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Amendment of Acid Soils with Crop Residues and Biochars*[1]

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ABSTRACT

The liming potential of some crop residues and their biochars on an acid Ultisol was investigated using incubation experiments. Rice hulls showed greater liming potential than rice hull biochar, while soybean and pea straws had less liming potential than their biochars. Due to their higher alkalinity, biochars from legume materials increased soil pH much compared to biochars from non-legume materials. The alkalinity of biochars was a key factor affecting their liming potential, and the greater alkalinity of biochars led to greater reductions in soil acidity. The incorporation of biochars decreased soil exchangeable acidity and increased soil exchangeable base cations and base saturation, thus improving soil fertility.

Key Words: alkalinity, exchangeable base cations, inorganic N, liming potential, soil acidity

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INTRODUCTION

There are large areas of acid soils distributed in subtropical regions of southern China and also in subtropical areas around the world. In recent decades various anthropogenic activities have accelerated soil acidification to a great extent. Acid deposition resulting from air pollution is a major cause for increased soil acidity (Reuss and Johnson, 1986). At present, acid deposition is still a serious factor that affects soil acidification in China (Vogt *et al.*, 2006; Hu *et al.*, 2007). Soil acidification can also be accelerated by applying excessive NH_4^+ based N fertilizers (Bolan *et al.*, 1991). Under the intensive land use in China, the sharp increase in application of N fertilizer in cropping systems has greatly accelerated soil acidification (Zhang *et al.*, 2008, 2009; Guo *et al.*, 2010).

Aluminum toxicity and reduced soil fertility are two important factors limiting plant growth in acid soils. Lime is usually used to ameliorate acid soils and so increase crop yields (Adams, 1984). There have been recent observations that some plant materials including crop straws can directly neutralize soil acidity (Noble *et al.*, 1996; Yan *et al.*, 1996; Pocknee and Sumner, 1997; Tang *et al.*, 1999; Xu and Coventry, 2003), but the liming potential of these plant materials on acid soils depends on the properties of both plant materials and soils. Organic anions associated with base cations Ca, Mg, K and Na in plant materials are the main source for ash alkalinity of the materials (Yan *et al.*, 1996; Wong *et al.*, 2000; Li *et al.*, 2008). Generally, legume materials have higher ash alkalinity than non-legume materials due to the unbalanced uptake of cations and anions, and thus should have greater amelioration effects on soil acidity than non-legume materials (Wang *et al.*, 2009). However, some investigators have reported that when acid soils were incubated with legume materials, soil pH increased early in the incubation, followed by an apparent decrease later in the incubation. This was due to the nitrification of NH_4^+ ions produced during the mineralization of organic N early in the incubation (Yan *et al.*, 1996; Tang *et al.*,

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1999; Xu and Coventry, 2003; Xu *et al.*, 2006a; Yan *et al.*, 2006). Therefore, the protons from the nitrification of the NH_4^+ that was produced from mineralization of organic N after incorporation of legume materials in acid soils may somewhat offset their amelioration effect on the soils (Wang *et al.*, 2010). If the transformation of organic N from legume materials is inhibited, their liming effect on soil acidity should be increased.

Pyrolysis of crop residues (thermoconversion of biomass under anaerobic conditions) produces renewable energy and also biochar (Gaskin *et al.*, 2008). Pyrolytic biochar can be used as a soil amendment to improve soil fertility and reduce soil acidity (Steiner *et al.*, 2007; Chan *et al.*, 2008). The amelioration effects with the direct incorporation of plant materials into soils cannot last for long time due to the decomposition of the plant materials by soil microorganisms (Tang *et al.*, 1999; Xu *et al.*, 2006b). While, research indicates that biochar is recalcitrant and it may persist for hundreds of years in soils (Rebecca, 2007; Steiner *et al.*, 2008). Natural coal and coal extracts have been shown to ameliorate acid soils and improve root growth (Yazawa *et al.*, 2000). However, little information is available on the comparison between the amelioration effects of biochars and their feedstock on soil acidity, and also the effects of biochars generated from different feedstock on soil acidity. Therefore, the objectives of this study were to compare the amelioration effects of biochars and their feedstock on an acid Ultisol and to investigate the effects of incorporation of biochars from crop residues on soil pH.

MATERIALS AND METHODS

Soil and plant materials

An Ultisol collected from Jiangxi Province of southern China was used in this study. The samples were taken from the topsoil (0–10 cm), air-dried, and then ground to pass a 2-mm sieve. The soil pH was 4.54 as determined in a 1:2.5 soil:water suspension. The soil organic matter content determined using dichromate method was 25.7 g kg^{-1}, and soil cation exchange capacity (CEC) determined with ammonium acetate method was 8.72 $cmol_c$ kg^{-1} (Pansu and Gautheyrou, 2006). Ten plant materials were used, including the non-legume materials of rice hulls and canola, wheat, rice and corn straws; and the legume materials of soybean, peanut, faba bean, pea and mung bean straws. All plant materials were obtained locally, oven-dried at 80 °C, and then ground to pass through a 0.83-mm sieve.

Preparation of biochars

The plant materials were packed tightly in ceramic pots with covers and then heated at 350 °C for 4 h in a muffle furnace to obtain biochars (Chun *et al.*, 2004). They were then cooled to room temperature, ground to powder, and passed through a 0.83-mm sieve. The pyrolysis was carried out in partial absence of oxygen.

Incubation experiments

Air-dried soil samples (350 g) were placed into plastic pots, and the ground samples of the plant materials or biochars were added at a rate of 10 or 20 g kg^{-1}, mixed thoroughly, and then wetted with deionized water to 70% of field capacity. All the pots were covered and a small hole was made to allow gas exchange but minimize moisture loss. The incubation was conducted at a constant temperature of 25 °C. Soil moisture was adjusted every 3 d throughout the experiment. The soils of 10 g were subsampled at specified intervals during the incubation to determine soil pH. At the end of the incubation, the remaining soil samples were removed from the pots, air-dried, and ground to pass a 0.3-mm sieve for determination of pH, exchangeable acidity, exchangeable base cations, ammonium nitrogen (NH_4^+-N) and nitrate. There were three replicates per treatment, and the soil sample without plant material and biochar added was also included as the control.

Analysis method

The alkalinity of the biochars was determined using a modified titration method similar to that for ash alkalinity of plant materials (Slattery *et al.*, 1991). The biochars (0.2 g) was put in 40 mL of 0.30 mol L^{-1} HCl, and titrated by a standardized solution of 0.25 mol L^{-1} NaOH to obtain their alkalinity after standing for 2 h.

The soil pH was determined in a 1:2.5 soil:water suspension using an Orion 720 pH meter with a combination electrode. The exchangeable acidity was extracted with 1.0 mol L^{-1} KCl, and then titrated with a standardized solution of 0.25 mol L^{-1} NaOH to pH 7.0 (Pansu and Gautheyrou, 2006). The exchangeable base cations were extracted with 1.0 mol L^{-1} ammonium acetate (Pansu and Gautheyrou, 2006). Ca and Mg were measured by atomic absorption spectrophotometry, and K and Na by flame photometry. The soil nitrate-N and ammonium-N were extracted by 2.0

mol L^{-1} KCl; the ammonia-N was determined by the indophenol blue colorimetric method, and the nitrate-N by UV spectrophotometry (Pansu and Gautheyrou, 2006).

Statistical analysis

The statistical package SPSS 15.0 (SPSS Inc., Chicago, IL, USA) was used for data analysis. One-way analysis of variance (ANOVA) was undertaken for each time interval of the incubations to determine significant differences between the treatments. Significant effects for various treatments were compared using *t*-test.

RESULTS AND DISCUSSION

Amelioration effects of plant materials and their biochars

When the Ultisol was incubated with rice hulls and rice hull biochar, the soil pH for all treatments decreased with incubation time (Fig. 1). The decline of soil pH was ascribed to the nitrification of NH_4^+ in soil. The incorporation of both rice hulls and rice hull biochar increased soil pH compared with controls ($P < 0.01$). At the early stage of incubation, soil pH with rice hull biochar incorporated was higher than that with rice hull due to the enriched alkali in rice hulls during pyrolysis ($P < 0.05$). At the later stage of incubation there was a reverse trend ($P < 0.05$); and at the end of incubation, soil pH for rice hull and rice hull biochar treatments was 0.46 and 0.39 higher, respectively, than for control. Rice hull inhibited nitrification of NH_4^+-N to a greater extent than for controls and the treatment using rice hull biochar (Fig. 2), which led to smaller decrease in soil pH later in the incubation. At the end of the incubation, soil NH_4^+-N for rice hull treatment was much higher than that for rice hull biochar and controls ($P < 0.01$), while there was a reverse trend for soil nitrate (Fig. 2) ($P < 0.01$). The inhibition of nitrification reduced H^+ release and increased soil pH.

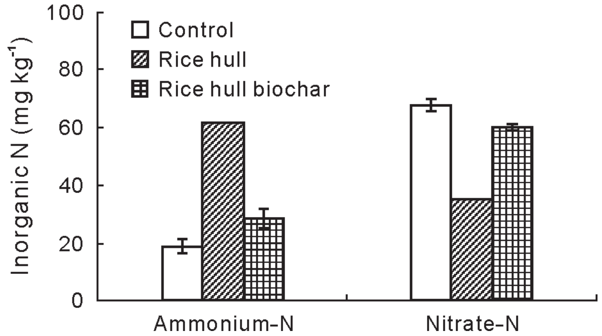

Fig. 2 Contents of soil ammonium-N and nitrate-N at the end of the incubation with rice hull and rice hull biochar. Vertical bars represent the standard error of the mean ($n = 3$).

For the two legume straws (soybean and pea straws), soil pH increased after incubation for 3 d, reached a maximum by 12 d, and then decreased with the incubation time (Fig. 3). The changes in soil pH were similar to those from a previous report for acid soils with lupin shoots added (Xu and Coventry, 2003). The transformation of N during the incubation caused the soil pH fluctuation of these legume treatments. The input of ash alkalinity and the mineralization of organic N are two main factors contributing to increased soil pH early in the incubation (Fig. 4), while nitrification of NH_4^+-N would contribute to decreased soil pH later in the incubation (Fig. 4), the balance of these reactions determined the final soil pH. Although

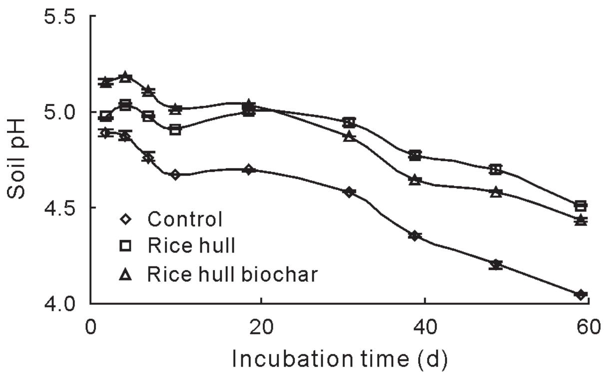

Fig. 1 Dynamics of soil pH during the incubation with rice hull (20 g kg^{-1}) and rice hull biochar (20 g kg^{-1}). Vertical bars represent the standard error of the mean ($n = 3$).

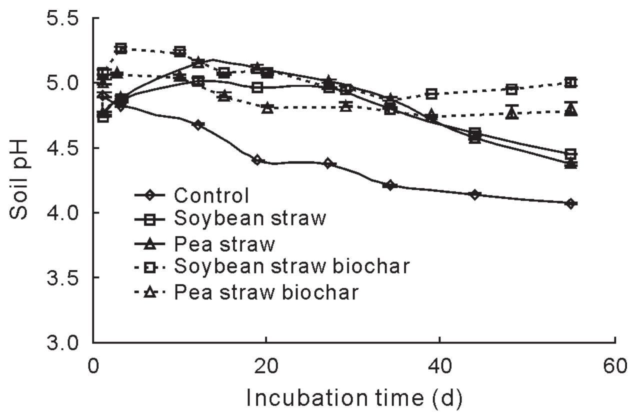

Fig. 3 Dynamics of soil pH during the incubation with legume straws (20 g kg^{-1}) and their biochars (10 g kg^{-1}). Vertical bars represent the standard error of the mean ($n = 3$).

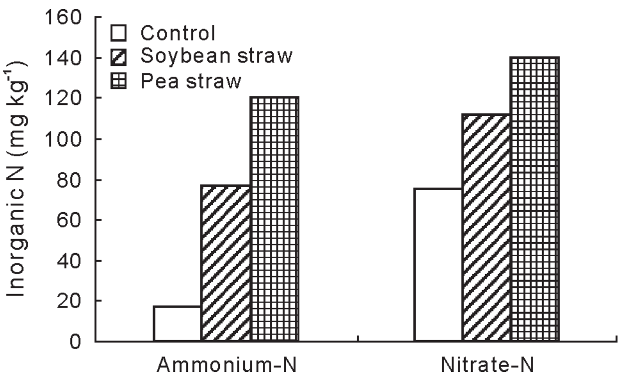

Fig. 4 Contents of soil ammonium-N and nitrate-N at the end of the incubation with straws of soybean and pea.

the amount of biochar added was only the half of the corresponding feedstock, the biochars showed greater liming potential than their feedstock at the early and later stages of the incubation. This suggested that the alkali in biochars was more easily released as compared with their feedstock. After 20 d, soil pH with incorporated biochars changed less compared with those treatments where feedstock was added directly. Therefore, pyrolysis of legume straws increased the liming potential of the pyrolytic products on acid soils compared to their feedstock.

Amelioration effects of biochars from different crop residues

The biochars from legume straws had higher liming potential than those from non-legume straws (Fig. 5) ($P < 0.05$), consistent with alkalinity of the biochars (Table I). The alkalinity of the biochars from legume straws was greater than that from non-legume straws ($P < 0.05$), thus the incorporation of legume biochars led to greater increases in soil pH compared with non-legume biochars ($P < 0.05$). At the end of the incubation, the biochars from straws of mung bean, peanut and faba bean increased soil pH by 0.68, 0.67 and 0.49, respectively. Among the biochars from non-legume crop straws that of canola had the highest liming potential, followed by rice and corn, and wheat had the least liming potential on the acid soil. At the end of the incubation, these incorporated biochars respectively increased soil pH by 0.35, 0.23, 0.16 and 0.10. These were generally consistent with their alkalinity. Therefore, alkalinity of biochars was a key factor affecting their liming potential on acid soils.

Values of pH of the Ultisol after incubation with crop residues and biochars for 50 days are listed in Table I. The results indicated that the treatments with

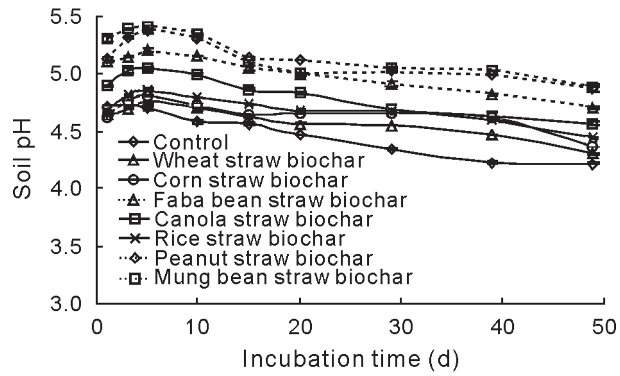

Fig. 5 Dynamics of pH in the Ultisol with different biochars (10 g kg^{-1}) during the incubation. Vertical bars represent the standard error of the mean ($n = 3$).

TABLE I

Alkalinity of biochars and the pH of the Ultisol after incubation with crop residues (20 g kg^{-1}) and biochars (10 g kg^{-1}) for 50 days

Treatment	Alkalinity of biochar	Soil pH with biochar added	Treatment	Soil pH with crop residues added
	$cmol_c$ kg^{-1}			
Control	-	4.21 ± 0.01a[a)]	Control	4.21 ± 0.01a
Canola straw biochar	191.4 ± 2.3f	4.56 ± 0.01b	Canola straw	4.56 ± 0.02b
Rice straw biochar	162.7 ± 3.5g	4.44 ± 0.02c	Rice straw	4.56 ± 0.02b
Corn straw biochar	180.0 ± 2.4h	4.37 ± 0.03d	Corn straw	4.66 ± 0.01c
Wheat straw biochar	120.1 ± 2.3i	4.31 ± 0.02e	Wheat straw	4.45 ± 0.02d
Mung bean straw biochar	326.1 ± 3.4a	4.88 ± 0.01f	Mung bean straw	4.90 ± 0.03e
Peanut straw biochar	292.7 ± 2.0b	4.87 ± 0.03f	Peanut straw	4.90 ± 0.01e
Soybean straw biochar	273.1 ± 3.5c	4.74 ± 0.01g	Soybean straw	4.44 ± 0.02d
Pea straw biochar	260.5 ± 2.5d	4.61 ± 0.02h	Pea straw	4.38 ± 0.01f
Faba bean straw biochar	216.7 ± 1.7e	4.70 ± 0.03g	Faba bean straw	4.71 ± 0.02g

[a)]Means ± standard errors followed by the same letter within a column are not significantly different at $P < 0.05$.

canola straw biochar and canola straw had the same soil pH. While the incorporation of rice straw, corn straw and wheat straw led to more increase in soil pH than the incorporation of the biochars derived from these crop straws ($P < 0.05$) although the ash alkalinity of these crop straws was much lower than the alkalinity of rice straw biochar, corn straw biochar and wheat straw biochar. The values of ash alkalinity for rice straw, corn straw and wheat straw were 33.6, 48.8 and 23.2 $cmol_c$ kg^{-1}, respectively. The differences between the effect of the straws of rice, corn and wheat and the effect of the biochars derived from these straws on soil pH were similar to the change of soil pH with incorporation of rice hull and rice hull biochar as shown in Fig. 1. The inhibition of nitrification in the soil by the straws of rice, corn and wheat was responsible for the more increase in soil pH induced by the incorporation of these straws compared with their biochars (Wang *et al.*, 2010). The contents of total N in the straws of soybean and pea were 23.8 and 35.0 g kg^{-1}, respectively. The NH_4^+ produced from the mineralization of organic N in these two legume straws during incubation accelerates the nitrification and release of H^+ and thus decreases the liming potential of these straws (Wang *et al.*, 2010). Therefore soybean straw biochar and pea straw biochar had higher ameliorating effect on the acid soil than their feedstock (Table I) ($P < 0.05$). The effect of the incorporation of mung bean straw, peanut straw and faba bean straw on soil pH was similar with that of the incorporation of their biochars due to relatively lower content of total N in these legume straws. The contents of total N in the straws of mung bean, peanut and faba bean were 14.5, 15.0 and 11.6 g kg^{-1}, respectively.

Effect of biochars on soil exchangeable acid and exchangeable base cations

The incorporation of biochars decreased soil exchangeable acidity and increased soil exchangeable base cations (Table II) ($P < 0.05$). The incorporation of biochars from legume straws led to greater decreases in soil exchangeable acidity than biochars from non-legume straws ($P < 0.05$), because the legume biochars had higher alkalinity and thus neutralized more exchangeable acidity of the soil. The legume biochars also resulted in greater increases in soil exchangeable base cations and the soil base saturation except for faba bean biochar. The legume straws contain higher amounts of base cations than the non-legume straws (Wang *et al.*, 2009), and the base cations were transferred from these straws to the biochars during the pyrolysis. When the biochars were incorporated into the soil, these base cations released into the soil and occupied soil exchange-sites. The higher content of base cations in the biochars led to greater increase in soil exchangeable base cations. Therefore the incorporation of biochars not only decreased soil acidity, but also improved soil fertility. The incorporation of legume biochars led to greater improvement of soil fertility than non-legume biochars

The rates of plant materials and biochar addition used in the incubation experiments in this study are equivalent to 15 to 30 t ha^{-1}. These rates are higher than the application rate of crop straws returned to fields in normal conditions, about 7.5 t ha^{-1} per year.

TABLE II

Effect of biochars on exchangeable acid, exchangeable base cations, ECEC and base saturation of the Ultisol

Treatment	Exchangeable acid	Exchangeable base cation	ECEC[a)]	Base saturation
	$cmol_c$ kg^{-1}			%
Control	6.61 ± 0.17a[b)]	3.33 ± 0.10e	9.94	33.5
Canola straw biochar	3.99 ± 0.16c	6.11 ± 0.05b	10.10	60.5
Rice straw biochar	4.70 ± 0.24b	5.79 ± 0.08c	10.49	55.2
Corn straw biochar	4.76 ± 0.48b	6.06 ± 0.07bc	10.82	56.0
Wheat straw biochar	5.36 ± 0.30b	4.77 ± 0.12d	10.13	47.1
Mung bean straw biochar	2.47 ± 0.11d	7.10 ± 0.01a	9.57	74.2
Peanut straw biochar	2.79 ± 0.11d	7.23 ± 0.17a	10.02	72.0
Soybean straw biochar	2.51 ± 0.15d	7.10 ± 0.08a	9.61	73.9
Pea straw biochar	3.12 ± 0.11d	7.00 ± 0.05a	10.02	69.9
Faba bean straw biochar	3.83 ± 0.16c	5.89 ± 0.18bc	9.72	60.6

[a)]Effective cation exchange capacity, the sum of exchangeable acid and exchangeable base cations; [b)]Means ± standard errors followed by the same letter(s) within a column are not significantly different at $P < 0.05$.

The amendments for acid soils such as lime are normally applied once in 4 to 5 years. Therefore, the results obtained in this study could provide references for the application of crop residues and their biochars as amendments for acid soils in field conditions.

CONCLUSIONS

The incorporation of both crop residues and their biochars could decrease soil exchangeable acidity and thus increase soil pH, exchangeable base cations and base saturation of acid soils. The liming potential of the biochars from legume materials is greater than that from non-legume materials and legume materials themselves. Ameliorating effect of non-legume materials on acid soils is greater than the biochars derived from these materials due to the inhibition of nitrification in soils by the non-legume materials. The biochars from legume materials are the better choices to be used as organic amendments for acid soils to reduce soil acidity and improve soil fertility.

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