar and its use and function
- 1431 in soil. Adv.Agron. 105, 47–82.
- Soinne, H., Hovi, J., Tammeorg, P.Turtola, E.,2014. Effect of biochar on phosphorus sorption
  and clay soil aggregate stability. Geoderma219–220, 162–167.
- Song, Y., Zhang, X., Ma, B., Chang, S.X.,Gong, J.,2013. Biochar addition affected the
  dynamics of ammonia oxidizers and nitrification in microcosms of a coastal alkaline soil.
  Biol.Fertil. Soils. DOI: 10.1007/s00374-013-0857-8.
- 1437 Spokas, K.A., Cantrellb, K.B., Novak, J.M., Archerc, D.W., Ippolitod, J.A., Collinse, H.P.,
- 1438 Boatengf, A.A., Limag, I.M., Lambh, M.C., McAloonf, A.J., Lentzd, R.D.Nicholsc,
- 1439 K.A., 2000. Biochar: A synthesis of its agronomic impact beyond carbon sequestration.
- 1440 J.Environ.l Qual. 41, 973–989.
- Steiner, C., Das, K.C., Melear, N.Lakly, D., 2010. Reducing nitrogen loss during poultry litter
  composting using biochar. J. Environ.l Qual. 39, 1236-1242.

- Stevenson, F.J., Cole, M.A.,1999. Cycles of the Soil, Second edition, John Wiley and Sons,
  Inc., New York, NY.
- Streubel, J.D., Collins, H.P., Garcia-Perez, M., Tarara, J. Granatstein, D., Kruger, C.E.,2011.
  Influence of biochar on soil pH, water holding capacity, nitrogen and carbon dynamics.
- 1447 Soil Sci.Soc. Am. J. 75, 1402–1413.
- Sun, Z., Bruun, E.W., Arthur, E., Jonge, L.W.D., Moldrup, P., Nielsen, H.H., Elsgaard, L.,
  2014. Effect of biochar on aerobic processes, enzyme activity, and crop yields in two
  sandy loam soils. Biol. Fertility Soils. 50. 10.1007/s00374-014-0928-5.
- Taghizadeh-Toosi, A., Clough, T., Sherlock, R., Condron, L., 2012a. Biochar adsorbed ammonia
  is bioavailable. Plant Soil, 350, 57-69.
- Taghizadeh-Toosi, A., Clough, T.J., Sherlock, R.R., Condron, L.M.,2012b. A wood based lowtemperature biochar captures NH<sub>3</sub>-N generated from ruminant urine-N, retaining its
  bioavailability. Plant Soil, 353, 73-84.
- Tammeorg, P.,Simojoki, A.,Mäkelä, P., Stoddard, F.,Alakukku, L.,Helenius, J., 2014. Biochar
  application to a fertile sandy clay loam in boreal conditions: Effects on soil properties
  and yield formation of wheat, turnip rape and faba bean. Plant Soil. 374.
- 1459 UNEP, 2017. The Emissions Gap Report 2017. United Nations Environment Programme1460 (UNEP), Nairobi.
- Uzoma, K.C., Inoue, M., Andry, H., Zahoor, A., Nishihara, E., 2011. Influence of biochar
  application on sandy soil hydraulic properties and nutrient retention. J.Food Agric.l
  Environ. 9, 1137–1143.

1464	Vaccari, F.P., Baronti, S., Lugato, E., Genesio, L., Castaldi S., Fornasie	er, F., Miglietta, F.,2011.
1465	Biochar as a strategy to sequester carbon and increase yield in	durum wheat. European
1466	J.Agron. 34, 231–238.	

- 1467 Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S., Cowie, A.
- 1468 2010. Effects of biochar from slowpyrolysis of papermill waste on agronomic performance
- and soil fertility. Plant Soil, 327:235–246
- 1470 Van Zwieten, L., Singh, B., Joseph, S., Kimber, S., Cowie, A., Chan, K.Y., 2009. Biochar and
- 1471 emissions of non-CO<sub>2</sub> greenhouse gasses from soil. In: Lehmann, J., Joseph, S. (Eds.),
- Biochar for environmental management: science and technology. Earthscan, London,
  Sterling, VA, pp. 227–249.
- Verheijen, F., Jeffery, S., Bastos, A.C., van der Velde, M.Diafas, F.,2010. Biochar application
  to soils. A critical scientific review of effects on soil properties, processes, and
  functions. Luxembourg pp. 149.
- Wen, P., Wu, Z., Han, Y., Cravotto, G., Wang, J., Ye, B.C., 2017. Microwave-Assisted Synthesis of a
  Novel Biochar-Based Slow-Release Nitrogen Fertilizer with Enhanced Water-Retention
  Capacity. ACS Sustain. Chem. Eng., 5, 7374-7382.
- Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J. Joseph, S.,2010. Sustainable
  biochar to mitigate global climate change. Nature Communications 1: Article number:
- 1482 56 (online journal). <u>www.nature.com/ncomms/journal/v1/n5/full/ncomms1053.html</u>.

1483	Wrobel-Tobiszewska, A., Boersma, M., Sargison, J.,	Adams, P.,	Jarick,	S.,2015.An
1484	economic analysis of biochar production using re	esidues from	Eucalypt	plantations.
1485	Biomass Bioenergy, 81, 177-82.			

Xie, Z.B., Xu, Y.P., Liu, G., Liu, Q., Zhu, J.G., Tu, C., Amonette, J.E., Cadisch, G., Yong,
J.W.H.Hu, S.J.,2013. Impact of biochar application on nitrogen nutrition of rice, green
house gas emission and soil organic carbon dynamics in two paddy soils of China. Plant
Soil, 370, 527–540.

Xu, Y., Seshadri, B., Sarkar, B., Wang, H., Rumpel, C., Sparks, D., Farrell, M., Hall, T., Yang,
X.Bolan, N., 2018a. Biochar modulates heavy metal toxicity and improves microbial
carbon use efficiency in soil. Sci. Total Environ.621, 148-159.

1493 Xu, G., Saho, H., Zhang,Y. Sun J.,2018b Non-additive effects of biochar amendments on soil
1494 phosphorusfractions in two contrasting soils. Land Degrad. Dev. 29, 2720-2727.

Yang, H., Sheng, K., 2012. Characterization of biocharproperties affected by different pyrolysis
 temperature using visible-near-infrared spectroscopy. International Scholarly Research
 Network, ISRN Spectroscopy, doi:10.5402/2012/712837.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P.Yang, L.,
2011. Removal of phosphate from aqueous solution by biochar derived from
anaerobically digested sugar beet tailings. J. Hazardous Materials 190(1-3), 501-507.

Yao, Y., Gao, B., Zhang, M., Inyang, M., Zimmerman, A.Z., 2012. Effect of biochar
amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy
soil. Chemosphere 89(11), 1467-1471.
- Yu, X., Wu, C., Fu, Y., Brookes, P.C.Lu, S.,2016. Three-dimensional pore structure and carbon
  distribution of macroaggregates in biochar-amended soil. European J. Soil Sci. 67(1),
  109–120.
- Yuan, J.H., Xu, R.K., Qian, W.Wang, R.H.,2011. Comparison of the ameliorating effects on an
  acidic Ultisol between four crop straws and their biochars. J. Soils Sediments11, 741–
  750.
- Yuan, J.H., Xu, R.K.Zhang, H.,2011. The forms of alkalis in the biochar produced from crop
  residues at different temperatures. Bioresource Technology 102, 3488–3497.
- Wang, S.P., Li, X.K., Lu, J.W., et al., 2013. Effects of combined application of urea and
  controlled-release urea on yield, profits of rapeseed and soil inorganic nitrogen. Chin. J.
  Oil Crop Sci. 35(3), 295-300
- 1515 Zhai, L., Cai Ji, Z., Liu, J., Wang, H., Ren, T., Gai, X., Xi, B., Liu, H., 2015. Short-term effects
- of maize residue biochar on phosphorus availability in two soils with different phosphorus
  sorption capacities. Biol. Fertil. Soils 51, 113–122.
- Zhang, A., Liu, Y., Pan, G., Hussain, Q., Li, L.Pan, G.,2012. Effect of biochar amendment on
  maize yield and greenhouse gas emissions from a soil organic carbon poor calcareous
  loamy soil from Central China Plain. Plant Soil, 351, 263–275.
- Zhang, H., Voroney, R.P.Price, G.W.,2015. Effects of temperature and processing conditions on
  biochar chemical properties and their influence on soil C and N transformations. Soil
  Biol.Biochem. 83, 19–28.

- 1524 Zhao, B., O'Connor, D., Zhang, J., et al., 2018. Effect of pyrolysis temperature, heating rate,
  1525 and residence time on rapeseed stem derived biochar. J. Clean. Prod.174, 977-987.
- 1526 Zheng, H., Wang, Z., Deng, X., Xing, B., 2013. Impact of pyrolysis temperature on nutrient
- 1527 properties of biochar, inXu, J., Wu, J., He, Y. (Eds.), Functions of Natural Organic Matter
- in Changing Environment. pp.975-978. 10.1007/978-94-007-5634-2\_179.
- 1529 Zhou, L., Cai, D., He, L., Zhong, N., Yu, M., Zhang, X., Wu, Z., 2015. Fabrication of a high-
- 1530 performance fertilizer to control the lossof water and nutrient using micro/nano net-works.
- 1531 ACS Sustain. Chem. Eng. 3, 645–653.
- 1532 Zhu, K.R., Fu, H., Zhang, J.H., Lv, X.S., Tang, J. Xu, X.H., 2012. Studies on removal of NHb 4
- 1533 -N from aqueous solution by using the activated carbons derived from rice husk.
  1534 Biomass Bioenergy 43, 18–25.
- 1535 Zimmerman, A.R., 2010. Abiotic and microbial oxidation of laboratory produced black carbon
  1536 (biochar). Environ.l Sci. Technol. 44, 1295–1301.

1537



Fig. 1. Pathways of biochar impact in soil for better crop production.  $\longrightarrow$  Indicate primary pathways as evident from previous literature while ----  $\rightarrow$  indicated possible pathways which needs to be validated with future research results.



Fig. 2. Effect of biochar (BC) application rate on soil pH





**Fig. 3.** Schematic diagram representing how biochar improves the retention of macro (N, P, and K) and micronutrients (Ca and Mg) and increases their availabilities in soils.



**Fig. 4.** Principal Component analysis with respect to soil type for effects of biochar on (a) soil chemical properties, and (b) crop yields. Point groups are enclosed by convex hulls. Numbers within the figure represent soil types.

In Fig. 4a 1–Acrisol; 2–Alfisol; 3–Anthrosols; 4–Calcarosol; 5–Cambisol; 6–Chernozem; 7– Entisol; 8–Eutric Cambisol; 9–Ferrosol; 10–Halpudept; 11–Haplustox; 12–Planosol; 13– Stagnosol.

In Fig. 4b 1–Acidic Aeronosol; 2–Acidic clay loam Ultisol; 3–Acid Ferrasol; 4–Acidic Oxisol; 5–Acidic sandy clay loam; 6–Acidic silty; 7–Alkaline Calcisol; 8–Alkaline sandy loam Inceptisol; 9–Neutral clay loam Oxisol; 10–Neutral Vertisol; 11–Slightly alkaline sandy loam Inceptisol.

### Highlights

- Nutrient value of biochar as impacted by pyrolysis conditions and feedstock types discussed.
- Impact of biochar on improvement of soil pH, CEC and buffering system delineated.
- Role of biochar on dynamics of nitrogen, phosphorus, potassium, secondary and micronutrients in soil elucidated.
- Effect of biochar on crop yields in different soils across the globe discussed.
- Meta-analysis of the established data by Principal component analysis was done to establish the role of biochar on soil chemical properties and crop yields
- Conclusions and future directions of biochar research

pH and nutrient composition of various biochar materials produced at different pyrolysis temperatures

(°C) (%) (%) (mg kg <sup>-1</sup> )	al et al.
(%) (%) (mg kg <sup>-1</sup> )	al et al.
	al et al.
Crop residues	al et al.
Corn cob 600°C 10.1 79.1 4.25 19 Mand (2017	)
Macadamia 450-480 8.76 78.03 0.43 182 0.24 2.19 0.37 0.17 1211 Wrob	el-
integrifolia °C Tobis (2015	zewska )
Giant reed 9.45 73.4 0.49 150 Zheng (Amundodongy)	g et al.
(Arunaddondx)       (2013)         Switch grass       400 °C       -       73.1       1.35       54       -       -       0.32       Purak	) ayastha
et al.	(2016)
Rice straw $450$ °C $/0.6$ $0.9/$ $0.218$ $26.4$ Peng (2011)	et al.
Wheat straw         400 °C         -         70.5         1.22         58         -         -         -         0.29         -         -         -         Purak	ayastha
et al. (	(2016)
(2012) Construction Construction (2012) Construction (2012)	)
Peanut hull         400 °C         65.5         2.0         33         0.00162         0.00153         0.00044         -         -         -         -         -         Gaski	n et al.
Pearl millet 400 °C 10.6 64 1.10 58 1.60 2.52 1.47 1.06 0.22 Purak	) avastha
et al.	(2015)
Soybean straw 500 °C 10.9 62.6 0.37 171 0.44 Yuan	et al.
Canola straw 500 °C 9.39 61.6 0.04 1610 0.27 (2011	a)
Corn stover         300 °C         7.33         59.5         1.16         51         0.137         1.705         0.648         0.588         0.070         132         -         963         142         -         Ender           (2012)	s et al. )
Sugarcane bagasse 350 °C 4.96 57 0.34 168 0.058 0.48 0.032	
Corn stover 400 °C - 55.3 1.30 43 0.20 Purak	ayastha
Rice hull 400 °C - 55 0.93 59 0.05 et al.	(2016)
Peanut straw 500 °C 10.86 48.5 1.51 32 0.95	
Rice husk 800°C 0.044 0.670 0.164 0.084 0.017 29 - 29 22 - Ender	s et al.
Soybean 500°C 0.056 3.779 1.565 1.171 0.112 28 - 699 58 - (2012 Woods	)
Bamboo chip 600°C 9.59 81.2 4.55 18 Mand	al et al.

Eucalyptus bark Spruce and pine chips	600°C 550- 600°C	9.37 10.8	79.1 87.8	4.20 0.62	19 142	0.001	3.23	- 4.44	- 0.72	- 0.019	- 470	- 10	- 7190	- 2570	- -	(2017) Tammeorg et
Hazelnut	400 °C	6.38	87.6	0.17	510	0.0298	0.429	0.282	0.0554	0.016	10	-	29	13	-	Enders et al. $(2012)$
Teak and Rose wood	300-400 °C	7.5	87.0	0.31	281	0.0048	0.12	0.044	0.036	Q						(2012) Asai et al.
Eucalyptus deglupta	C	7.0	82.4	0.573	144	0.6	-	-	-	-	-	-	-	-	-	Rondon et al.
Eucalyptus camaldulensis L.,	800°C	8.92	81.50			0.086	0.781	1.042	0.059				0.229			(2007) Butnan et al. (2015)
Oak	400 °C	4.58	78.8	0.17	468	0.0005	0.147	0.106	0.0061	0.008	33	-	169	15	-	Enders et al. (2012)
Douglas-fir wood pellets	500°C	7.2	78.2	0.13	602	0.022	0.10	0.20	0.03	0.017	29.1	3.1	250	93.3		Streubel et al. $(2011)$
Pine	400°C	4.6	76.3	0.1	763	0.0035	0.037	0.225	0.048	0.010	66	-	1166	258	_	()
Wood chips	400- 450°C	10.9	74.8	0.15	499	0.04	0.23	0.59	0.13	0.03	-	-	4200	-	-	Saarnio et al., (2013)
Cooking wood	500- 700°C	9.20	72.9	0.76	121	0.0030	0.046	0.033	0.0048	-	-	-	-	-	-	Major et al. $(2012)$
Douglas-fir wood bark	500°C	7.6	72.7	0.35	208	0.047	0.10	1.07	0.048	0.023	40.9	6.8	700	266		Streubel et al.
Yellow pine chipped	400 °C	5.96	71	0.1	710	0.017	0.18	-	-	0.01	-	-	-	-	-	White Jr. et al. (2015)
Hardwood			70.3	0.30	234	0.0278	0.000241	0.00027	-	-	-	-	-	-	-	Gaskin et al. $(2009)$
Pine chips			67.0	0.14	479	0.0235	0.000197	0.00017	-	-	-	-	-	-	-	Gaskin et al.
Eucalyptus camaldulensis L., traditional kilp	300 °C	6.52	61.86	-	-	0.05	0.51	0.541	0.043	-	-	-	0.05	-	-	(2005) Butnan et al. (2015)
Sesbaniaroxburghii	400 oC	9.0	57.7	3.50	17	-	-	-	-	-	-	-	-	-	-	Chen et al. $(2014)$
Manure																(2011)
Bull manure	600 °C	9.5*	76.0	0.8	95	0.295	3.582	0.938	0.507	0.102	193	-	311	165	-	Enders et al. $(2012)$
Anaerobic digested	500°C	9.3	65.8	2.23	30	0.76	1.17	2.40	0.70	0.30	230	163	1280	184	-	Streubel et al.
Bull manure	300 °C	8.2*	60.6	1.3	47	0.301	2.002	0.941	0.395	0.110	162	-	376	137	-	Enders et al. (2012)
				X												

Digested dairy manure	600°C	9.94	59.4	0.225	28	0.827	1.494	2.65	0.850	0.286	200	-	2356	191	-	Enders et al. (2012)
Digested dairy manure	400°C	9.22	57.7	0.242	26	0.645	1.66	2.2552	0.973	0.272	131	-	1656	145	-	Enders et al. (2012)
Dairy manure	700°C	9.9	56.7	1.51	38	1.69	2.31	4.48	2.06	0.15	423	163	44800	867	10.0	Cantrell et al. (2012)
Dairy manure	350°C	9.2	55.8	2.60	22	1.00	1.43	2.67	1.22	0.11	361	99.0	26700	525	7.8	Cantrell et al. (2012)
Paved-feedlot	350°C	9.1	53.3	3.64	15	1.14	3.20	2.27	0.76	0.45	359	91.7	22600	259	6.2	Cantrell et al. (2012)
Paved-feedlot	700°C	10.3	52.4	1.70	31	1.76	4.91	3.50	1.22	0.44	448	136	34500	388	6.3	Cantrell et al. (2012)
Swine solids	350°C	8.4	51.5	3.54	15	3.89	1.78	3.91	2.44	0.80	3181	1538	48400	1453	18.3	Cantrell et al. (2012)
Poultry litter	350°C	8.7	51.1	4.45	12	2.08	4.85	2.66	0.94	0.61	712	213	13200	640	11.0	Cantrell et al. (2012)
Turkey litter	350°C	8.0	49.3	4.07	12	2.62	4.01	4.04	0.85	0.55	690	535	27800	710	7.16	Cantrell et al. (2012)
Poultry litter	700°C	10.3	45.9	2.07	22	3.12	7.40	4.02	1.45	0.63	1010	310	18900	948	13.0	Cantrell et al. (2012)
Turkey litter	700°C	9.9	44.8	1.94	23	3.63	5.59	5.61	1.24	0.41	909	762	36500	986	10.1	Cantrell et al. (2012)
Swine solids	700°C	9.5	44.1	2.61	17	5.90	2.57	6.15	3.69	0.85	4981	2446	74800	2240	27.4	Cantrell et al. (2012)
Poultry litter	400 °C	7.7	38.3	2.0	19	0.9	1.0	2.5	0.3	-	238	57	2695	265	5	Macdonald et al. (2014)
Cow manure	500°C	9.20	33.6	0.15	22	0.814	0.005	0.042	0.034	-	-	-	-	-	-	Uzoma et al. (2011)
Poultry manure	500 °C	10.57	25.4	1.41	18	3.055	2.811	20.42	1.044	0.459	601	-	2034	566	-	Enders et al. (2012)
Poultry manure	600 °C	10.65	23.6	0.94	28	2.359	2.74	24.28	0.877	0.349	595	-	1522	466	-	Enders et al., (2012)
<i>Waste materials</i> Brush	500°C	8.4	84	0.1	840	0.013	0.087	0.756	0.044	0.011	59	-	94	142	-	Enders et al. $(2012)$
Whole tree residue	600°C	7.5**	78	0.14	557	0.009	0.055	0.140	0.040	0.004	25	3.1	2600	56	<1.2	Van Zwieten
Orchard pruning	500°C	9.8	77.8	0.91	63.5	2.33	1.39	2.5	2.87	0.048	.010	.009	.033	.008	-	Baronti et al. $(2014)$
Leave waste	500°C	9.0	60.7	1.1	55	0.207	1.084	5.455	0.361	0.103	70	-	1504	555	-	Enders et al. (2012)

Switchgrass	500°C	9.4	59.2	1.99	30	0.47	3.28	0.87	0.46	0.11	33.7	7.7	620	109		Streubel et al. (2011)
Grass waste	500°C	9.6	53.5	4.9	11	1.197	6.129	2.062	0.618	0.629	150	-	1557	360	-	Enders et al. $(2012)$
Food waste	400 °C	8.27	52.4	3.65	14	0.5007	1.456	5.174	0.534	0.083	39	-	4431	179	-	Enders et al., 2012
Paper mill waste	550°C	8.2	50.5	0.31	104	0.009	0.029	-	-	-	-	-	-	-	-	Van Zwieten et al. (2010)
Green waste	450°C	9.4	36	0.18	200	0.040	0.819	0.008	0.013							Chan et al. $(2007)$
Paper mill sludge	300 °C	-	23.4	0.22	106.2	-	-	-		0.32	-	-	-	-	-	Devi and Saroha (2015)
Paper mill sludge	300°C	7.8	21.2	0.3	71	0.083	0.278	25.81	0.243	0.031	26	-	4274	136	-	Surona (2010)
Paper mill sludge Waste water sludge	600°С 550°С	11.5 8.2	-	0.1 2.3	192	0.094 0.110	0.385 0.009	31.12 0.66	0.294 0.043	0.031 -	51 -	-	6037 -	160 -	-	Hossain et al. (2010)

\*pH measured in 1 N KCl instead of water. \*\* pH measured in CaCl<sub>2</sub>

Soil	pH and CEC as influenced b	v feedstock types.	temperature and addition rates of biochar
~ ~ ~ ~ _		,,,,,,,,, _	

Feedstock	Temperature (°C)	Application rate	Soil type		рН	CEC (cmc	ol <sup>(+)</sup> kg <sup>-1</sup> )	References
		(Mg ha <sup>-1</sup> )		Control	Treatment	Control	Treatment	
Greenwaste	450	10	Alfisol	4.5	4.75			Chan et al. (2007)
		50			5.38			
		100			5.99			
Poultry litter	550	10	Alfisol	4.5	6.66			Chan et al. (2008)
		25			7.29			
		50			7.78			
Sludge + wood chip	550	10	Ferrosol	4.2	5.93	4.03	10.5	van Zwieten at al. (2010)
			Calcarosol	7.67	7.67	31.0	29.3	
Wheat straw	350-550	10	Anthrosols	5.6	5.70			Cui et al. (2012)
		20			5.81			
		40			5.86			
Spruce + pine chips	550-600	5	Stagnosol	6.6	6.7			Tammeorg et al. (2014)
		10			6.7			
Switch grass	500	10-40	Entisol	7.2	7.9			Streubel et al. (2011)
Wood bark		10-40			8.0			
Digested fibre		10-40			8.0			
Wood pellet		10-40			7.2			
Sludge	550	10		4.0	4.86			Khan et al. (2013)
		20			5.39			
Hardwood	500	22.4	Haplocalcids	7.7	7.7			Lentz and Ippolito (2012)
Wood chip	450	25	Eutric Cambisol	6.8	6.8			Quilliam et al.(2013)
		50			6.8			
Mix wood chips	525	90	Planosol	5.3	6.9	75.1	101.1	Kloss et al. (2014)
Wheat straw					6.5		94.0	
Vinevard pruning					6.6		96.5	
Canola straw	350	4	Acrisol	3.99	4.7	9.1	11.4	Yuan et al. (2011b)
Rice straw					4.5		10.7	
Sovbean straw					52		10.6	
Soj obuli biluti					2.2			

							L	
Pea straw					5.0		10.5	
Wood chip	<550	72	Chernozem	7.4	7.4	201	208	Karer et al. (2013)
			Cambisol	6.3	6.7	187	214	
Oak + Hickory		5	Hapludolls	6.4	6.4	17.1	19.8	Laird et al. (2010b)
		10			6.9		20.7	
		20			7.1		20.8	
Cow manure	500	10		6.40	7.1	0.8	0.9	Uzoma et al. (2011)
		15			7.34		1.2	
		20			8.0		1.3	
Poultry litter	700	4		5.9	9.7			Novak et al. (2009)
Pecan shell	700	4			7.5			
Wheat Straw	350-550	10	Halpudept	6.5	6.75			Zhang et al. (2012)
		20			6.77			
		40			6.77			
Birch wood	500	10	Hapludalf	6.6	6.7			Sun et al. (2014)
		20			6.6			
		50			6.8			
Eucalyptus	350	6	Haplustox	5.0	5.0	108.2	118.5	Rondon et al. (2007)
		12			5.2		131.7	
		18			5.4		131.5	

Biochar	Pyrolysis temperature	Soil	Rate	Nitroger	1*						Р	K	Ca	Mg	S	Zn	Cu	Fe	Mn	Reference
				TSN	AN	MN	IM	N/D	NO <sub>3</sub> -	NH <sub>4</sub> <sup>+</sup>										
Maize	350°C	Arable	-	$\uparrow$	-	1	-	↑(N)	1	Ļ		-	-	-	-	-	-	-	-	Nelissen et al.
	550 °C		-	<b>↑</b>	-	-	-	-	Ļ	1	-	-	-	-	-	-	-	-	-	(2012)
Cotton stalks	650 °C	Sandy loam	-	-	-	-	-	↑(N)	-	1	-	-	-	-	-	-	-	-	-	Song et al. (2013)
Corn stalk	450 °C	Clayey Oxisol	-	-	-	<b>↑</b>	Î	-	-	-					1					Blum et al. $(2013)$
Rye grass	450 °C	Forest Cambisol	-	1	-	<b>↑</b>		↑(N)	Ļ	$\downarrow$										Maestrini et
Poultry manure	400 °C	Vertisol and Alfisol		-	-	-	-	↑ (D)	-	Ļ	-	-	-	-	-	-	-	-	-	Clough and Condon (2010)
Douglas fir	410 °C	-	-	-	-	<b>↑</b>	-	<u> </u>	-	-	-	-	-	-	-	-	-	-	-	Pereira et al.
wood	510 °C	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	(2015)
Hog waste wood	600 °C	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	
	700 °C	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	
Loliumperenne	350°C	-	-	-	$\boldsymbol{\wedge}$		-	↑ (N)	-	-	-	-	-	-	-	-	-	-	-	Rosa and Knicker
Oak wood	200 °C	-	-	-		↑	-	-	-	-	-	-	-	-	-	-	-	-	-	(2011) Zhang et al.
	400 °C	-	-	-		↑	-	↑ (NI)	-	-	-	-	-	-	-	-	-	-	-	(2015)
	600°C	-	-	-		No effect	-	$(\mathbf{N})$ $\uparrow$ $(\mathbf{D})$	-	-	-	-	-	-	-	-	-	-	-	
Willow (Salix viminalo)	470 °C	Flinty clay loam	-	-	-	-	ſ	-	$\downarrow$	$\downarrow$	-	-	-	-	-	-	-	-	-	Prayogo et al. (2014)
Japanese larch wood				-	-	-	ſ	-	-	-	-	-	-	-	-	-	-	-	-	Makoto et al. (2011)
(Larixgmetintt)																				

Effect of biochar on nutrient contents and nitrogen transformations in soil at different pyrolysis temperatures

														K						
Bamboo	500°C		-	-	-	-	-	-	-	↑	-	-	-	-	-	-	-	-	-	Asada et al.
( <i>Bumbusu</i> sp.)	700°C	-	-	-	-	-	-	-	-	$\downarrow$	-	-	-	-	-	-	-	-	-	(2002)
Bamboo ( <i>Bambusa</i> sp.)	600 °C	Sandy silt soils	-	-	-	-	-	-	-	$\downarrow$	-	5	-	-	-	-	-	-	-	Ding et al. (2010)
Pine chips ( <i>Pinus</i> sp.) wood	-	-	-	-	-	-	-	-	ſ	Ļ			-	-	-	-	-	-	-	Bai et al. (2015)
Eucalyptus	600 °C	Acidic Grey OrthicTenosol	5-25 Mg ha <sup>-1</sup>	-	-	Ļ	Ţ	-	-	-	-	-	-	-	-	-	-	-	-	
Sugarcane	400 °C	-	-	-	$\downarrow$	-	-	-	↓	-	-	-	-	-	-	-	-	-	-	Kameyama et
bagasse	800 °C	-	-	-	$\downarrow$	-	-	-	Ļ		-	-	-	-	-	-	-	-	-	al. (2012)
Poultry litter and wheat straw	-	Acidic ferrasol and alkaline	5 & 10 Mg	Ţ	-	-	-	-			-	-	-	-	-	-	-	-	-	Macdonald et al. (2014)
Rice husk	-	calcisol Acidic Gleysols	ha <sup>-1</sup> 41 Mg ha <sup>-1</sup>	ſ	-	-	-	7	-	-	Ţ	-	-	-	-	-	-	-	-	Haefele et al. (2011)
Lump biochar	-	Loamy soils		ſ	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Laird et al. $(2010a)$
Maize stover and wheat straw	400°C	Sandy loam alluvial soil	-	-	Ť		-	-	-	-	1	1	-	-	-	-	-	-	-	Purakayastha et al. (2015)
Charcoal	-	Base rich soils	-	-	-		-	-	Î	-	-	-	-	-	-	-	-	-	-	Borchard et al. (2014)
		Extremely acidic soils	-	-	-	- /	-	-	Ļ	-	-	-	-	-	-	-	-	-	-	()
Chicken manure	-	-	-	-	<b>↑</b>	-	-	-	-	-	1	1	-	-	-	-	-	-	-	Chan and Xu (2009)
Peanut straw	400 °C	Oxisol	-	-		-	-	-	-	-	-	-	1	<b>↑</b>	-	-	-	-	-	Jiang et al.
Rice straw			-	-	<b>-</b>	-	-	-	-	-	-	-	$\downarrow$	↓	-	-	-	-	-	(2015)
Mixed hardwood	500 °C – 575 °C	-	-	$\leq$	-	-	-	-	-	-	-	-	ſ	1	-	ſ	ſ	↓	$\downarrow$	Rogovska et al. (2014)

\*TSN: total soil nitrogen; AN: available nitrogen; MN: mineralization; IM: immobilization; N: nitrification; and D: denitrification.

## Effect of biochar on crop yield

Table 4						
Effect of biochar on crop yield						
Biochar feedstock	Application rate (t ha <sup>-1</sup> )	Soil Type	Test crop	Yield increase/decrease* (%)	Country	Reference
	30	Acidic silty	Wheat	+28.2	Italy	Vaccari et al. (2011)
Poultry manure Wheat straw	$12 \\ 10 - 40$	Alkaline alluvial Fine loamy Gleysols	Wheat Rice	+38 Neutral	China China	Lashari et al. (2013) Huang et al. (2013)
Wheat straw 450 °C	1	Acid Ferrasol	$\sim$	+19	Germany	Macdonald et al. (2014)
Wheat ( <i>Triticum aestivum</i> L.) straw (1 yr + Pyrogallol)	5 10 12			+79 +51 +60		(2011)
Wheat straw, 350-500 °C	10 20		Rice	+28 +9	China	Zhang et al. (2012)
Biochar 450 °C 1 <sup>st</sup> yr	40 25	Acidic sandy clay loam, Cambisol	Maize	+22 Neutral	UK	Jones et al. (2012)
2 <sup>nd</sup> yr 3 <sup>rd</sup> yr Wood 300 °C 1 <sup>st</sup> ur		Acidic Ovical	Maize	Neutral +78 +28	Colombia	Major et al. $(2010)$
2nd yr 3rd yr		Acture Oxisor	Iviai2C	+30 +140	Cololilola	Major et al. (2010)
Birch wood (Hordeumyulgare L.)	20	Acidic sandy loam soil	Oat	Neutral	Denmark	Sun et al. (2014)
(nor dealler angure E.)			Spring barley	+6		
Poultry litter 450 °C	50 1	Acid Ferrasol	Maize	-22-24 +24	Germany	Macdonald et al. (2014)
	5 10 1 5	Acidic Aeronosol		+101 +144 Neutral Neutral		. /

	10			21		
	10			-21		
	1, 5, 10	Alkaline Calcisol		Neutral		
		Neutral Vertisol		Neutral		
Domestic green waste biochar 550 °C	25		Wheat	+7.54	Australia	Farrel et al. (2014)
Wheat straw, 400 °C	12	Slightly alkaline sandy loam	Rice	Neutral	China	Xie et al. (2013)
		Inceptisol				× ,
Corn stover 400 °C	12	Acidic clay loam Ultisol				
Maize biochar 400 °C	20	Alkaline sandy loam Inceptisol	Maize	+3.68	India	Purakayastha (2010)
Rice biochar 400 °C	5	Alkaline sandy loam Inceptisol	Rice	+24.3	India	Bera (2014)
	5	Acidic sandy loam Alfisol	Rice	+31.3		
Eucalyptus deglupta 350 °C	90‡	Neutral clay loam Oxisol	Bean	+46	Colombia	Rondon et al. (2007)
	60‡		Bean	+39		

\*Values of yield indicated by '+' and '-' represent yield increase and decrease, respectively.

<sup>‡</sup>Biochar application rate in g kg<sup>-1</sup> soil

Eigenvalues, percentage of variation explained by the principal components, and Eigenvectors of Principal Component Analysis (PCA)

Eigenvalues and percentage of variations												
Dringing	Soil chemic	al properties			Crop yie	elds						
component	Eigenvalue	% variance	e % va (cum	riance ulative)	Eigenva	lue	% variance	% variance (cumulative)				
1	1.57	39.3	39.3		1.38		45.9	45.9				
2	1.40	35.0	74.3		0.93		30.9	76.8				
3	0.62	15.5	89.8		0.70		23.2	100				
4	0.41	10.2	100		-		-	-				
Eigenvector	'S											
Principal	Soil chemical p	roperties			(	Crop yield	ls					
component	Temp	AppRate	d_pH	d_CEC	Г	ſemp	AppRate	Yield				
1	0.27	0.64	0.43	0.58	-	0.67	0.48	0.57				
2	0.67	-0.25	0.54	-0.43	0	0.06	0.79	-0.61				
3	0.51	0.48	-0.65	-0.29	0	).74	0.37	0.56				
4	0.46	-0.54	-0.32	0.63	-		-	-				