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Biochar Phosphorus Sorption-Desorption: Potential Phosphorus Eutrophication Mitigation Strategy

Lucy W. Ngatia, Johnny M. Grace III, Daniel Moriasi, Alejandro Bolques, George K. Osei and Robert W. Taylor

Abstract

Phosphorus (P) eutrophication in the water bodies is of global concern. The role of biochar in the mitigation of (P) eutrophication has recently received substantial attention. Agriculture is the main source of P in the water bodies, as a result of excessive fertilizer and manure application. Excessive P results in excessive primary production in the water bodies, leading to anoxic conditions, growth of toxic algae blooms, altering plant species composition and biomass. Therefore, resulting in food web disruption, fish kill, toxins production and recreation areas degradation. When biochar is applied on farm, it has potential to sorb/adsorb P, immobilizing it, slowing its translocation to the water bodies. However, biochar effectiveness in P sorption is influenced by both feedstock type and pyrolysis temperature. The interaction between feedstock type and pyrolysis temperature influences the biochar pH, surface area, aromatic carbon, cation exchange capacity, surface charge density, biochar internal porosity and polar and nonpolar surface sites that promote nutrient absorption. Hence, biochar properties have a broad spectrum that influences how biochar reacts with P sorption; therefore, it is not appropriate to extrapolate observed results to different materials. Biochar that promote P sorption rather than desorption should be considered and designed to meet specific management practices.

Keywords: biochar, desorption, eutrophication, phosphorus, mitigation, sorption

1. Introduction

Phosphorus (P) eutrophication is a major problem globally. Increased aquatic primary production attributed to P over enrichment results in eutrophication [1, 2]. Aquatic systems affected by eutrophication often exhibit harmful algal blooms, which foul water intakes and waterways, disrupt food webs, fuel hypoxia and produce secondary metabolites that are toxic to water consumers and users including human, cattle, zooplankton, shellfish, domestic pets and fish [3]. Agriculture is the main pollutant of aquatic systems [4]. Overapplication of P fertilizer and manure to soil is in itself wasteful and causes P accumulation in the soil, but the transport of P to aquatic ecosystems by erosion is also causing widespread problems

of eutrophication [5–8]. Soil P exists in both organic and inorganic forms [9]; the inorganic P is highly influenced by soil pH and is mainly coupled with amorphous and crystalline forms of Fe, Al, and Ca [10]. Biochar exhibits potential to mitigate P eutrophication when applied on farm as a result of its high capacity to sorb P [1]. Biochar is a by-product of pyrolysis process, whereby in an energy-limited world, biomass is converted to energy products through pyrolysis process [11]. Biochar nutrient sorption capacity has been reported to exceed that of natural organic matter by a factor of 10–100 in some cases [12]. However, its capacity for P sorption is influenced by both feedstock type and pyrolysis temperature [13]. The interaction between feedstock type and pyrolysis temperature influences biochar characteristics resulting in wide spectrum of biochar properties that influence P sorption [1, 14]. Therefore, extrapolation of P sorption findings from one material to another is not appropriate; as a result of diversity of biochar response to P sorption, every material needs to be studied and designed to address the set P sorption objectives.

2. Forms of phosphorus

Soil P exists as either organic or inorganic compounds that differ significantly in their biological availability in the soil environment [9]. Phosphorus goes through different geochemical processes in soil which include adsorption, solubilization, precipitation and complexation that determine its mobility and fate [15]. The inorganic P compounds mainly couple with amorphous and crystalline forms of Fe, Al, and Ca [10] and are highly influenced by soil acidity and alkalinity [1]. Soil acidity and alkalinity influence the impact of solubilization, complexation, adsorption and precipitation on P retention and release. In acidic soils P is fixed by sorption to oxides and hydroxides of Al and Fe through formation of insoluble Al and Fe phosphates by ligand exchange and precipitation reactions [16, 17]. In alkaline soils, P is made unavailable due to formation of metal complexes such as Mg-P and Ca-P [18, 19]. The organic P in most soils is dominated by a mixture of phosphate monoesters (e.g., inositol phosphates and mononucleotides) and phosphate diesters (mainly phospholipids and nucleic acids), with smaller amounts of phosphonates (compounds with a direct carbon-phosphorus bond) and organic polyphosphates (e.g., adenosine triphosphate) [20]. Plants can acquire P from organic compounds through various mechanisms; some of the mechanisms allow plants to utilize organic P as efficiently as inorganic phosphate [21, 22]. Different environmental conditions influence availability and sorption of P, for example anaerobic condition leads to the release of P resulting from reduction of ferric to ferrous iron [23]. The presence of sulfate could lead to reaction of ferric iron with sulfate and sulfide to form ferrous iron and iron sulfide resulting in the release of P [24]. Increased temperature can reduce adsorption of P by mineral complexes in the sediment [25]. Other physicochemical processes affecting the release of P from the sediment include redox, temperature, reservoir hydrology, pH potential and environmental conditions [26]. These processes are further complicated by the influence of biological processes, for example mineralization, leading to a complex system regulating the release of P across sediment water interface [26]. Understanding of P retention and release mechanism enhances effective management of P enhancing crop production and promoting sustainability of soil and water quality [11].

3. Agriculture: the major source of phosphorus to water bodies

Increasing human population calls for increased food production. Increased food production requires increased fertilizer application which includes P fertilizer

(**Figure 1**) [27]. Today agriculture is heavily dependent on P derived from phosphate rock. Phosphorus is a nonrenewable resource and it is expected that economically mineable P reserves will be exhausted within 50–100 years (**Figure 2**) [27]. Crop and livestock production systems are the major cause of human alteration of the global P cycles [28]. The major source of P input to water bodies is the excessive application of fertilizer or manure on farm which causes P accumulation in soils [5]. Excess P or poor-timed application could mobilize P through runoff, negatively impacting water quality of water bodies and causing eutrophication [29, 30].
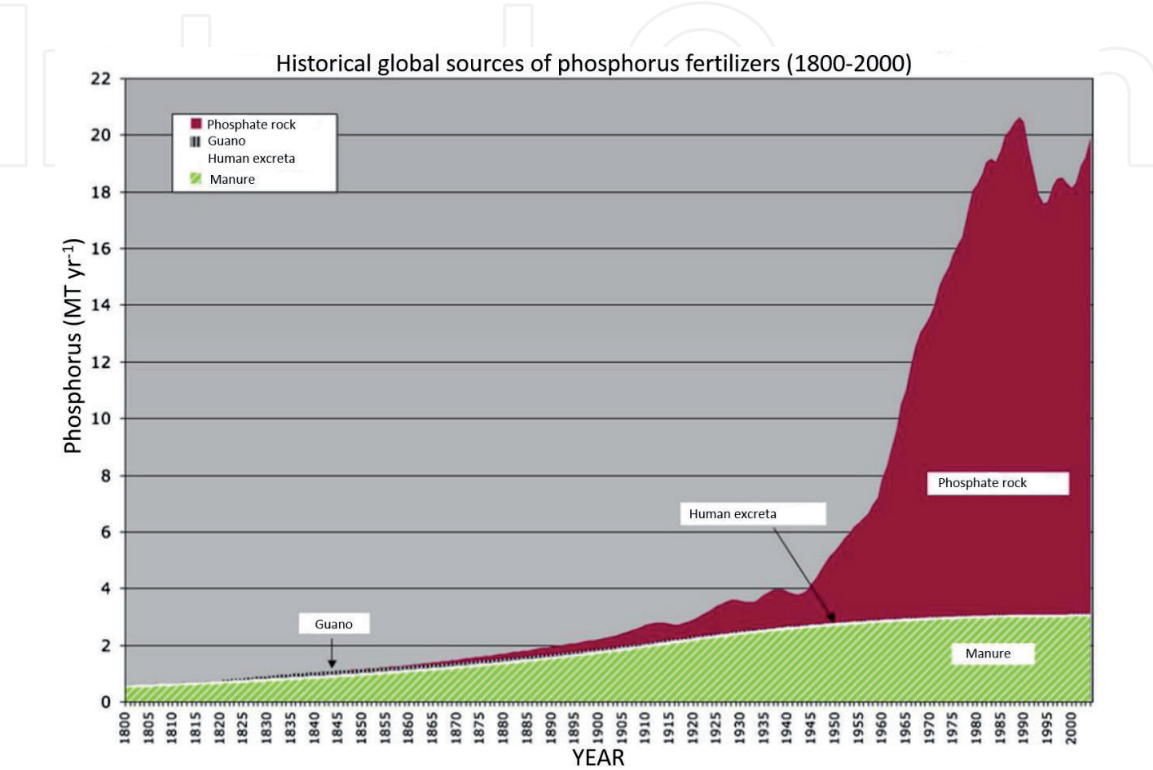

Figure 1.
Historical sources of phosphorus for use as fertilizers, including manure, human excreta, guano and phosphate rock (1800–2000). Modified from [27].
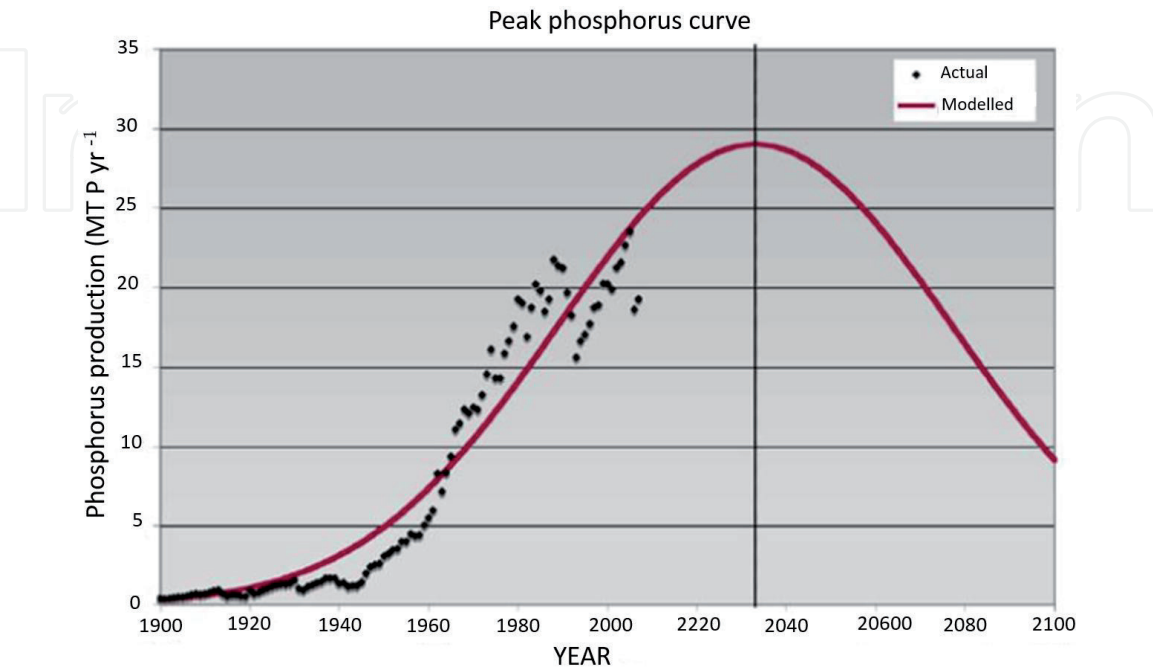

Figure 2.
Indicative peak phosphorus curve, illustrating that, global phosphorus reserves are likely to peak after which production will be significantly reduce. Modified from [27].

3

In many cases, P enters aquatic ecosystems sorbed to soil particles that are eroded into rivers, lakes and streams; any factor elevating soil P concentration or accelerating soil erosion potentially increase P runoff to aquatic system [31, 32]. Mobilization of P involves chemical, biochemical and biological processes. The processes are grouped into detachment or solubilization mechanisms and are defined by the physical size of the P compounds that are mobilized [33]. Potential for solubilization increases with increasing concentrations for extractable P. Depending on site conditions, diffuse P transport occurs as particulate or dissolved P in overland flow, drainage, channelized surface runoff or groundwater [34].

4. Phosphorus sorption is dependent on biochar properties

Biochar exhibits variable properties which are related to its formation; biochar properties are mainly influenced by method of pyrolysis, temperature of pyrolysis, feedstock type, particle size, pyrolysis retention time and furnace oxygen level [35–38]. Biochar has been reported to increase soil pH and cation exchange capacity (**Figure 3**) [1, 39]. Biochars exhibit high surface charge density, and CEC values up to 112 cmolc kg^{-1} have been observed [40]. The high surface charge density allows biochar to retain cations by cation exchange, whereas biochar internal porosity, high surface area and presence of both polar and non-polar surfaces sites promote absorption of nutrient [41]. Biochar is also reported to contain essential nutrients [41, 42] that could be retained and slowly released over time [43, 44].

As a result of biochar variable properties, the P sorption findings by different studies are inconsistent; some previous studies indicated no increase in P sorption
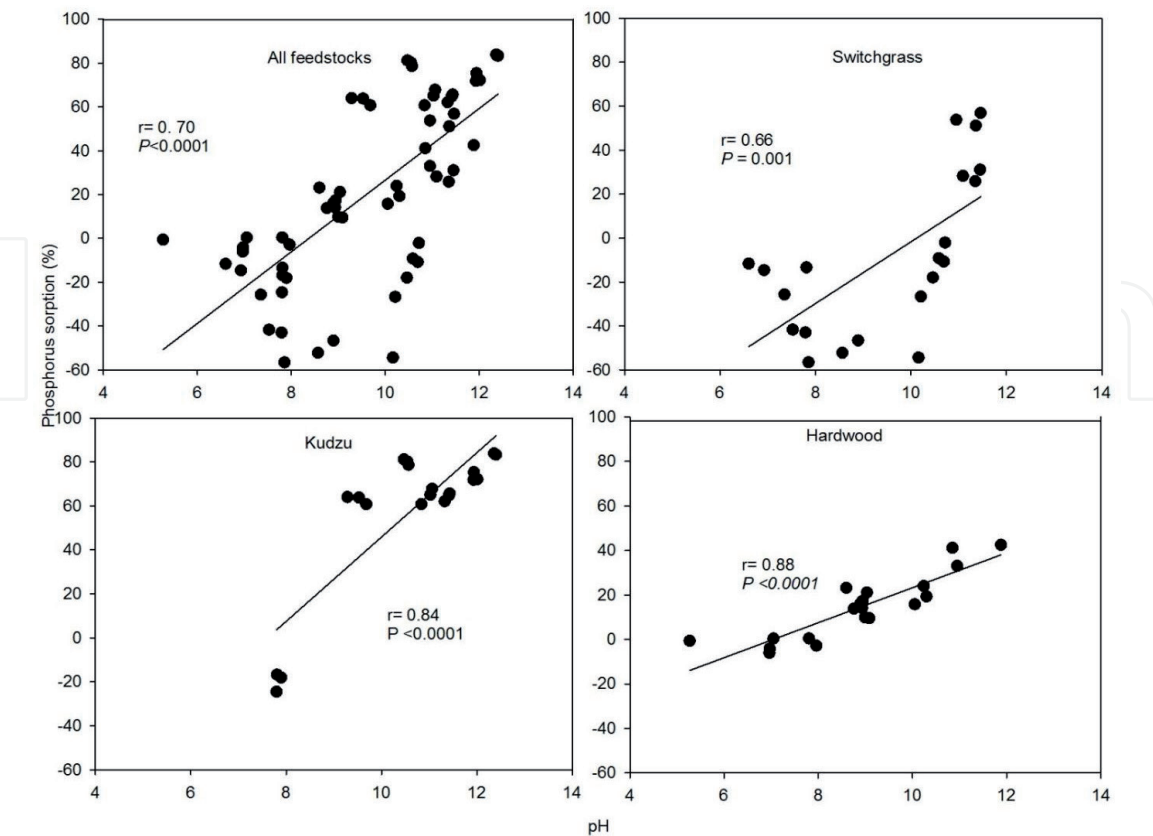

Figure 3.
Relationship between biochar phosphorus sorption and pH for all feedstocks, switchgrass, kudzu and Chinese tallow. Modified from [1].

of the sandy and clayey soils after addition of biochar [45]. There was no P sorption observed with corn biochar produced at 350 and 550°C pyrolysis temperatures [46]. Biochar produced from sugarcane bagasse, peanut hull, Brazilian pepper wood and bamboo at 200, 450 and 600°C did not indicate any clear trend in phosphorus sorption [47]. However, other studies indicated reduction of P leaching after biochar application [41, 48]. Further, biochar addition reduced P leaching after manure addition and in green roof discharge water [41, 49]. Application of 2% biochar to agricultural soil amended with swine manure resulted in reduction of P leaching by 69% [41]. Addition of 2% pecan shell biochar to loamy soil reduced P leachate by 40% [50]. Orange peel pyrolyzed at between 250 and 700°C improved P sorption by 8–83% [51]. [1] indicated that biochar pyrolyzed from kudzu and Chinese tallow at 300–700°C temperature exhibited increased P sorption; when switchgrass was pyrolyzed at 300–500°C, it exhibited P desorption, but when pyrolyzed at 500–700°C temperature, it exhibited P sorption, clearly demonstrating that feedstock type and pyrolysis temperature are major determinant of P sorption capacity (**Figures 4** and **5**).

In [1], it is also demonstrated that increasing temperature resulted in loss of O-alkyl carbon and accumulation of aromatic carbon that favored P sorption (**Figure 6**). This variability in biochar capacity to sorb P suggests that understanding each biochar type is important to ensure appropriate application to meet target objectives.
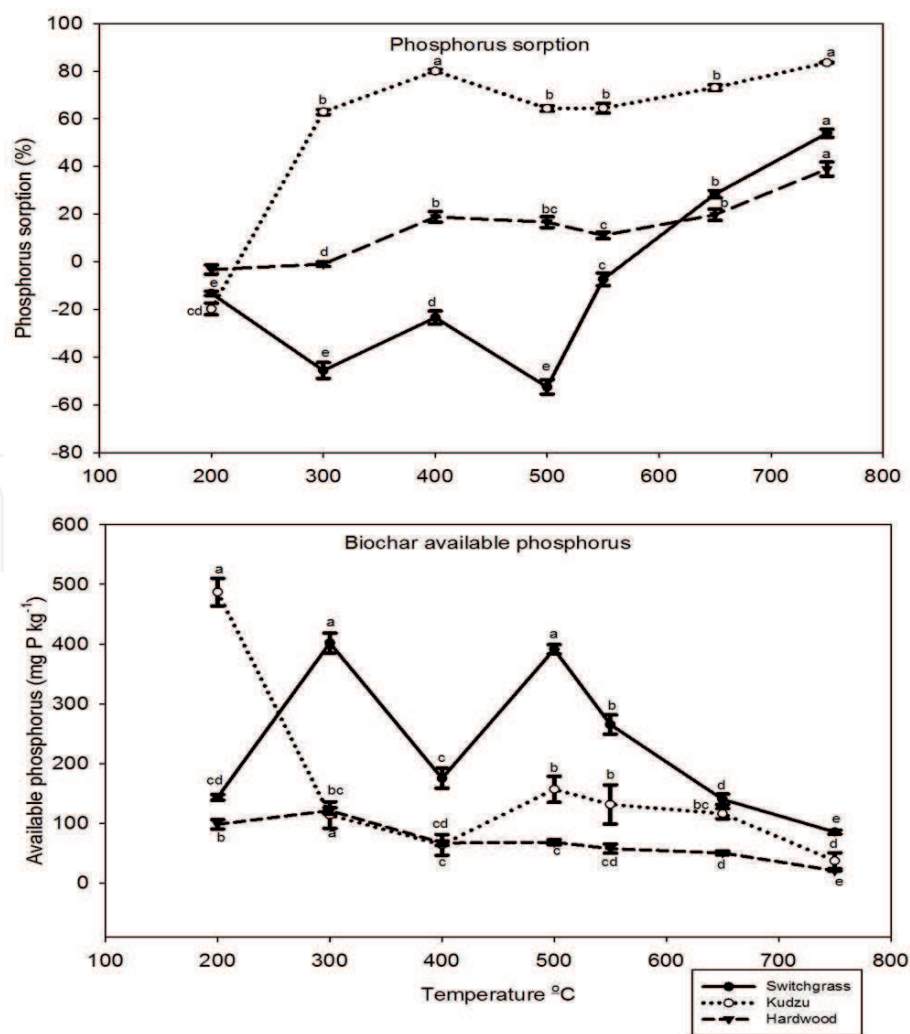

Figure 4.
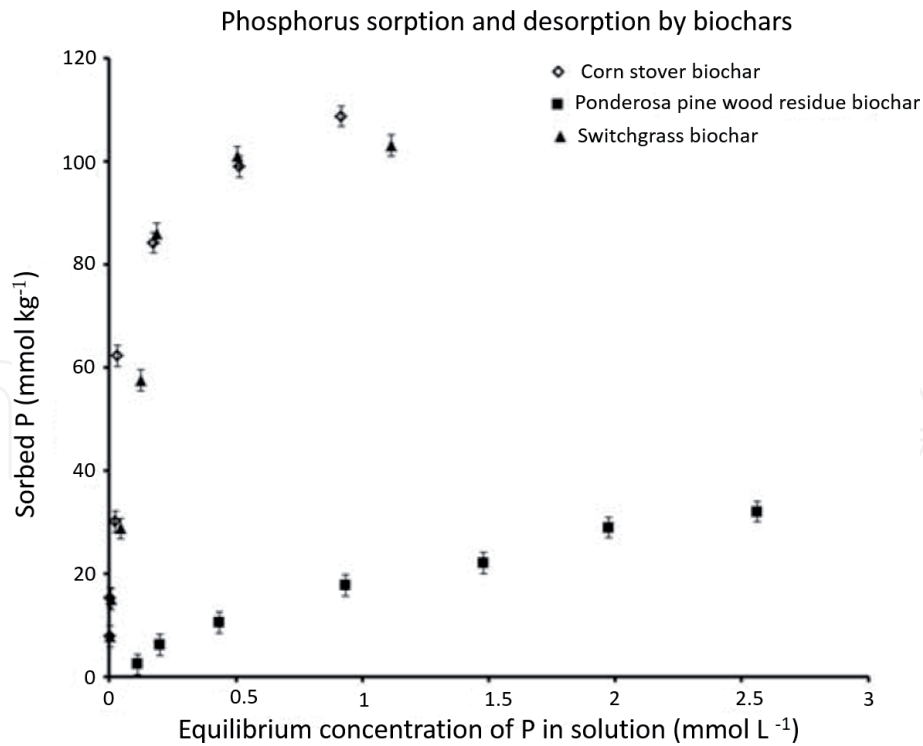*Biochar phosphorus adsorption; Modified from [1].*

Figure 5.
Phosphorus sorption by corn stover, Ponderosa pine wood residue, and switchgrass biochars. Each data point is the mean of four replications with standard error. Modified from [11].
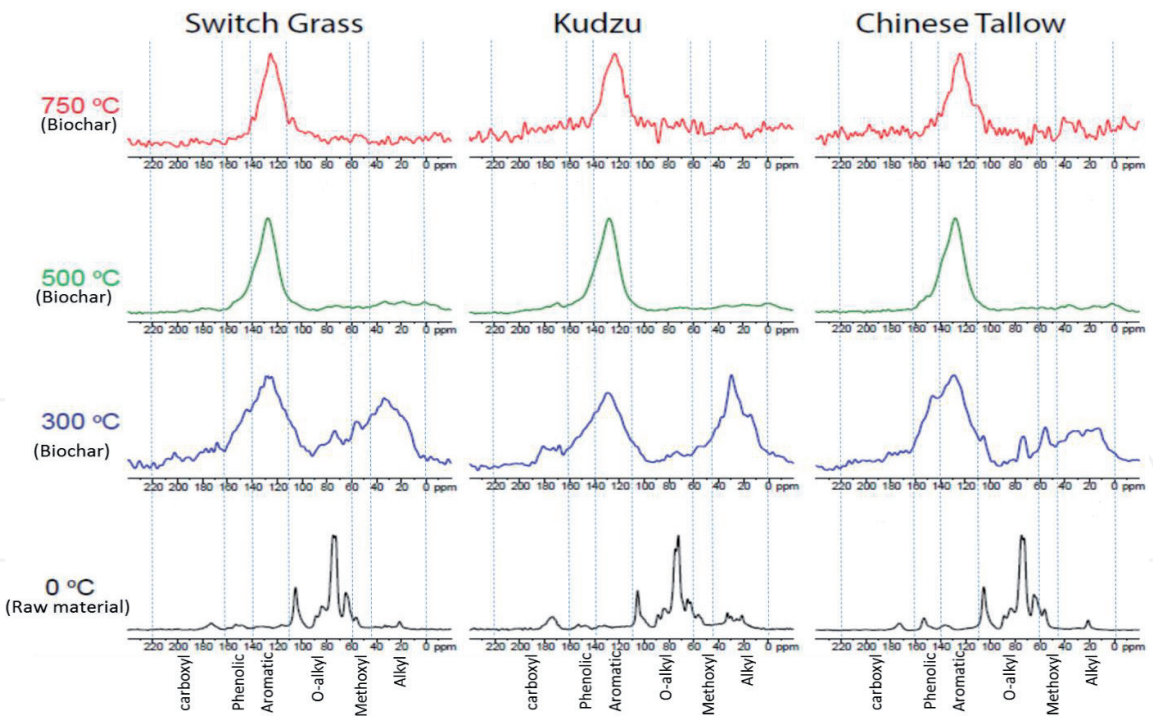

Figure 6.
Biochar carbon functional groups as determined by Nuclear Magnetic Resonance (NMR); modified from [1].

5. Biochar pH influence phosphorus sorption–desorption

The influence of the changes in pH after biochar application seems to vary between different studies. Biochar application reduces soil acidity altering P complexity with metals such as Al^{3+}, Fe^{3+} and Ca^{2+} affecting P availability, sorption and desorption (**Figure 3**) [13, 52]. As a result of higher alkalinity, biochars from legume plants increase pH much compared to biochars from non-legume plants [52].
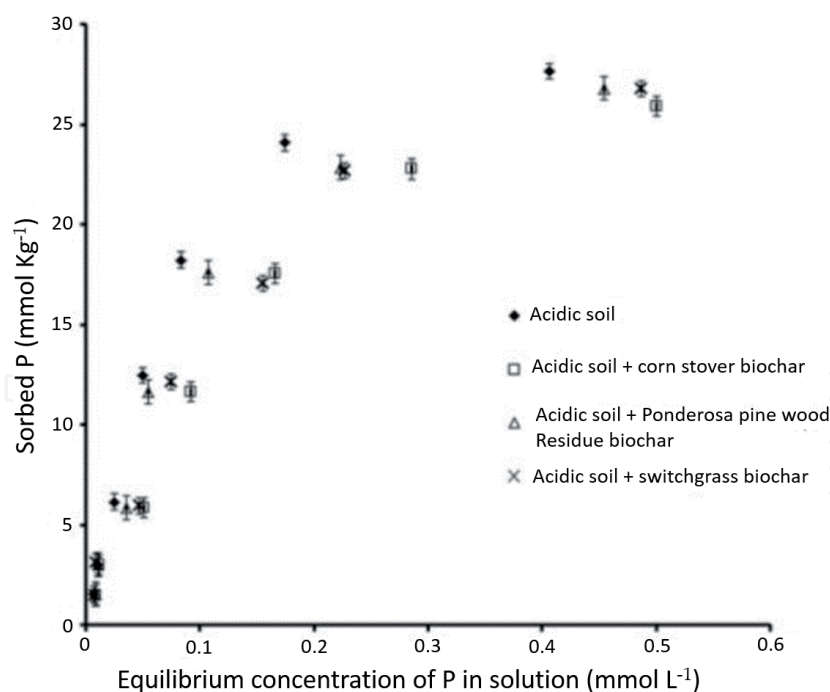
Figure 7.
P sorption by acidic soil and acidic soil (Grummit series) incubated with corn stover, Ponderosa pine wood residue or switchgrass biochars at 4 g/kg soil for 30 days. Each data point is the mean of four replications with standard error. Modified from [11].

Biochar has potential to adsorb cations such as Al^{3+}, Fe^{3+} and Ca^{2+}, which can lead to delayed P adsorption or precipitation; in addition organic molecules could sorb onto biochar reducing its capacity to chelate with Al^{3+}, Fe^{3+} and Ca^{2+} in soil (**Figure 7**) [53]. Ref. [53] reported that P sorption was increased in acidic soil but decreased in alkaline soil, and attributed increased P sorption after biochar addition to Ca induced P sorption/precipitation and also reported that P sorption was less affected by Fe and Al oxides. In contrast, incorporation of 4% biochar into acidic soil reduced the P sorption and increased availability of sorbed P, whereas application of alkaline biochars to calcareous soil increased P sorption significantly and decreased availability of sorbed P [11]. The increase in soil pH reportedly enhances the solubility of P [54] but, in contrast [1], demonstrated that addition of biochar with high pH, Ca concentration and aromatic C reduced P solubility (**Figures 3–5**). Ref. [55] indicated that colloidal and nano-sized MgO (periclase) particles on the biochar surface played the key role in providing adsorption sites for aqueous phosphate [55]. In addition, initial solution pH and coexisting anions have potential to affect adsorption of P on biochar.

6. Feedstock/biomass type and pyrolysis temperature influence phosphorus sorption

There have been diverse findings on the effect of biochar on P sorption, and in some studies, biochar application promoted availability and uptake of P as a result of biochar high anion exchange capacity; reduction of availability of Al and Fe in soil resulted in less P fixation (**Figure 8**) [50, 56]. Biochar feedstock and pyrolysis temperature affect its chemical composition and surface characteristics influencing biochar P sorption and desorption capacity [1, 11, 13]. Biochar produced from different biomass often has very different chemical characteristics and as a result influences the P sorption capacity of biochar [1, 11]. In [1], it is reported that corn stover biochar (79%) had greater sorption followed by switchgrass biochar (76%),
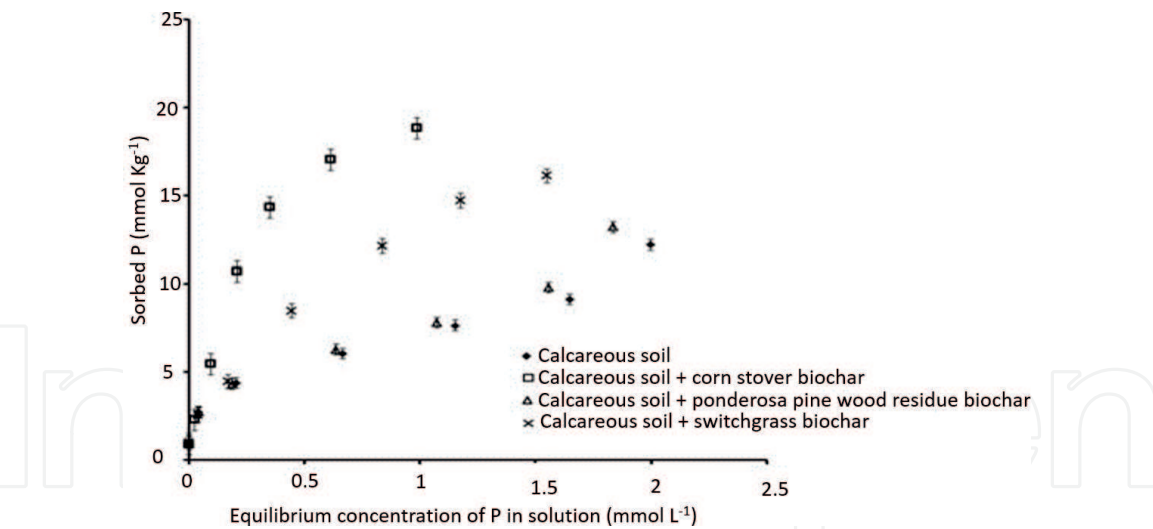
Figure 8.
P sorption calcareous soil (Langhei series) and calcareous soil incubated with corn stover, Ponderosa pine wood residue, and switchgrass biochars at 40 g/kg soil for 30 days. Each data point is the mean of four replications with standard error. Modified from [11].

Temperature	200°C	300°C	400°C	500°C	550°C	650°C	750°C	*P*-value
Switchgrass								
BC recovery (%)	78.0±1.5[a]	46.2±1.1[b]	31.7±1.3[c]	35.4±2.0[c]	24.9±0.3[d]	24.1±0.2[d]	22.8±0.2[d]	<0.0001
pH	7.1±0.4[b]	8.0±0.3[b]	9.3±1.0[ab]	9.0±0.7[ab]	10.7±0.04[a]	11.3±0.1[a]	11.3±0.1[a]	0.0001
Kudzu								
BC recovery (%)	74.0±2.3[a]	38.8±0.2[b]	29.8±2.0[c]	26.0±1.1[cd]	26.9±0.5[cd]	24.6±0.1[cd]	23.4±0.2[d]	<0.0001
pH	7.8±0.03[e]	9.5±0.1[d]	10.5±0.03[c]	11.3±0.1[b]	11.1±0.2b	12.0±0.03[a]	12.4±0.01[a]	<0.0001
Chinese Tallow								
BC recovery (%)	80.0±0.4[a]	36.5±2.6[b]	23.7±0.3[c]	22.2±0.3[cd]	20.6±0.9[cd]	20.8±0.8[cd]	17.5±0.6[d]	<0.0001
pH	7.0±0.03[c]	7.0±0.9[c]	8.8±0.1[b]	8.9±0.05[b]	8.9±0.1[b]	10.2±0.1[ab]	11.2±0.3[a]	<0.0001

Data indicate mean ± SEM (standard error of mean) between temperatures. Different letters superscript along the row indicate Tukey HSD significant difference between means of biochar recovery and pH under different temperatures. Modified from [1].

Table 1.
Biochar recovery and pH.

while Ponderosa pine wood residue biochar (31%) exhibited the lowest biochar sorption. Increasing biochar pyrolysis temperature leads to loss of the volatile compounds and increased aromatic carbon, elevated pH, biochar yield decreases (**Table 1**), increased surface area and decreased surface functional groups that provide exchange capacity (**Figures 4** and **5**) [1, 14]. Beet tailing biochar pyrolyzed at 600°C adsorbed P; the adsorption was suggested to have occurred due to binding sites contained in colloidal and nano-sized MGO particles on the biochar surface [55]. [57] indicated that similar to P sorption, desorption is also influenced by feedstock, for example Inga exhibited less sorption of P compared to Lacre and Embauba feedstocks but also desorbed less P (**Figures 9** and **10**) [57].
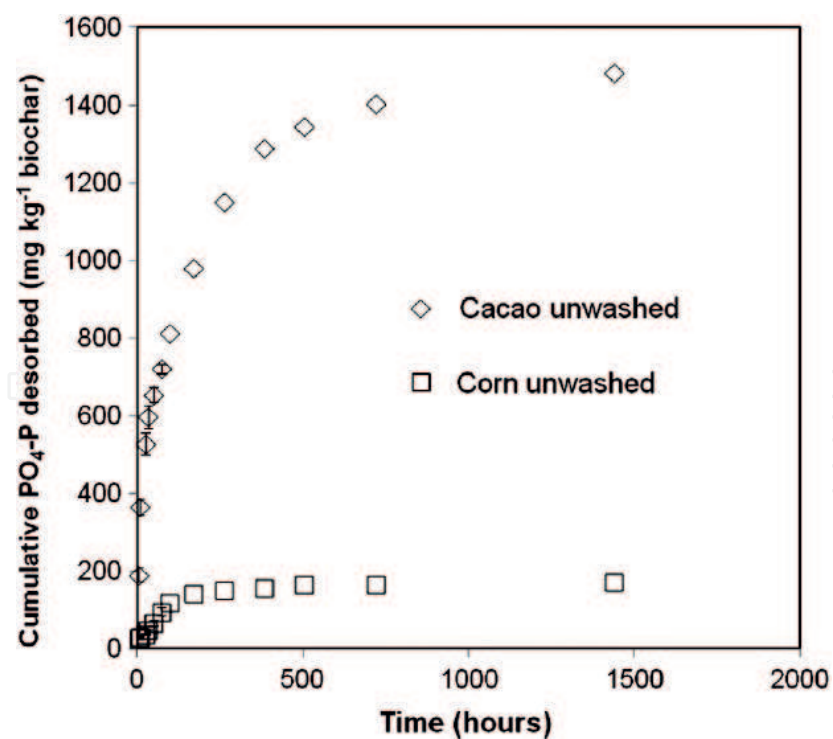
Figure 9.
Desorption of PO⁴–P from washed biochars plotted as the cumulative fraction desorbed. Modified from [58].
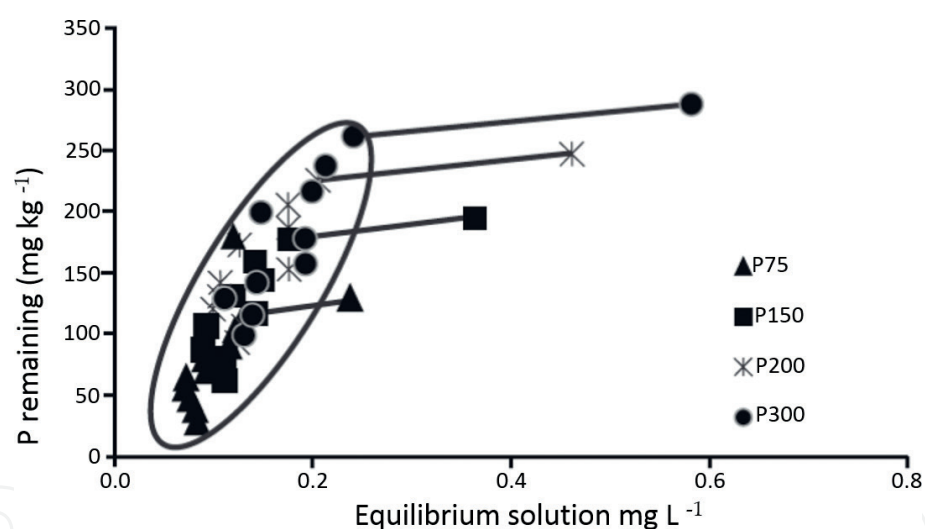

Figure 10.
Phosphorus desorption curve data for the sequential desorption of P from a degraded tropical soil with biochar added. The points represent desorption of P from the soil/biochar complex after the addition of 75, 150, 200 and 300 mg P/kg. The encircled area represents a uniform desorption curve common to all treatments with a Kd between solution concentrations of 0.1 and 0.2 mg/L of approximately 1230 L/kg. Modified from [57].

Therefore, P sorption–desorption varies between feedstock type and pyrolysis temperature levels, providing a possibility of designing biochars for specific soil management objectives (**Figures 4**, **5** and **10**) [57].

7. Biochar potential to mitigate phosphorus eutrophication

Biochar has potential to mitigate P eutrophication in the water bodies through its application in the farm. However, it is clear that biochar P sorption capacity is feedstock specific and is highly influenced by pyrolysis temperature [1]. Therefore,

it is important to understand the interaction between feedstock type and pyrolysis temperature and how they influence biochar acidity/alkalinity, surface area, aromatic carbon, cation exchange capacity, surface charge density, biochar internal porosity and presence of both polar and non-polar surfaces sites that promote nutrient absorption [1, 13, 39, 41]. Biochar that promotes P sorption rather than release of P should be considered for P eutrophication mitigation, and biochar should be designed to meet specific management practices [57]. When applying biochar on farm, it is also important to consider the erodibility of biochar to water bodies; P is easily translocated to water bodies as particulate P [32, 34]. Therefore consideration of influence of biochar on erosion is important, for example in conditions where biochar reduces soil erosion, it results in reduced particulate P losses [59].

8. Conclusion

Biochar has potential to mitigate P eutrophication in the water bodies through biochar application on farm. However, biochar exhibits broad spectrum of properties which are mainly influenced by feedstock type and pyrolysis temperature and as a result influences P sorption. Some biochars have exhibited P sorption while others exhibited P desorption. Carbon composition of biochar and pH values of biochar and soils are major drivers of P sorption. It is not appropriate to extrapolate any single study findings to any other material as a result of the wide diversity in terms of biochar influence on P sorption. Therefore every material needs to be evaluated and its potential for P sorption determined. The usefulness of biochar on P sorption is dependent on its characteristics; to mitigate P eutrophication, employment of biochar with high P sorption is important.

Acknowledgements

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