Biochar: a potential route for recycling of phosphorus in agricultural residues

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Abstract

Phosphorus (P) is a finite and dwindling resource, while an enormous amount of P flows to agricultural residues with increasing agricultural production. Therefore, the recycling of P in agricultural residues is critical for P sustainability in agricultural systems, which is dominated by the route of direct land application. Biochar production from agricultural residues and its subsequent land application have been suggested as solutions for waste biomass disposal, carbon sequestration, soil amendment/remediation, and crop production promotion. However, little attention has been paid to the contrasting effects of the land application of biochar vs. agricultural residues on the recycling of P accumulated in agricultural residues. Phosphorus in agricultural residues can be retained and transformed into stable forms of P in the resulting biochar. Thus, compared to agricultural residues, biochar provides lower amounts of labile P and releases its P more slowly while providing a long-lasting P source, and the loss potential of P from biochar is reduced by low mobility of its P, indicating that biochar-based P recycling route could substantially promote P recycling by acting as sustainable P source and diminishing the loss of P applied to soil.

Keywords: agricultural residues, biochar, biochar-based phosphorus recycling, phosphorus loss potential, phosphorus recycling, phosphorus sustainability

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Introduction

Phosphorus (P) is a finite and dwindling resource (Elser & Bennett, 2011). Most mined P is used as fertilizer (Cordell et al., 2009) to enhance food production and support earth’s rapidly growing population (Metson et al., 2014), which result in that agricultural production is the largest driver in the alteration of the global P cycle (Bouwman et al., 2013). With increasing agricultural production, the most important flow of P has been evolved into a one-way movement from fertilizer to crops to livestock (Cordell et al., 2009; Bouwman et al., 2013; Metson et al., 2014), causing P accumulation in agricultural residues (i.e., crop residues and manure) (Cordell et al., 2009). Therefore, the recycling of P in agricultural residues is essential for the sustainability of agriculture and food security (Cordell et al., 2009).

Sustainable P recycling in agricultural residues requires a maximal utilization by crops and minimal loss of P applied from agricultural residues. However, direct land application of agricultural residues is the dominant route for recycling of P in agricultural residues. The high mobility of P in agricultural residues not only impairs the efficiency of P recycling, but also results in serious P loss to the surrounding environment (Giles et al., 2015). Thus, the control of P mobility in agricultural residues prior to land application will probably enhance the efficiency of P recycling in agricultural systems, reduce P loss potential, and further favor sustainable availability of P in agricultural systems.

The production of biochar, combined with its application in soils, has been suggested as promising strategies for the disposal of waste biomass (Jeffery et al., 2015), for mitigating climate change (Cusack et al., 2014; Smith, 2016), and for simultaneously amending soil (Gul et al., 2015; Puga et al., 2015) and enhancing crop production (Dickinson et al., 2015). However, little attention has been paid to the contrasting effects of the land application of biochar vs. agricultural residues on the recycling of P originally accumulated in agricultural residues (Withers et al., 2015). Most fractions of P in biomass are...
converted to stable P during the carbonization of biomass (Uchimiya & Hiradate, 2014; Dai et al., 2015), which can reduce the mobility of P. Therefore, compared to agricultural residues-based P recycling route, the biochar production and its storage in agricultural soil may have an effect on recycling of P originally accumulated in agricultural residues.

Here, we aimed to elucidate the contrasting effects of agricultural residues-based and biochar-based P recycling routes on the recycling of P in agricultural residues and then to apply this information to recycle agricultural residues as biochar to improve sustainable P recycling. First, we estimate the P amount in main agricultural residues and agricultural residues with maximum availability for biochar production. Then, we synthesize current findings related to the forms of P in biochar. Next, we analyze the input of different P species during the land application of agricultural residues and biochar. In particular, we compare the P release process and the potential loss of P applied from agricultural residues and biochar to soil. Finally, we suggest biochar as a potential route for recycling of P in agricultural residues.

**Phosphorus in agricultural residues and their biochar**

**Phosphorus budgets in agricultural residues**

Crop residues with very small amount (e.g., oat straw), with high water content (e.g., potato residue), or without high global significance are excluded from this analysis (Lal, 2005). Thus, in this analysis, cereal residues include residues from rice, wheat, maize, barley, and sorghum; sugar crop residues only include sugarcane residue; oil crop residues only include rapeseed straw, and legume residues only include soybean straw. Considering the amount of the selected crop residues (Table S1) (Lal, 2005), crop residues are divided into five categories (rice, wheat, maize, sugarcane, and other selected crops with relatively lower amount). Despite the P content in crop residues is typically <0.1% (Table S1), the amount of P in crop residues totals 4.35 Tg P y⁻¹ (Fig. 1) because of the enormous amount of crop residues humans produce (3519 Tg DM y⁻¹, Table S1) (Lal, 2005; Woolf et al., 2010). The global dominant crops (i.e., rice, wheat, and maize) account for ~53% of the total amount (Fig. 1). Even though the amount of manure produced globally (1794 Tg DM y⁻¹, Table S2) represents about 51% of crop residues (Woolf et al., 2010), the amount of P in manure is about four times higher than that in crop residues (Fig. 1). Thus, the sustainability of maintaining adequate P in agricultural systems is dominated by the effects of manure production (Bouwman et al., 2013).

The P amounts in crop residues and manures with maximum potential for biochar production are 2.35 and 6.94 Tg P y⁻¹, which account for ~54% and 41% of the P amounts in crop residues and manure, respectively (Fig. 1). Cattle are the largest driver of the global P flow into manure, which accounts for nearly 75% of the P in total manure (Fig. 1). However, cattle are not mainly held in housing or confined areas, so the availability of cattle manure for thermal treatment and subsequent agricultural application is lower than that of swine and poultry (Hoogwijk et al., 2003). Therefore, the maximum amount of P in cattle manure available for biochar is only 25% of the total P in cattle manure. In comparison, the maximum amount of P in swine and poultry manure available for biochar is 90% of the total P in swine and poultry manure (Fig. 1).

**Phosphorus forms in agricultural residues and biochar**

Most P in crop residues is in the form of organic P (OP). The P in poultry manure is dominated by OP in the form of phosphate monoesters (almost entirely as phytic acid). In cattle and swine manure, P is dominated by inorganic P (IP), with a small proportion of OP. For example, Turner & Leytem (2004) reported that OP, readily soluble IP, P bound to Fe and Al, and P bound to Ca and Mg accounted for 58%, 30%, 2%, and 7% of the total P (TP) in broiler litter, respectively. While IP accounted for more than 79% of the TP in cattle and

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Fig. 1 Phosphorus budgets in each agricultural residue and the agricultural residue with maximum potential for biochar production. The P contents in crop residues and manure are obtained from Preston (2013) and Muller (1980), respectively (Tables S1 and S2 in Supporting Information). The amount of rice hulls is directly collected from Woolf et al. (2010) (Table S1), and the amounts of other selected crop residues (except maize cob) are directly obtained from Lal (2005) (Table S1). The amount of maize cob is calculated according to the ratio of cob to stover [0.16, collected from Halvorson and Johnson (2009)].

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swine manure, and most parts of the IP are readily soluble, a small proportion of IP is held as P bound to Fe, Al, Ca, and Mg (Turner & Leytem, 2004).

Nearly all the P in agricultural residues can be retained during the process of carbonization (Azuara et al., 2013). Biochar is much richer in P content than agricultural residues. Moreover, creating biochar modifies the forms of P in biomass significantly (Fig. 2) (Qian & Jiang, 2014; Dai et al., 2015), leading to a remarkable reduction of P solubility compared to that in uncharred biomass (Wu et al., 2012). The presence of multivalent metal cations, such as Al, Ca, Mg, and Fe, is responsible for the formation of insoluble phosphate in the resulting biochar (Fig. 2) (Uchimiya et al., 2015). The OP will be transformed into IP during the decomposition of organic matter under thermal treatment (Qian & Jiang, 2014). Soluble P will be immobilized as insoluble Al, Fe-P (e.g., AlPO₄), insoluble Ca, Mg-P (e.g., apatite), or other kinds of P-containing minerals (e.g., stanfieldite), during thermal treatment (Fig. 2) (Heilmann et al., 2014; Qian & Jiang, 2014).

The environmental fate of P is highly correlated with its form and solubility. The P losses from agricultural soil are generally dominated by the solubility of P (Elliott & O’Connor, 2007; McDowell, 2012). Soluble P in surface runoff will be directly increased with increasing solubility of P from various P sources (Shigaki et al., 2007), which is immediately bio-available. While the insoluble P, including the P that is bound in compounds of Fe, Al, Ca, and Mg, is not readily available, it can provide a long term source of P for biota (McDowell, 2012). The various forms of OP also have different levels of mobility. For example, the OP bound to organic matter and containing an abundance of O-alkyl groups (e.g., phytic acid) is more labile than that bound to organic matter containing ample refractory alkyl and aromatic carbon groups (e.g., nucleic acid and phospholipid) (Hamdan et al., 2012). Hence, the production of biochar can change the fate of P by altering P forms in agricultural residues.

**Land application of agricultural residues and biochar**

A large proportion of P flows in agricultural systems and ends in manure, and land application is the predominant method for disposing of agricultural residues and recycling its nutrients (Ribaudo, 2007). This process is essential for the sustainable recycling of P in agricultural systems (Fig. 3). To highlight the different effects of agricultural residues- and biochar-based routes on recycling P in agricultural residues (Fig. 3), this subsection specifically compares P loads from manure and biochar, their P release characteristics, and loss potential of the P from these sources.

**Phosphorus loads from manure and biochar**

The TP and AP loads from cattle manure at the application rate of 1% are 156 and 124.8 kg ha⁻¹, respectively (Table 1), which are far more than the P removal capacities of crops (Sadras, 2006). In contrast, the TP and AP loads from cattle manure-derived biochar at a 1% application rate are 401.7 and 4.02 kg ha⁻¹, respectively (Table 1). Even though the TP load from biochar is twice higher than that from manure, the AP load from biochar is >30 times lower than that from manure (Table 1). The AP load from biochar at the rate of 10% is still as low as 40.2 kg ha⁻¹, which is still in the range of P removal capacities of crops (Sadras, 2006). Moreover, at the same application rate of AP, the amount of biochar applied to soil is >30 times higher than that of cattle manure (Table 1). Considering these facts, the partial immobilization of manure-derived P in biochar
prior to land application will avoid oversupply of AP, mitigate the potential loss of P and improve the ability of land to accommodate manure.

Actually, the change of AP in soil after the application of P source (e.g., chemical P fertilizer, manure and biochar) is not equivalent to the amount of AP input from P source to soil, which is controlled by the properties of P source and soil. The P content in cattle manure and its biochar is assumed as 0.8% (Muller, 1980) and 2.06% [average from the results of Cao & Harris (2010), Cantrell et al. (2012), and Liang et al. (2014)], respectively. The fractions of total P that are available in cattle manure and biochar made from this feedstock are typically set as 80% and 1%, respectively.

The application rate (1%, 5%, and 10%) is the percentage of the weight of agricultural residues or biochar to soil, assuming the average soil density of 1.3 ton per m³. The input of P and AP is calculated according to the P and AP contents in cattle manure and its biochar. The P content in cattle manure and its biochar is assumed as 0.8% (Muller, 1980) and 2.06% [average from the results of Cao & Harris (2010), Cantrell et al. (2012), and Liang et al. (2014)], respectively. The fractions of total P that are available in cattle manure and biochar made from this feedstock are typically set as 80% and 1%, respectively.

### Table 1: Input of phosphorus (P) and available phosphorus (AP) to the upper 15 cm soil layer from cattle manure and its biochar at various application rates

| Rate (%) | Cattle manure (kg P ha⁻¹) | Cattle manure biochar (kg P ha⁻¹) |
|----------|---------------------------|-----------------------------------|
|          | P    | AP  | P    | AP  |
| 1        | 156  | 124.8 | 401.7 | 4.017 |
| 5        | 780  | 624  | 2008.5 | 20.085 |
| 10       | 1560 | 1248 | 4017  | 40.17 |

The application rate (1%, 5%, and 10%) is the percentage of the weight of agricultural residues or biochar to soil, assuming the average soil density of 1.3 ton per m³. The input of P and AP is calculated according to the P and AP contents in cattle manure and its biochar. The P content in cattle manure and its biochar is assumed as 0.8% (Muller, 1980) and 2.06% [average from the results of Cao & Harris (2010), Cantrell et al. (2012), and Liang et al. (2014)], respectively. The fractions of total P that are available in cattle manure and biochar made from this feedstock are typically set as 80% and 1%, respectively.

Phosphorus in manure is normally released rapidly, while in biochar, P is released much more slowly because labile P has been transformed into Ca-P or Mg-P during thermal treatment (Christel et al., 2014; Liang et al., 2014; Wang et al., 2015). The stable P in biochar is not water extractable, yet it is proton releasable (Wang et al., 2015). For example, about 12% of the TP in dairy manure was released to water during 240 h, while only 1% of the TP in dairy manure biochar (prepared at 450 °C) was released during the same time period (Liang et al., 2014). Even though the TP in dairy manure biochar was about three times higher than that of dairy manure, the increase of soluble P in soil amended with dairy manure biochar (at an application rate of 2.5%) after 2-day incubation was about 13 times lower than that in the soil amended with dairy manure (Liang et al., 2014). With increasing incubation time, the soluble P in soil amended with dairy manure decreased significantly, while that in the soil amended with dairy manure biochar, the soluble P remained almost stable (Liang et al., 2014). Thus, P in manure can be recycled in biochar as a slow-releasing but long-lasting P source to improve the efficiency of P recycling and to reduce the need for chemical P fertilizer.

### Phosphorus release characteristics of manure and biochar

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### Loss potential of P applied from manure and biochar

The P loss potential is the risk of P loss through runoff or leaching. Compared to the loss of P applied from

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**Fig. 4** The illustration of the direct effects of biochar-based agricultural P recycling route.

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agricultural residues (especially manure), little is known about the loss potential of P applied from biochar. The loss of P is strongly related to the P source coefficient (PSC) and the total P application rate (i.e., total AP applied to soil) (Elliott & O’Connor, 2007; Borda et al., 2011). The PSC is viewed as a measure of the applied P that is susceptible to runoff or leaching; it is applied as a P risk assessment tool (Elliott & O’Connor, 2007; Shoher & Sims, 2007). According to the Pennsylvania P index (Beegle et al., 2006), all of the P contained in swine manure may be released into the soil after application as fertilizer, while 80% of the P in cattle or poultry manure can be released into soil, indicating the PSC for manure is >80%. The PSC for biochar will be much lower than that of manure due to its much lower P solubility. For example, poultry litter biochar would supply 24% of the applied P to soil (Wang et al., 2015). Therefore, the P loss potential of biochar is much lower than that of manure.

The P in biochar is resistant to loss, and, on most occasions, the application of biochar results in a reduction of P loss from soil. The P loss potential of soil can be influenced by modifying its physical, chemical, and biological properties (e.g., pH, CEC, P adsorption capacity, contents of multivalent metal cations, water-holding capacity, bulk density, structure, aggregate stability, dissolved organic matter concentration, microbial structure, and activity) (Major et al., 2015). However, in some situations, the application of biochar showed negative or neutral effects in P loss potential of soil. For example, the application of rice husk biochar to a sandy soil (Nampong soil) showed no significant effects on P loss amounts compared to that of untreated soil (Kongthod et al., 2015). The application of wood biochar to significantly increased P leaching from soil in an apple orchard (Hardie et al., 2015).

Biochar-based agricultural P recycling route

Biochar is a feasible route for recycling of P in agricultural residues. Phosphorus in agricultural residues can be recycled by direct application to nearby agricultural land, in biochar by pyrolysis or hydrothermal carbonization, in ash by incineration, and in phosphates by precipitation of anaerobic digested effluents. The least expensive disposal pathway is direct land application; however, this poses potential environmental risks (Schoumans et al., 2010). Although the production of biochar from manure is much more expensive than the production of ash, the price of biochar is higher than ash because of the versatility of biochar (Schoumans et al., 2010). Moreover, the net total cost of manure processing via biochar is similar to the production of mineral P fertilizer from manure (Schoumans et al., 2010).

Biochar-based agricultural P recycling route means recycling of P in agricultural residues by the application of biochar-derived from agricultural residues (Fig. 4). Compared to the direct application of agricultural residues, this route can decrease the amount of labile P applied to soil, while provide long-lasting P source to soil and reduce the loss of P applied to soil. In particular, in areas with intensive livestock farming that have a serious surplus of P, these two routes can make difference in the management of P derived from manure (Fig. 4). Even though beneficial outcomes of biochar production and its land application have been identified in many fields, there is still a lack of awareness related to biochar-based agricultural P recycling route (Fig. 4). The lab- and field-scale comparisons are lacking related to the transport and fate of P in agricultural residues and biochar during their soil application. These comparisons are beneficial to help researchers determine the effects of biochar-based route on recycling of P in agricultural residues. Moreover, considering the negative or neutral impacts of biochar on P availability and loss potential of soil in some situations, the specific effects of specific types of biochar on specific soil in specific region for specific cropping systems have to be investigated for positively using biochar to maintain the sustainable availability of P in agricultural systems (Major et al., 2015).

Conclusions

An enormous amount of P flows into agricultural residues (i.e., crop residues and manure), while mineral P resource is shrinking with increasing agricultural production. Therefore, the recycling of P in agricultural residues is crucial to the sustainability of P availability for agricultural production. However, because of the high mobility of P in agricultural residues, especially in manure, the direct land application of those residues may pose a threat to the environment. The sustainability of P availability in agricultural systems requires P to be recycled with maximal efficiency and minimal loss. The control of P mobility in agricultural residues prior to land application is a possible strategy that can promote the recycling of agricultural residue that generates P in agricultural systems.

Nearly, all P in agricultural residue can be retained in biochar and in a much more stable form, resulting in a reduction of P mobility. Compared to the direct application of agricultural residues, the biochar-based P recycling route can decrease the amount of labile P applied to soil, provide long-lasting P source to soil, and reduce the loss potential of P applied to soil. Therefore, we suggest biochar as a potential route for recycling of P in agricultural residues.
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Supporting Information

Additional Supporting Information may be found online in the supporting information tab for this article:

**Data S1.** Data collection and estimation of phosphorus budget in agricultural residues.
**Table S1.** The amount of different crop residues and their maximum availability for biochar production, and the P content in crop residues.
**Table S2.** The amount of different manures and their maximum availability for biochar production, and the P content in different manures.
**Table S3.** Phosphorus budgets in each agricultural residue and the agricultural residue with maximum potential for biochar production.