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Comparison of the ameliorating effects on an acidic ultisol between four crop straws and their biochars

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Abstract

Purpose The amelioration effects of crop straws and their biochars on an acidic ultisol were compared in incubation experiments to determine suitable organic amendments for acid soils.

Materials and methods Four crop straws, including non-legumes (canola straw and rice straw) and legumes (soybean straw and pea straw) were used to prepare biochars using a low temperature (350°C) oxygen-limited pyrolysis method. Two application rates of 1% and 2% were used for both crop straws and their biochars in incubation experiments lasting 90 days. Soil pH (1:2.5 soil to water), soil exchangeable acidity, soil exchangeable base cations, and soil cation exchange capacity (CEC) were determined to evaluate the amelioration effects of these crop straws and their biochars on an acidic ultisol.

Results and discussion The incorporation of crop straws increased or decreased the soil pH depending on the relative contribution of alkalinity of the straws, mineralization of organic N and nitrification of NH_4^+. The incorporation of biochars produced from crop straws increased the soil pH, and their ameliorating effects increased with the application rates of biochars. The biochars from legume straws induced more increase in soil pH than non-legume biochars. The addition of both crop straws and their biochars decreased soil exchangeable acidity and exchangeable Al^{3+}, and increased soil exchangeable base cations and base saturation degree. The biochars (especially legumes) induced a greater decrease in soil exchangeable acidity and a greater increase in soil exchangeable base cations compared to their feedstock due to their much higher contents of base cations. The CEC of biochars were 10–20 times that of soil CEC and thus biochar incorporation increased the soil CEC significantly, as well as the retention of Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ by acid soils.

Conclusions The biochars produced from legume crop straws were better choices as amendments for acid soils than their feedstock. Organic anions and carbonates were the main forms of alkali in the biochar; both contributed to neutralizing soil acidity and increasing soil pH. The incorporation of biochar cannot only neutralize soil acidity, but can also improve soil fertility.

Keywords Amelioration of soil acidity · Biochar · Crop straws · Soil pH · Ultisol

1 Introduction

In recent decades, various anthropogenic activities have greatly accelerated soil acidification. Acid deposition is a serious factor that accelerates soil acidification (Vogt et al. 2006; Hu et al. 2007), which can also be accelerated by applying excessive ammonium-based fertilizers (Bolan et al. 1991). Under the intensive land use in China, the sharp increase in the application of nitrogen (N) fertilizers in cropping systems has greatly accelerated soil acidification (Zhang et al. 2008, 2009; Guo et al. 2010). The increases in air temperature induced by rising atmospheric greenhouse gases have also enhanced soil acidification through the

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acceleration of N mineralization and nitrification (Murdoch et al. 1998).

Aluminum toxicity and soil infertility are two important factors limiting plant growth in acid soils and thus reducing crop yields. 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; Xu et al. 2006b; Wang et al. 2009, 2010; Mao et al. 2010), but the ameliorating effects of these plant materials on acid soils depends on the properties of both plant materials and soils (Pocknee and Sumner 1997; Wang et al. 2009, 2010). Organic anions in plant materials are the main source for their ash alkalinity (Yan et al. 1996; Li et al. 2008). Generally, there is higher ash alkalinity in legume than non-legume materials due to the unbalanced uptake of cations and anions, and thus legume materials should have greater amelioration effects on soil acidity (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 later decrease. This was due to nitrification of ammonium (NH_4^+) ions produced during the mineralization of organic N early in the incubation (Yan et al. 1996, 2006; Tang et al. 1999; Xu and Coventry 2003; Xu et al. 2006a). The protons from nitrification of the NH_4^+ after incorporation of legume materials in acid soils may somewhat counteract their amelioration effect on the soils. When the legume materials were incorporated into acidic soils in combination with dicyandiamide (a nitrification inhibitor), the nitrification of the NH_4^+–N produced by ammonification of organic N in legume materials was inhibited and thus their ameliorating effects on soil acidity were increased greatly (Mao et al. 2010).

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 increase pH of acid soils (Steiner et al. 2007; Chan et al. 2008; Novak et al. 2009; Yuan and Xu 2011) because biochar contains some alkaline substances and has an alkaline pH (Yuan et al. 2011). The incorporation of biochars from legume materials resulted in greater increases in soil pH than from non-legume materials and a close linear correlation was observed between soil pH and biochar alkalinity (Yuan and Xu 2011). The amelioration effects on soils by direct incorporation of plant materials cannot last long due to their decomposition by soil microorganisms (Tang et al. 1999; Xu et al. 2006b). Research indicates that biochar is recalcitrant and may persist for hundreds of years in soils (Rebecca 2007; Christoph et al. 2008); however, there is little information comparing the amelioration effects of biochars and their feedstock on soil acidity. Therefore, straws of canola, rice, soybean, and pea were chosen to prepare biochar samples at 350°C, and the amelioration effects on an acid ultisol of biochars and their feedstock were compared. The ameliorating mechanisms of biochar and crop straws on acid soils were also investigated based on the data obtained.

Organic anions and organic N mineralization of crop straws contribute to the neutralization of soil acidity, while nitrification of NH_4^+ counteracts the amelioration effects of these organic materials. Pyrolysis of crop residues leads to the change of chemical components in these materials and thus the amelioration effect of pyrolytic biochar on acid soils and related mechanisms should be different from its feedstock. Therefore, the objectives of this study are to compare the amelioration effects of crop straws and their biochars on an acidic ultisol under the same conditions and to recommend suitable organic amendments for acid soils.

2 Materials and methods

2.1 Soil, crop straws, and biochar

The acidic ultisol (U.S. Soil Taxonomy; Haplic Acrisol in the WRB Taxonomy) used in this study was collected from a cropland of Langxi, Anhui Province, China (31°6′ N, 119°8′ E). The soil is derived from Quaternary red earth. The sample was taken from the topsoil (0–10 cm), air-dried, and ground to pass a 2-mm sieve. The soil pH was 4.31 as determined in a 1:2.5 soil to water suspension; the soil organic matter was 16.49 gkg^{-1}, the soil cation exchange capacity (CEC) was 9.36 $cmol_{(+)}kg^{-1}$, and soil exchangeable H^+, Al^{3+}, K^+, Na^+, Ca^{2+}, and Mg^{2+} were 0.20, 5.97, 0.53, 0.68, 4.92, and 0.35 $cmol_{(+)}kg^{-1}$, respectively.

The straws of canola (*Brassica campestris* L.), rice (*Oryza sativa* L.), soybean (*Glycine max* L.), and pea (*Pisum sativum* L.) were collected from a cropland in a suburb of Nanjing, China. These straws were air-dried at room temperature and ground to pass a 1-mm sieve. The ground straws were then placed in ceramic crucibles, each covered with a fitting lid, and pyrolyzed under oxygen-limited conditions in a muffle furnace (Shanghai Yi Zhong Electricity Furnace, Inc., Shanghai, China). The pyrolysis temperature was raised to the selected value of 350°C at a rate of approximately 20°C per minute and held constant for 4 h (Chun et al. 2004), then the biochar was allowed to cool to room temperature and ground to pass a 1-mm sieve. There were three replicates for each crop straw during the biochar-generating process.

2.2 Determination of physical and chemical properties of crop straws and their biochars

The ash alkalinity of the crop straws was determined using a modified titration method (Slattery et al. 1991); 0.5000 g of the ground straw (1-mm sieve) was heated at 200°C for 1 h and then at 500°C for an additional 4 h in a muffle furnace. When the furnace cooled to room temperature, the ash was dissolved in 25.0 mL of 1.0 M HCl, and 5.0 mL of the solution was taken and titrated against a standard 0.25 M NaOH solution to determine ash alkalinity. Then 1.0 mL of the solution was taken to analyze the chemical compositions. The K^+ and Na^+ concentrations in the solution were determined by flame photometry, and Ca^{2+} and Mg^{2+} by atomic absorption spectrometry (AAS). The total P in the solution was determined by ascorbic acid–NH_4–molybdate blue colorimetry at 700 nm (Wang et al. 2009). The total C and N contents of the straws and biochar were determined using a Leco CN-2000 analyzer (Leco Corp., St. Joseph, MI, USA) at 1,200°C.

The pH of the straws and biochar were measured in deionized water at 1:5 biochar to water (Gaskin et al. 2008). The straws and biochar were each thoroughly mixed and allowed to equilibrate for 1 h. The pH was then measured using an Orion 720 pH meter with a combination electrode. The biochar CEC was measured by a modified ammonium acetate compulsory displacement method (Gaskin et al. 2008). Of the biochar, 0.2000 g was leached with 20 mL of deionized water five times, and the leachate collected together. The K^+, Na^+, Ca^{2+}, and Mg^{2+} in the leachate were determined as the soluble base cations of the biochar. After the fifth run of the leaching with deionized water, the biochar was leached with 20 mL of 1.0 M sodium acetate (pH 7.0) five times, and the leachate collected together. The biochar was then washed with 20 mL of ethanol five times to remove the excess Na^+. Afterwards, the Na^+ on the exchangeable sites of the biochar was displaced by 20 mL of 1.0 M ammonium acetate (pH 7.0) five times, and the CEC of the biochar calculated from the Na^+ displaced by NH_4^+. The K^+ and Na^+ in the leachate were determined by flame photometry, and Ca^{2+} and Mg^{2+} by AAS.

The carbonate (CO_3^{2-}) content in biochar was determined by volumetric analysis of the carbon dioxide liberated by adding 4 M HCl solution to the biochar. About 5 g of $CaCO_3$ was dried at 104°C and then 0.0000, 0.1000, 0.2000, and 0.3000 g of the dried $CaCO_3$ were each weighed as standard substances. Of the prepared biochar (0.154-mm sieve) sample, 2.0000 g was weighed in three replicates to determine the CO_3^{2-} content.

The Fourier transform mid-infrared photoacoustic spectroscopy (FTIR-PAS) spectra were recorded for all the biochar samples using a Nicolet 380 spectrophotometer (Thermo Fisher Scientific, USA) equipped with a photoacoustic cell (Model 300, MTEC, USA) (Du et al. 2009). After a sample was placed in the cell holding cup (diameter, 5 mm; height, 3 mm) and the cell purged with dry helium at 10 mL min^{-1} for 10 s, the sample was scanned from 500 to 4,000 cm^{-1} with a resolution of 8 cm^{-1} and a mirror velocity of 0.48 cm s^{-1}.

2.3 Incubation experiments

Air-dried soil samples of 250 g were placed in plastic cups, and each crop straw or biochar was added at 10 gkg^{-1} (1%) and 20 gkg^{-1} (2%), respectively. The soil and crop straws or biochar were mixed thoroughly and then wetted with deionized water to 70% of field water holding capacity of the soil. All cups were covered with plastic film, and a small hole was made to allow gaseous exchange but to minimize moisture loss, and then incubated at a constant 25°C. The cups were weighed every 3 days, with water added to maintain a constant moisture content throughout the experiment. The soils were subsampled after 1, 3, 6, 10, 20, 30, 40, 50, 60, 70, 80 and 90 days to determine the soil pH (Yan and Schubert 2000). There were three replicates for each treatment with the controls having no incorporated crop straws or biochar. After 90 days of incubation, the soil samples were removed from the cups, air-dried, and ground to pass a 0.3-mm sieve.

2.4 Soil analyses after incubation

After incubation, soil exchangeable H^+ and Al^{3+} were extracted with 1.0 M KCl, and then titrated by 0.25 M NaOH to pH 7.0 (Pansu and Gautheyrou 2006). The CEC of the soil samples was measured by ammonium acetate compulsory displacement method, exchangeable base cations were extracted with 1.0 M ammonium acetate (pH 7.0) (Pansu and Gautheyrou 2006), Ca^{2+} and Mg^{2+} were measured with AAS, and K^+ and Na^+ with flame photometry. The soil NH_4^+–N and NO_3^-–N were extracted by 2.0 M KCl using 1:5 soil to solution (Pansu and Gautheyrou 2006), and then were determined by the continuous flow analytical system (Skalar San^{++}, The Netherlands).

2.5 Statistical analyses

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

3 Results and discussion

3.1 Chemical compositions and properties of crop straws and their biochars

The chemical compositions of crop straws and biochar tested are presented in Tables 1 and 2. All biochars had a higher pH than their corresponding crop straws, indicating the higher alkalinity of biochar compared with the straws and suggesting the concentrating of alkaline substances in crop straws during pyrolysis. We found that the total elemental concentration of feedstock had a significant influence on the chemical composition of biochar (see Tables 1 and 2). Gaskin et al. (2008) observed a similar relationship between elemental concentration of the feedstock and the chemical composition of the biochar. The legume straws of soybean and pea had higher contents of total base cations and total N than the non-legume straws of canola and rice (see Table 1) ($P<0.05$), and thus the biochars produced from the legumes had higher contents of total base cations and total N than those from the two non-legume straws (see Table 2) ($P<0.05$). The highest P content was found in the biochar from the pea straw compared with the other straws (see Table 2) ($P<0.05$), and was attributed to the much higher P content in pea straw (see Table 1) ($P<0.05$). Therefore, the higher contents of base cations, N and P in feedstock resulted in the greater concentrations for these elements in biochar. The contents of base cations and total P in biochar were higher than in the feedstock—also evident for total N in biochars from straws of rice, soybean, and pea. These results suggest that the chemical components were concentrated in the biochar during pyrolysis, leading to higher contents of these chemical components in biochar compared to the feedstock. The CEC of biochars from the non-legume straws was much higher than that from legumes ($P<0.05$), and canola straw biochar had the highest CEC (see Table 2). All biochars had abundant soluble base cations and exchangeable base cations. These base cations can be released into acid soils easily, thus incorporation of biochar can improve soil fertility.

3.2 Amelioration effects of crop straws on the acid ultisol

There were some fluctuations in soil pH during incubations for the treatments with legume straws incorporated, but soil pH changed little for treatments with non-legume straws (Fig. 1). Soil pH decreased with the increased incubation time for controls, and the incorporation of canola and rice straws somewhat inhibited the decrease of soil pH ($P<0.05$). At the end of the incubation, soil pH was 0.43 and 0.29 units higher for the treatments with 1% canola and rice straws incorporated than for controls, respectively, the corresponding data were 0.45 and 0.36 for treatments with 2% of canola and rice straws (Table 3). It is interesting that soil pH did not increase significantly with the increased addition level of canola and rice straws. Nitrification of NH_4^+ in controls is the main reason for the decreased soil pH with incubation time because $(NO_3^-+NO_2^-)$–N increased with incubation time and NH_4^+ changed oppositely in the control soil (Fig. 2). The canola and rice straws inhibited the decrease of soil pH through the release of alkaline substances and the inhibition of nitrification during incubation. The $(NO_3^-+NO_2^-)$–N content was much lower for treatments with canola and rice straws incorporated than for controls and changed less with incubation time (see Fig. 2) ($P<0.05$). There was no significant difference in soil $(NO_3^-+NO_2^-)$–N content between the two addition levels of the rice straw, and the content of $(NO_3^-+NO_2^-)$–N for the treatment with 1% canola straw added was slightly higher than for the 2% canola straw added. This was consistent with the change of soil pH in the corresponding treatments. These results suggest that the inhibition of nitrification is the main mechanism for the ameliorating effect of the straws of canola and rice on soil acidity.

The pH change for the treatments with legume straws incorporated differed from that for the non-legume systems. The soil pH increased with incubation time, reached a maximum at 30 days and then decreased sharply (see Fig. 1). The changing trends of the soil pH for these treatments were similar to those for a study in which acid

Table 1 Chemical compositions for the straws of canola, rice, soybean and pea

Crop straw	pH	Ash alkalinity	Total base cations	Total P	Total N	Total C	C/N
		(cmol kg^{-1})		(g kg^{-1})			
Canola straw	6.34	43.3c	35.0d	1.07b	1.9d	457a	24
Rice straw	6.81	33.6d	45.0c	1.11b	8.7c	412d	47
Soybean straw	6.29	72.0a	49.9b	0.90c	23.8b	440b	18
Pea straw	6.27	61.6b	79.5a	4.62a	35.0a	436c	12

The total base cations are the sum of total Ca^{2+}, Mg^{2+}, K^+, and Na^+. The data followed by the different letters within a row are significantly different at the 5% level ($P<0.05$)

Table 2 pH, CEC, chemical compositions of the biochar samples produced from the straws of canola, rice, soybean, and pea at 350°C

Biochar	pH	CEC	Total base cations	Soluble base cations	Exchangeable base cations	Carbonate	Total P	Total N	Total C	C/N
		(cmol kg^{-1})					(g kg^{-1})			
Canola straw biochar	8.00	180a	186c	72c	87b	56.2a	2.2d	1.7d	617a	364
Rice straw biochar	7.69	152b	151d	98b	68d	44.2d	3.3c	16.5c	425d	26
Soybean straw biochar	9.02	98d	236b	50d	96a	56.0a	7.2b	36.2b	541b	15
Pea straw biochar	10.26	104c	330a	184a	78c	51.2c	16.6a	40.3a	533c	13

Total base cations are the sum of total Ca^{2+}, Mg^{2+}, K^+, and Na^+. Soluble base cations are the sum of soluble Ca^{2+}, Mg^{2+}, K^+, and Na^+. Exchangeable base cations are the sum of exchangeable Ca^{2+}, Mg^{2+}, and K^+. The data followed by the different letters within a row are significantly different at the 5% level ($P<0.05$)

soils were treated with lupin shoots (Xu and Coventry 2003). A similar phenomenon was also reported by Wang et al. (2010) when an acidic ultisol was incubated with 1% straws of pea and soybean and 1% Chinese milk vetch shoots. The maximum value of soil pH increased with the increased addition level of the two straws (see Fig. 1). However, at the end of the incubation, the incorporation of 2% of soybean and pea straws increased soil pH by 0.11 and 0.03 units, respectively, while addition of 1% pea straw led to a decrease of 0.09 units (see Table 3). There was no significant difference in soil pH between the control and the treatments with 1% straws of soybean and pea and 2% pea straw added (see Table 3).

The transformation of N during incubation was responsible for the soil pH fluctuation for the treatments with legume straws added due to their relatively higher N contents compared to non-legume straws (see Table 1). The input of ash alkalinity and the mineralization of organic N are two main factors increasing the soil pH early in the incubation while subsequent nitrification of NH_4^+–N would have contributed to declines in soil pH later in the incubation. This is due to the release of protons from the reaction, and the dependence of the final soil pH on the balance of these reactions (Xu and Coventry 2003; Wang et al. 2010). Therefore, the nitrification of NH_4^+ counteracted the amelioration effects of these two legume straws on the acid ultisol. The results of the NH_4^+–N and (NO_3^-+NO_2^-)–N analyses obtained during the incubation also support this explanation. The NH_4^+–N increased with the incubation duration and reached a maximum at 30 days, prior to decreasing later in the incubation while the (NO_3^-+NO_2^-)–N always increased with longer incubation (see Fig. 2). These results suggest that the mineralization of organic N in these two legumes increased the soil NH_4^+–N early in the incubation, and that nitrification of NH_4^+–N later in the incubation increased the (NO_3^-+NO_2^-)–N. The trends of the changes in the soil NH_4^+–N and (NO_3^-+NO_2^-)–N were consistent with the soil pH change discussed above and provide evidence accounting for the change in soil pH during incubation.

3.3 Amelioration effects of biochars from crop straws on the acid ultisol as compared with their feedstock

Soil pH decreased with incubation time for all treatments with biochar incorporated, similar to the trend for soil pH in controls (Fig. 3). The nitrification of NH_4^+ originated from the soil in the controls and with biochar added was responsible for the decreased soil pH during incubation. The incorporation of biochars both from legume and non-legume materials increased soil pH ($P<0.05$). The ameliorating effects were greater for the biochars derived from

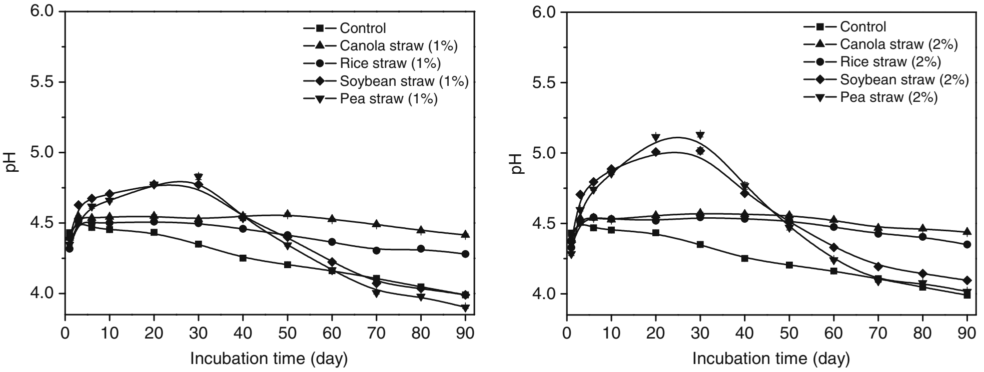

Fig. 1 Dynamics of soil pH during incubation of an ultisol with straws of canola, rice, soybean, and pea incorporated

Table 3 Soil pH and the difference of soil pH between the treatments with crop straws and their biochars and control (ΔpH) at the end of the incubation

Treatment with straw	Soil pH	ΔpH	Treatment with biochar	Soil pH	ΔpH
Control	3.99±0.018e	–	Control	3.99±0.018h	–
Canola straw (1%)	4.42±0.006a	0.43	Canola straw biochar (1%)	4.35±0.027f	0.36
Rice straw (1%)	4.28±0.004c	0.29	Rice straw biochar (1%)	4.26±0.005g	0.27
Soybean straw (1%)	3.99±0.013e	0.00	Soybean straw biochar (1%)	4.49±0.010d	0.50
Pea straw (1%)	3.90±0.009f	−0.09	Pea straw biochar (1%)	4.42±0.002e	0.43
Canola straw (2%)	4.44±0.002a	0.45	Canola straw biochar (2%)	4.65±0.017c	0.66
Rice straw (2%)	4.35±0.007b	0.36	Rice straw biochar (2%)	4.46±0.004de	0.47
Soybean straw (2%)	4.10±0.010d	0.11	Soybean straw biochar (2%)	5.19±0.029a	1.20
Pea straw (2%)	4.02±0.010de	0.03	Pea straw biochar (2%)	4.99±0.018b	1.00

Soil pH was presented as means ±standard error, the data followed by the different letters within a row of soil pH are significantly different at the 5% level ($P<0.05$)

legumes than from non-legumes and followed the order: soybean straw>pea straw>canola straw>rice straw, consistent with the ash alkalinity of these straws (see Table 1); at the end of the incubation, these biochars increased soil pH by 0.50, 0.43, 0.36 and 0.27 units at the addition level of 1%, respectively, and by 1.20, 1.00, 0.66 and 0.47 units at 2% addition level (see Table 3). The effect of incorporated biochar on soil pH increased markedly with increased addition level, especially for biochars from legumes ($P< 0.05$). Compared with biochars from non-legume materials, when biochars from legumes were incorporated into acid soils, their higher pH and greater alkalinity led to a greater increase in soil pH.

The biochars from the two non-legumes and their feedstock had similar ameliorating effects on the acid soil at an addition level of 1%, but the ameliorating effects of biochar were greater than the feedstock at 2% addition level due to the different ameliorating mechanisms of the non-legume straws and their biochars. The non-legume straws inhibited the decrease of soil pH mainly through the inhibition of nitrification during incubation. Biochar increased soil pH through the release of alkaline substances into the soil and thus its ameliorating effect increased with an increase in the application rates.

The ameliorating effects of the biochars from the legume straws on the acid soil were much greater than that for their feedstock, especially at high application rates (see Figs. 1 and 3). Although the ash alkalinity of legume straws was high (see Table 1), the nitrification of NH_4^+ from the mineralization of organic N in the legume straws counter-

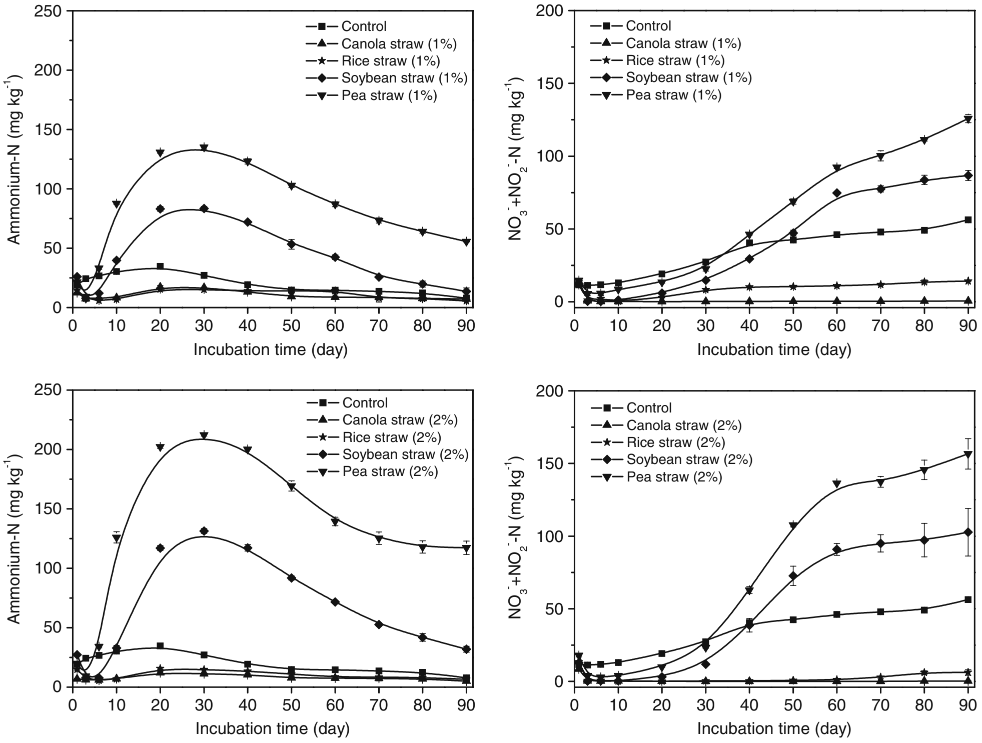

Fig. 2 Dynamics of soil NH_4^+–N and $(NO_3^-+NO_2^-)$–N during incubation with straws of canola, rice, soybean, and pea

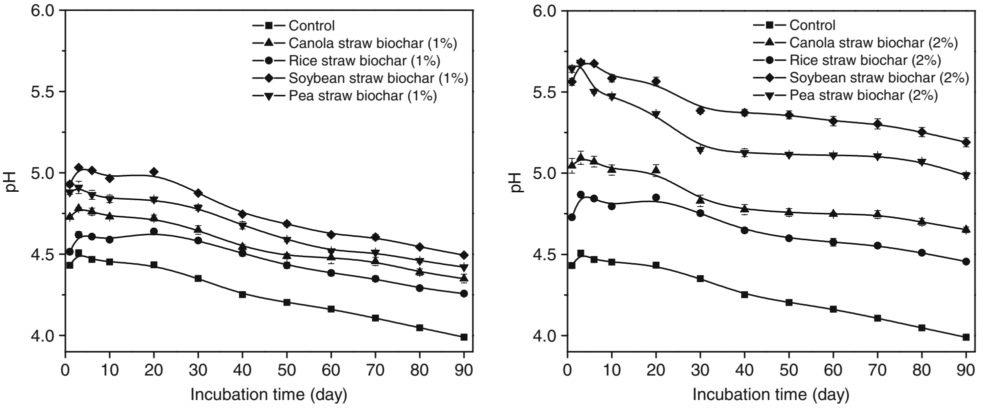

Fig. 3 Dynamics of soil pH during incubation of an ultisol with incorporation of biochars produced from straws of canola, rice, soybean, and pea

acted their ameliorating effects on soil acidity. The pyrolysis of legume straws made the organic N in biochar unavailable to soil microorganisms. The N in the biochar exists mostly as organic N, with inorganic N representing no more than 0.1% of total N. Therefore, although the C/N ratio of the biochars from legume straws was close to that of their feedstock, the organic N is difficult for microorganisms to utilize, and so mineralization of organic N and subsequent nitrification of NH_4^+ from biochar is weak in soil. The NH_4^+ in the nitrification reaction mainly came from the original soil NH_4^+, not from biochar (Fig. 4). The effect of nitrification on soil pH for treatments with biochar added was similar to that for controls (see Fig. 3), in contrast to treatments with legume straws added (see Figs. 1 and 2). Thus, pyrolysis made the pyrolytic products of legume straws more effective in ameliorating soil acidity than their feedstock. The biochars produced from legume straws were better amendments for acid soils than their feedstock and also the biochars from non-legume straws.

3.4 Ameliorating mechanisms of the biochar from crop straws

Organic anions associated with base cations Ca^{2+}, Mg^{2+}, K^+, and Na^+ in plant materials are the main source of alkalinity in plant materials (Yan et al. 1996; Wong et al.

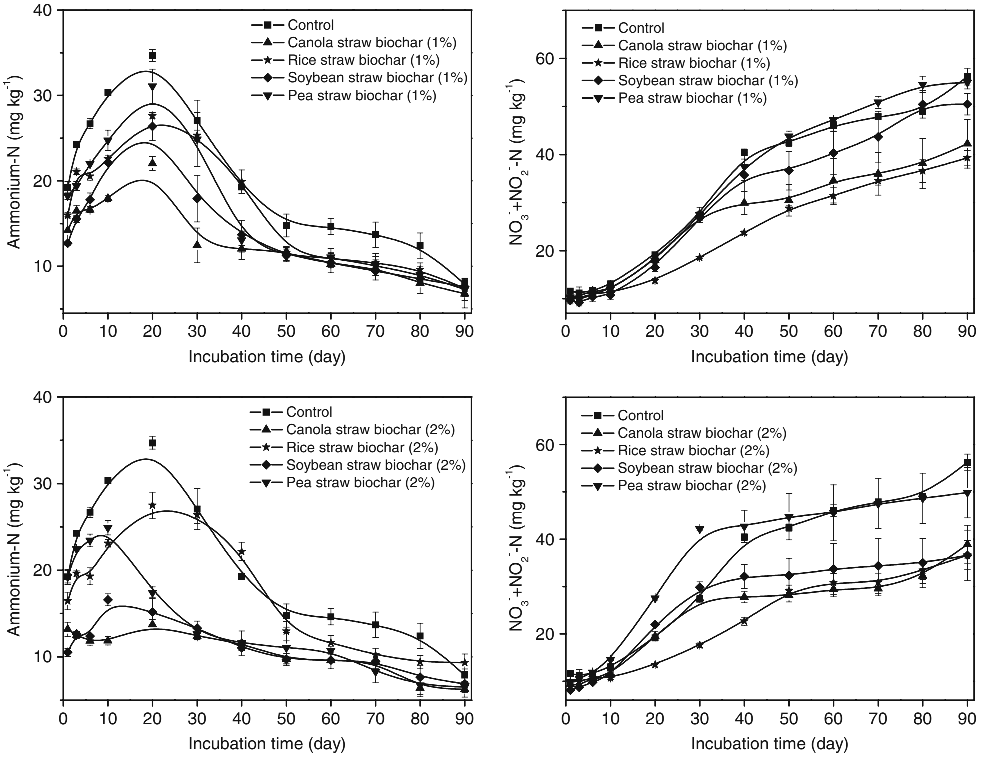

Fig. 4 Dynamics of soil NH_4^+–N and $(NO_3^-+NO_2^-)$–N during incubation with biochars produced from straws of canola, rice, soybean, and pea

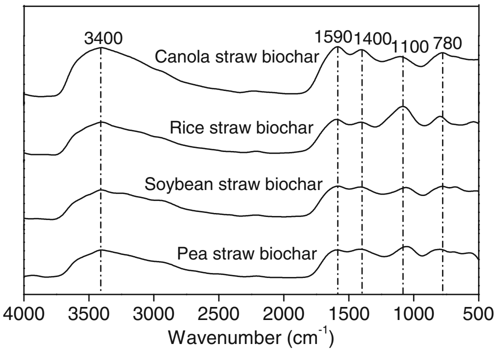

Fig. 5 The FTIR-PAS (Fourier transform mid-infrared photoacoustic spectroscopy) spectra for biochars produced from straws of canola, rice, soybean and pea

2000; Li et al. 2008). When plant materials are returned to and decomposed in soils, the decarboxylation of organic anions in the materials consumes protons and thus neutralizes soil acidity (Yan et al. 1996). Generally, legume materials have higher alkalinity than non-legume materials due to more uptake of cations than anions during the growth of legumes, and thus more organic anions accumulate in legume materials. The data of the present and previous reports (Chan et al. 2007; Novak et al. 2009) indicate that biochar is commonly alkaline, and so can be used as soil amendments to neutralize soil acidity and increase soil pH. However, the forms of the alkalis in biochar are not understood.

To probe the functional groups on the surfaces of the biochars, their FTIR-PAS spectra were collected (Fig. 5); the absorption peaks at 780 and 1,400 cm^{-1} in the spectra were assigned to the carboxylate (–COO^{-}) deviational vibration and symmetric stretching (Cheng and Lehmann 2009; Fu et al. 2009; Lammers et al. 2009). The peaks at 1,590 cm^{-1} were assigned to –COO^{-} antisymmetric stretching (Qiu et al. 2008). The peaks at 3,400 cm^{-1} were assigned to hydroxyl (–OH) stretching (Yaman 2004; Özçimen and Ersoy-Meriçboyu 2010). The FTIR-PAS spectra indicated that there were ample amounts of oxygen-containing functional groups (e.g., –COO^{-} and –OH) on the biochar. The –COO^{-} and –O^{-} groups should buffer the acid addition and contribute to alkalinity of the biochar through association of these groups with H^{+}. Organic anions on the surface of biochar are an important source of alkalinity, similar to their feedstock.

The peaks at 1,100 cm^{-1} of the FTIR-PAS spectra were assigned to the bands of the out-of-plane bending for CO_3^{2-} (Lammers et al. 2009; Michel et al. 2009; Nguyen et al. 2009), indicating the presence of CO_3^{2-} in the biochar. This is in agreement with other data (see Table 2) showing that the biochar contained some CO_3^{2-}. Therefore, CO_3^{2-} is also an important source of alkalinity and can contribute to neutralizing soil acidity and increasing soil pH.

Although, it is impossible to quantify the relative contribution of organic anions and CO_3^{2-} to alkalinity of the biochar samples in the present study, it can be

Table 4 Effect of crop straws and their biochars on soil exchangeable properties

Treatment	Exchangeable acidity (cmol$_{(+)}$kg^{-1})	Exchangeable Al^{3+}	Exchangeable base cations	CEC	Base saturation Percent
Control	4.92±0.46a	4.76±0.51a	5.02±0.04j	9.12±0.05g	55.02±0.40i
Canola straw (1%)	3.45±0.53c	3.22±0.56c	5.50±0.06i	9.35±0.12fg	58.85±0.96h
Rice straw (1%)	3.92±0.14bc	3.73±0.20bc	5.70±0.04i	9.17±0.08g	62.17±0.71h
Soybean straw (1%)	4.11±0.17b	3.85±0.13bc	6.09±0.14h	9.18±0.05g	66.32v1.31g
Pea straw (1%)	4.49±0.12ab	4.14±0.13b	6.18±0.11h	9.35±0.02fg	66.07±1.32g
Canola straw (2%)	3.69±0.16bc	3.49±0.13c	6.23±0.13h	9.35±0.12fg	66.66±2.02g
Rice straw (2%)	3.45±0.07c	3.23±0.06c	6.66±0.15g	9.16±0.02g	72.69±1.76f
Soybean straw (2%)	3.18±0.12cd	2.95±0.15cd	7.29±0.14f	9.35±0.13fg	77.99±1.12e
Pea straw (2%)	3.53±0.15c	3.22±0.14c	7.69±0.07e	9.44±0.01f	81.44±0.72de
Canola straw biochar (1%)	3.40±0.03c	3.15±0.03c	6.90±0.04g	10.65±0.02bc	64.79±0.51gh
Rice straw biochar (1%)	3.61±0.05bc	3.38±0.05c	6.82±0.10g	10.20±0.03d	66.92±1.14g
Soybean straw biochar (1%)	2.61±0.09de	2.40±0.10d	8.25±0.11d	10.10±0.04de	81.67±1.16d
Pea straw biochar (1%)	2.68±0.10d	2.48±0.10d	8.56±0.01cd	9.91±0.09e	86.45±0.72c
Canola straw biochar (2%)	2.08±0.12e	1.90±0.11d	9.56±0.04b	11.41±0.18a	83.87±1.53cd
Rice straw biochar (2%)	2.18±0.05de	2.02±0.07d	8.87±0.10c	10.72±0.08b	82.82±0.76d
Soybean straw biochar (2%)	0.55±0.03f	0.50±0.04e	11.62±0.22a	10.60±0.04bc	109.60±1.93b
Pea straw biochar (2%)	0.66±0.04f	0.55±0.06e	11.86±0.20a	10.46±0.07c	113.38±1.31a

All data in table were presented as means±standard error, the data followed by the different letters within a row are significantly different at the 5% level ($P<0.05$)

confirmed that both organic anions and CO_3^{2-} are alkaline components in the biochars produced from the crop straws and have important contributions to ameliorating effect of biochar on acid soils.

3.5 Effect of crop straws and their biochars on soil exchangeable properties

The incorporation of both crop straws and their biochars decreased soil exchangeable acidity and exchangeable Al^{3+} and increased soil exchangeable base cations (Table 4). The incorporation of biochar led to greater decreases in soil exchangeable acidity and exchangeable Al^{3+} and a greater increase in soil exchangeable base cations than for the corresponding straws, especially for the legume biochar. This is consistent with a previous report (Topoliantz et al. 2005). Both crop straws and their biochars contained base cations of Ca^{2+}, Mg^{2+}, K^+, and Na^+; when these straws and biochar were incorporated into the acid soils, the base cations exchanged with exchangeable Al^{3+} and H^+ on soil negative-charge sites and thus decreased soil exchangeable acidity and increased soil exchangeable base cations. The contents of base cations in the biochar were much greater than that in the corresponding crop straws, and biochars from legumes contained more base cations than those from non-legumes (see Tables 1 and 2). The increase in soil pH is another important reason for the decrease of soil exchangeable acidity. The incorporation of the legume biochar induced a greater increase in soil pH (see Table 3). The combination of these two factors led to the greater decrease of soil exchangeable acidity and the greater increase of soil exchangeable base cations for the treatments with the biochars from the straws of soybean and pea. Consequently, crop straws and their biochars increased the soil base saturation degree, and the increases were greater for treatments incorporating legume biochar.

The incorporation of biochar led to a significant increases ($P<0.05$) in soil CEC (see Table 4), suggesting that biochar made soil negative surface charge more negative. This is in agreement with the CEC of the biochar samples (see Table 2). The biochar from canola straws had the highest CEC of the four biochars and thus incorporation of canola biochar led to the greatest increase in soil CEC. The values of biochar CEC were 10–20 times the CEC of the soil used in this study (see Table 2); although the application rates of the biochar were only 1–2% of the soil samples, it still increased the soil CEC. The application of biochar will increase the retention of Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ in acid soils and thus improve soil fertility. This is consistent with other reports (Steiner et al. 2007; Novak et al. 2009). In a field experiment in Brazil, significantly more nutrients (P, K, Ca, Mg, and N) were exported from the plots of charcoal from forest wood plus mineral fertilizer, while the available nutrient contents of an Oxisol did not decrease in comparison to plots with only mineral fertilized added (Steiner et al. 2007). The addition of pecan shell-based biochar increased soil Ca, K, and P and significantly improve fertility of an acidic soil from the southeastern USA (Novak et al. 2009). However, the additions of charcoal and biochar did not increase the soil CEC in these studies, which differed from the observations in the present study.

4 Conclusions

The incorporation of crop straws can increase or decrease soil pH depending on the relative contribution of alkalinity of the straws, mineralization of organic N and nitrification of NH_4^+. The incorporation of biochars produced from the crop straws increased soil pH and the ameliorating effects of biochars on soil pH clearly increased with increased biochar application rates. The biochars from legume straws induced greater increases in soil pH than non-legume biochars. Organic anions and CO_3^{2-} were the main forms of alkali in the biochars, and both can contribute to neutralize soil acidity and increase soil pH. The addition of both crop straws and their biochars decreased soil exchangeable acidity and exchangeable Al^{3+}, and increased soil exchangeable base cations and base saturation degree. The biochars (especially legumes) induced a greater decrease in soil exchangeable acidity and a greater increase in soil exchangeable base cations due to much higher contents of base cations relative to their feedstock. The values of biochar CEC were 10–20 times that of soil CEC and thus incorporation of biochar significantly increased soil CEC and retention of Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ by acid soils. The biochars from legume straws were better choices as amendments for acid soils.

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