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# Characteristics of biomass ashes from different materials and their ameliorative effects on acid soils

Renyong Shi<sup>1,2</sup>, Jiuyu Li<sup>1</sup>, Jun Jiang<sup>1</sup>, Khalid Mehmood<sup>1,2</sup>, Yuan Liu<sup>1,2</sup>, Renkou Xu<sup>1,\*</sup>, Wei Qian<sup>1</sup>

1. State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China. E-mail: [ryshi@issas.ac.cn](mailto:ryshi@issas.ac.cn)

2. University of Chinese Academy of Sciences, Beijing 100049, China

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## ABSTRACT

The chemical characteristics, element contents, mineral compositions, and the ameliorative effects on acid soils of five biomass ashes from different materials were analyzed. The chemical properties of the ashes varied depending on the source biomass material. An increase in the concrete shuttering contents in the biomass materials led to higher alkalinity, and higher Ca and Mg levels in biomass ashes, which made them particularly good at ameliorating effects on soil acidity. However, heavy metal contents, such as Cr, Cu, and Zn in the ashes, were relatively high. The incorporation of all ashes increased soil pH, exchangeable base cations, and available phosphorus, but decreased soil exchangeable acidity. The application of the ashes from biomass materials with a high concrete shuttering content increased the soil available heavy metal contents. Therefore, the biomass ashes from wood and crop residues with low concrete contents were the better acid soil amendments.

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## Introduction

The increase in CO<sub>2</sub> emissions has led to an increase in global temperatures. It is widely accepted that biomass energy is a renewable power source that does not release net CO<sub>2</sub> during the combustion process (Mckendry, 2002; Cherubini and Strømman, 2011). Currently, biomass energy contributes 8%–15% of the world energy supplies, including heat, electricity and fuels, and the contribution is predicted to rise to 33%–50% by 2050 (Vassilev et al., 2013). In 2005, the generating capacity from biomass combustion in China was about 2.0 gigawatt (GW), which is expected to rise to 24 GW in 2020. It has been reported that 5%–10% on a dry weight basis forms ash during biomass combustion (Wang et al., 2011). As biomass energy

becomes more wide spread, there will be increasing numbers of different biomass ashes produced. Hence, there is a need to reuse and manage biomass ash if the benefits to the economy, environment, and society brought about by biomass power generation are to be realized.

Previous studies have shown that biomass ashes from wood and crop straw not only contain some alkaline substances, but also contain high levels of nutrients, such as K, Ca, Mg, P, and trace elements (Etiegni and Campbell, 1991; Mozaffari et al., 2000). They could therefore be used to ameliorate soil acidity and increase soil nutrient contents (Muse and Mitchell, 1995; Nkana et al., 1998; Demeyer et al., 2001; Mozaffari et al., 2002; Park et al., 2005). However, these investigations just focused on the biomass ashes from single

\* Corresponding author. E-mail: [rkxu@issas.ac.cn](mailto:rkxu@issas.ac.cn) (Renkou Xu).

biomass fuel, such as wood ash, rather than from co-firing different bio-waste materials in biomass power plants. Biomass ashes showed clear variations in properties and composition due to the differences in the raw biomass materials (Werkelin et al., 2005, 2010; Vassilev et al., 2010). Thus, it is needed to study the various properties and composition of ashes how to affect their amelioration on acidic soils.

In the subtropical area of China, there is about 2.03 million km<sup>2</sup> of land covered in acid soils, which accounts for 22% of the total arable soil. Over recent decades, the acidification rate of the soil has been accelerated due to acid precipitation (Reuss and Johnson, 1986; Hu et al., 2007) and excess applications of NH<sub>4</sub><sup>+</sup> and R-NH<sub>2</sub> fertilizers to farmland (Bolan et al., 1991; Zhang et al., 2009; Guo et al., 2010). Aluminum (Al) toxicity and deficiencies of nutrients induced by soil acidification limit the growth of crops in acidic soils (Von Uexküll and Mutert, 1995). So, it would be a valuable and sustainable way if the plant ashes could be used as ameliorant for acid soils in southern China. On the other hand, it has also been reported that biomass ashes contain heavy metals to varying extents (Pastircakova, 2004; Wang et al., 2011; Williams et al., 2012; Vassilev et al., 2014; Saqib and Backstrom, 2015). To ensure environmental security of the ashes, the potential risk from these heavy metals has to be considered well when ashes were returned back to soils.

This study was designed to (1) examine the physicochemical properties of biomass ashes produced from different mixed biomass materials; (2) investigate the ameliorative effects of various biomass ashes on acid soils; and (3) evaluate the potential environmental risk of heavy metals in biomass ashes when they are applied as soil amendments. The results obtained in this study can provide practical, technical support for appropriate management programs, and will improve and increase the use of biomass ashes derived from the co-firing of mixed biofuels in power plants to ameliorate acidic soils.

## 1. Materials and methods

### 1.1. Soil samples and biomass ashes

Two acidic Ultisols were collected from Anhui and Guangdong Provinces. The soil samples were taken from the topsoil (0–15 cm), air-dried, and then ground to pass through a 2-mm sieve. The soils were then reserved for the incubation experiment. Some basic properties of the soils used are listed in Table 1. Soil pH was measured with Orion 720 pH meter (Orion Research Incorporated, Boston, Massachusetts, USA) in

a 1:2.5 solid:water suspension. Soil exchangeable H<sup>+</sup> and Al<sup>3+</sup> were extracted with 1.0 mol/L KCl and then titrated with 0.01 mol/L NaOH. Soil exchangeable base cations were extracted with 1.0 mol/L ammonium acetate. Ca<sup>2+</sup> and Mg<sup>2+</sup> in the extractants were measured with atomic absorption spectrophotometry (nov AA350, Analytik, Jena AG, Germany), and K<sup>+</sup> and Na<sup>+</sup> were measured using flame photometry (FP640, Aopu, Shanghai, China).

The ash samples were obtained from five power plants with circulating fluidized bed belonging to Sunshine Kaidi New Energy Group Co., Ltd. in China. Biomass ash-1 (BA-1), biomass ash-3 (BA-3) and biomass ash-5 (BA-5) were collected from power plants located in Chongqing, Hunan, and Hubei provinces, respectively, and biomass ash-2 (BA-2) and biomass ash-4 (BA-4) were collected from power plants located in Anhui Province. All samples are bottom ash, which were collected from ash pits. Each ash sample was collected from ten sites in the pit and mixed thoroughly. The biofuels burned were mainly a mixture of crop husks, woody byproducts and concrete shuttering. The same mixed waste biofuels were used during the total combustion process. The specific compositions of the ashes are shown in Table 2.

### 1.2. Analyses of the properties and compositions of the biomass ashes

The pH and electrical conductivity (EC) of the biomass ashes (BA) were measured in suspensions with a solid:water ratio of 1:5 by an Orion 720 pH meter (Orion Research Incorporated, Boston, Massachusetts, USA) and an EC 215 conductivity meter (Hanna instruments, Padova, Italy), respectively. The acid–base titration curves of the biomass ashes were measured using an automatic titrator (T50 Titrator, Mettler Toledo, Urdorf, Switzerland), which titrated a 60 mL suspension containing 0.250 g biomass ashes to pH 2.5 using 0.2 mol/L HNO<sub>3</sub>. The acid consumptions down to pH 5.0 were regarded as the acid neutralization capacities (ANC) of the biomass ashes (Wong et al., 1998). The biomass ashes were digested in a mixture of HF–HClO<sub>4</sub>–HNO<sub>3</sub> and dissolved by HNO<sub>3</sub> to determine the K, Na, Ca, Mg, Fe, Mn and P contents using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, VISTA-MPX, Varian, Palo Alto, California, USA), and Cr, Pb, Ni, Cu, Zn, Co, Mo and Cd were analyzed by ICP-mass spectrometry (VG PQ II Agilent 7500a, Agilent, California, USA). Mercury, arsenic and selenium levels in the biomass ashes were measured by atomic fluorescence spectrometry (AFS3300, Beijing Titan Instruments Co. Ltd., Beijing, China) after microwave digestion with HNO<sub>3</sub>. To evaluate the solubility of nutritional ions in the biomass ashes, 0.200 g biomass ash was leached with 20 mL distilled

Table 1 – Basic properties of Ultisols used.

Location	Utilization	pH	OM (g/kg)	CEC	Exchangeable acidity	Exchangeable base cations (cmol <sub>(+)</sub> /kg)				BS (%)
						K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	
Anhui	Farmland	4.60	18.0	14.3	4.59	0.31	0.34	3.16	0.63	49.17
Guangdong	Forest	4.56	11.9	8.1	3.19	0.02	0.17	0.15	0.10	12.12

OM: organic matter; CEC: cation exchange capacity; BS: base saturation.

**Table 2 – Biomass material compositions for the different biomass ashes.**

Biomass ash	Location of power plant	Composition of biomass materials (%)			
		Crop husk	Woody byproduct	Concrete shuttering	Others
BA-1	Fengdu, Chongqing Province	25	10	65	0
BA-2	Huoshan, Anhui Province	33.3	33.3	33.3	0
BA-3	Shuangfeng, Hunan Province	30	70	0	0
BA-4	Nanling, Anhui Province	15	55	25	5
BA-5	Songzi, Hubei Province	40	40	20	0

BA-1: biomass ash-1; BA-2: biomass ash-2; BA-3: biomass ash-3; BA-4: biomass ash-4; BA-5: biomass ash-5.

water five times, and the leachates were collected together. The  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  in the leachates were measured by ICP-AES as the soluble base cations of ashes. The total C and N in the biomass ashes were measured by a Leco CN-2000 carbon and nitrogen analyzer (Leco Corp., St. Joseph, MI, USA).

X-ray diffraction (XRD) analyses of the biomass ashes were conducted using a Rigaku X-ray diffractometer equipped with an incident beam graphite monochromator (Rigaku, D/max-IIIIC, Tokyo, Japan), using Cu  $K\alpha$  radiation generated at 40 kV and 20 mA. The identification of the main crystalline phase was performed using the JADE 6.0 software package (MDI, Livermore, CA, USA) and the PDF2-2004 diffraction database.

Fourier Transform Infrared Spectra (FT-IR) of the biomass ashes were recorded using KBr pellets of the ash samples in the  $4000\text{--}400\text{ cm}^{-1}$  range on a Thermo Nicolet Avatar 380 FT-IR spectrophotometer (Thermo Fisher Scientific, San Jose, California, USA).

### 1.3. Experimental design

Exactly 300 g of the air-dried soil samples were thoroughly mixed with 2.40 g biomass ashes (0.8%) and then placed in plastic beakers. Then they were wetted with deionized water to reach 70% of the field water-holding capacity of the treatments with and without each biomass ash. There were three replicates for each treatment. All the beakers were covered with plastic film to avoid moisture loss, but there was a small hole to allow gas exchange. The incubation was conducted in an incubator at a constant temperature of  $25^\circ\text{C}$  for 58 days. During the incubation, soil moisture was controlled to the constant value with distilled water every three days.

During the incubation, sub-samples were taken at 1, 3, 7, 14, 21, 28, 35, and 58 days from each beaker to measure soil pH in a 1:2.5 solid:water suspension using an Orion 720 pH meter. The data were used to show the changes in pH. After incubation, soil exchangeable  $H^+$  and  $Al^{3+}$ , and soil exchangeable base cations were extracted and determined with the same methods as mentioned above. The available P was extracted by  $NH_4F\text{--}HCl$  solution and determined by ascorbic acid- $NH_4\text{--}molybdate$  blue colorimetry at 700 nm. The available heavy metals in the soil samples were measured by ICP-AES after extraction with 1 mol/L HCl.

### 1.4. Statistical analysis

The SPSS 20.0 software package (SPSS Inc., Chicago, IL, USA) was used for statistical analysis. A one-way analysis of variance (ANOVA) was used to test for significant differences

among the treatments. The means were compared by a least significant difference (LSD) test at  $p < 0.05$ .

## 2. Results and discussion

### 2.1. Basic properties and compositions of the different biomass ashes

The basic properties and elemental compositions of the ash samples are summarized in Table 3. The five biomass ashes

**Table 3 – Chemical properties and elemental contents of biomass ashes.**

Properties and composition	BA-1	BA-2	BA-3	BA-4	BA-5
pH	11.89	12.61	12.09	12.53	12.55
Electric conductivity (mS/cm)	21.33	9.49	13.92	7.95	6.79
ANC (mol/kg)	5.32	2.68	0.39	0.79	1.01
Total C (%)	0.80	1.00	0.43	0.86	1.71
Total N (%)	ND	ND	ND	ND	ND
Total content					
Ca (g/kg)	218.26	76.69	63.72	58.95	47.53
Mg (g/kg)	26.99	19.75	9.94	7.94	13.30
K (g/kg)	46.25	29.59	56.14	37.35	24.28
Na (g/kg)	11.37	8.63	3.31	6.78	3.41
P (g/kg)	2.11	2.84	5.63	3.10	3.43
Fe (g/kg)	18.05	18.22	16.38	18.27	16.64
Mn (g/kg)	1.03	1.06	3.84	1.77	1.33
Al (g/kg)	17.57	35.85	20.49	22.56	26.26
Cr (mg/kg)	93.76	37.32	139.63	32.91	37.73
Cd (mg/kg)	3.90	2.18	2.54	2.58	4.14
Cu (mg/kg)	82.58	47.45	44.32	64.39	36.58
Co (mg/kg)	22.15	8.13	7.95	7.07	7.58
Ni (mg/kg)	24.73	21.78	30.57	19.76	18.20
Zn (mg/kg)	643.00	456.32	253.92	323.91	131.55
Mo (mg/kg)	5.09	2.02	3.79	4.67	4.00
Pb (mg/kg)	276.80	66.70	34.30	102.99	31.05
Hg (mg/kg)	ND	0.19	0.24	0.13	0.16
As (mg/kg)	21.72	10.04	17.47	19.31	16.18
Se (mg/kg)	1.37	0.84	0.40	1.25	0.77
Water extractable (g/kg)					
Ca	37.53	31.34	5.16	12.01	11.74
Mg	0.04	0.05	0.14	0.08	0.23
K	41.44	1.77	25.07	4.42	0.56
Na	7.75	0.35	0.70	0.79	0.09

ANC: acid neutralization capacity; ND: not determined.

were all alkaline. BA-2 had the highest pH (12.61) and BA-1 had the lowest pH (11.89). The variation in pH among the different biomass ashes was small. However, clear ANC differences were observed between the different biomass ashes. The BA-1 ANC was much greater than the other four ashes, whereas the BA-3 ANC was much smaller than the other four ashes (Table 3). These data demonstrated that the biomass ash pHs did not fully reflect their alkalinity and that ANC more accurately predicted the liming potential of the biomass ashes. The ash ANCs had significant linear positive correlations ( $R^2 = 0.90$ ) to the concrete shuttering content in the biomass materials (Table 2). Therefore, the concrete shuttering content of the biomass materials made a major contribution to the biomass ash ANCs due to the concrete residues left behind in the ash after biomass combustion. One major component of concrete is CaO, which increases the alkalinity of biomass ashes that contain concrete.

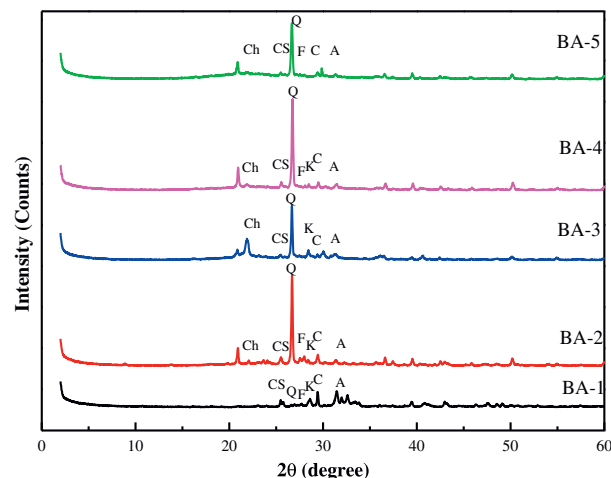
The five biomass ashes contained high levels of Ca, Mg, K, and P, which is very useful when ameliorating acid soils. However, their contents varied in the ashes (Table 3). The Ca and Mg contents in BA-1 and BA-2 were higher than those in the other three ashes, and this was due to the higher concrete shuttering contents in their biomass materials and the high Ca and Mg levels in concrete. The K contents in the biomass materials varied from 24.28 to 56.14 g/kg. BA-3 had the highest K content due to higher levels of wood and crop residues in the biomass material (Vassilev et al., 2010). The P content in the biomass ashes varied from 2.11 to 5.63 g/kg. It was much greater in BA-3 than the others, which indicated that wood and crop residue materials could increase P accumulation in biomass ashes. The electrical conductivity (EC) of the biomass ashes reflected the soluble salt contents in the ashes. The ECs of the five ashes followed the order: BA-1 > BA-3 > BA-2 > BA-4 > BA-5 and was related to the base cation contents, especially K and Na. This is because the solubility of K- and Na-containing compounds are higher than Ca- and Mg-containing compounds.

The heavy metal contents also varied. BA-1 contained more heavy metals, especially Cu, Co, Zn and Pb, than the other ashes, and this was mainly due to the concrete residue content. In contrast, BA-5, which had the highest percentage of crop residues in the raw material, contained the least heavy metals. Thus, during the generation of electricity, biomass fuels that include crop straws would help control the level of heavy metals in biomass ashes. The heavy metal contents in the five biomass ashes, except for Zn in BA-1, were all less than the standard limits for the application of sewage sludge to agricultural soils in China (GB4284-1984). Furthermore, the heavy metal contents of all the biomass products, including Zn in BA-1, were below the standard limits for the application of sewage sludge to agricultural soils in the European Union (Commission of the European Communities, 1986).

The total C in all ashes was very low and varied from 0.43% to 1.71%, which implied that the biomass had been efficiently combusted during the generation of electricity. No N was detected in any of the biomass ashes.

## 2.2. XRD analyses of biomass ashes

The XRD spectra of the different biomass ashes are shown in Fig. 1. The mineral compositions of BA-2 to BA-5 were similar.



**Fig. 1 – X-ray diffraction spectra of the different biomass ashes. Ch: christobalite; CS: CaSO<sub>4</sub>; Q: quartz; F: feldspar; K: KCl; C: calcite; A: apatite.**

They contained considerable amounts of crystalline quartz mineral and a little calcite, apatite, CaSO<sub>4</sub>, and KCl (Table 4), which was consistent with the elemental composition of biomass ashes (Table 3). Some studies have reported that the large number of silica minerals in biomass ashes is mainly generated by biomass materials that contain silicon, such as rice husk (Thy et al., 2006). Although the four biomass ashes contained some K, little crystal KCl was detected by the XRD analysis (Table 4). This may be due to the interaction between most K compounds and silicates, which then melt into the glass phase (Wang et al., 2011). Apatite and calcite were observed in BA-1 primarily, which was different from the XRD spectra of the other four ashes (Table 4). This correlated with the high Ca content in the ash (Table 3). The Ca in the ash mainly came from the concrete residues in the biomass materials. Although BA-1 contained large amounts of Ca, dissoluble Ca only accounted for 19% of the total Ca in the ash due to its mineral crystal stability. In general, silica minerals, such as quartz, easily form when rice husk and other silica containing crop residues are present, while the presence of concrete shuttering probably induced calcium-containing crystal minerals to form, such as apatite, calcite, and calcium sulfate. These components are all useful during acid soil amelioration.

## 2.3. FTIR study of biomass ashes

The FT-IR spectra of the five biomass ashes are shown in Fig. 2. For BA-2, BA-3, BA-4, and BA-5, the central prominent peaks at 1100 cm<sup>-1</sup> were attributed to Si–O–Si asymmetric stretching, and the second-highest peaks, at around 470 cm<sup>-1</sup>, were caused by Si–O and Al–O in-plane flexural vibration modes (Chindapasirt et al., 2009). The peaks in the four ashes at 792 cm<sup>-1</sup> corresponded to Si–O–Si symmetrical stretching in the framework structures (Majchrzak-Kucęba and Nowak, 2011). A strong peak at 1125 cm<sup>-1</sup> appeared in the



**Table 4 – Primary mineral composition of biomass ashes.**

Biomass ash	Primary mineral composition (%)						
	Calcite	Apatite	KCl	CaSO <sub>4</sub>	Feldspar	Quartz	Christobalite
BA-1	12	68	4	10	4	2	–
BA-2	8	4	1	10	15	61	1
BA-3	3	13	3	5	–	48	28
BA-4	6	6	2	8	1	73	4
BA-5	9	3	–	6	4	74	4

–: not detected.

BA-1 spectrum, but there were no peaks at 470 and 792  $\text{cm}^{-1}$ , which suggested that little silica mineral and much more apatite were observed in BA-1 XRD spectrum. Thus, the peak at 1125  $\text{cm}^{-1}$  for BA-1 may be due to the P–O asymmetrical stretching of pyrophosphate. There were considerably weak peaks at 3000–3500  $\text{cm}^{-1}$  in all the spectra, which corresponded to the –OH functional group. This may be due to the presence of water in the ashes (Chindaprasirt et al., 2009). The peaks at 876, 1424, and 712  $\text{cm}^{-1}$  in the BA-1, BA-2, and BA-4 spectra match the out-of-plane bend, asymmetric stretch, and the in-plane bend mode for powdered CaCO<sub>3</sub>, which suggests that these three ashes contained some Ca, K and Mg carbonates (Ohno, 1992). The peak around 1400  $\text{cm}^{-1}$  in the BA-3 and BA-5 spectra could be due to sulfate S–O vibrations (Abraham et al., 2013). There were a few peaks in the 700–500  $\text{cm}^{-1}$  range in the BA-1 spectrum, which were associated with Cu–O and Zn–O vibrations and reflected the high heavy metal content in BA-1. The lack of a carbon functional group absorption peak in all five ashes showed that the biomass materials had been efficiently combusted.

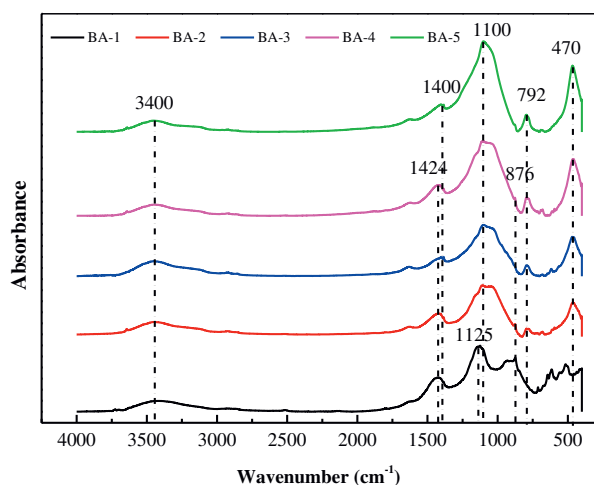
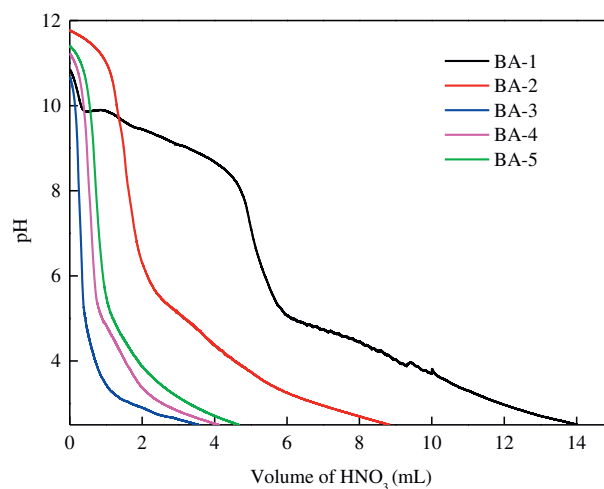
#### 2.4. Acid–base titration curves for the biomass ashes

The H<sup>+</sup> consumption and its influence on different biomass ashes were examined because the pH of biomass ashes did not reflect their ANC values (Table 3). The acid–base titration curves of the ashes were measured by an automatic titrator. The pH changes in the acid–base titration curves were similar for BA-3, BA-4, and BA-5 (Fig. 3). The pH of the suspensions

decreased slowly at the beginning. As the addition of H<sup>+</sup> increased, the pH dropped rapidly between pH 11 and 5, which suggested that these ashes had a relatively low buffering capacity for acids. These three ashes consumed 0.43, 0.89, and 1.19 mL HNO<sub>3</sub>, respectively, when the pH declined to 5.0. The decline in pH was relatively slow below pH 5.0, which showed that these ashes had a relatively high buffering capacity in this pH range compared to the other pH ranges. When the system pH decreased from 5.0 to 2.5, a total of 3.18, 3.22, and 3.47 mL HNO<sub>3</sub>, respectively, were consumed and there was little difference between the three ashes, which indicated that their acid buffering capacities were similar in this pH range.

The pH changes in the acid–base titration curve of BA-2 were similar to BA-3, BA-4, and BA-5 (Fig. 3), but more acid was consumed by BA-2 than the other three ashes. A total of 3.18 mL HNO<sub>3</sub> was consumed by BA-2 when the pH decreased to 5.0, and 5.64 mL was consumed when the pH decreased from 5.0 to 2.5. These results suggested that the acid buffering capacity of BA-2 was greater than BA-3, BA-4, and BA-5, which may be due to the higher concrete shuttering content in the BA-2 biomass materials.

The acid–base titration curve for BA-1 was different from the titration curves for the other four ashes. The pH decreased rapidly at the beginning to 10.0 and then a plateau region occurred between pH 10.0 and 8.0, which suggested that BA-1 had a relatively higher acid buffering capacity in this pH range. The 4.14 mL HNO<sub>3</sub> consumed by BA-1 in this pH range

**Fig. 2 – FT-IR spectra of the different biomass ashes.****Fig. 3 – Acid–base titration curves for the different biomass ashes.**

was much greater than BA-2, BA-3, BA-4, and BA-5, which were 0.11, 0.33, 0.16, and 0.18 mL, respectively. Between pH 8.0 and 5.0, the BA-1 pH declined rapidly, and then slowly between pH 5.0 and 2.5. These change trends were similar to the other four ashes, but the  $\text{HNO}_3$  consumed by BA-1 (7.89 mL) was much greater than other four ashes. The greater acid buffering capacity of BA-1 was probably due to the higher concrete shuttering content in the BA-1 biomass materials.

## 2.5. Effects of different biomass ashes on soil pH

During incubation, the pH increased considerably on the first day and then the pH variation was small for both Ultisols when BA-1, BA-2, and BA-5 were added (Fig. 4), which demonstrated that the alkali in these three ashes neutralized the acidity of the soils within one day. In the BA-3 and BA-4 treatments that used the Ultisol from Guangdong, the soil pH increased gradually with the number of incubation days until the 21st day and then the rate of change fell, which suggested that the release of alkali from BA-3 and BA-4 was slower than for the other three ashes. A similar trend was also observed when BA-3 was added to the Ultisol from Anhui.

At the end of incubation, all five biomass ashes had increased the pH of the Ultisols compared to the control (Fig. 4). The amelioration effects of the different ashes were as follows: BA-1 > BA-2 > BA-3  $\approx$  BA-4  $\approx$  BA-5. The increases in

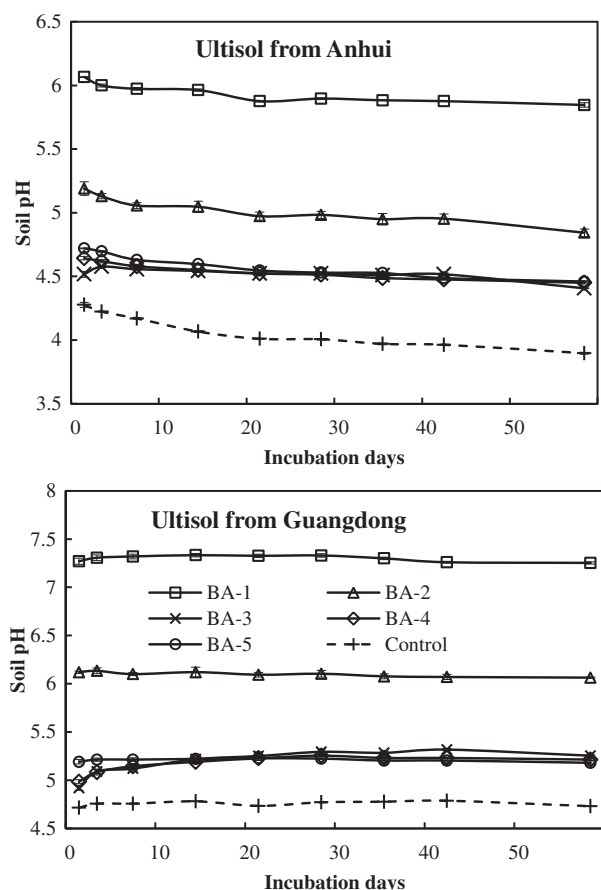
soil pH induced by the different ashes were significantly correlated to their ANCs, which indicated that the ANC of biomass ashes represented their ability to ameliorate soil acidity better than their pH. When the same biomass ash was incorporated, the soil pH increase in the Ultisol from Guangdong was greater than for the Ultisol from Anhui, which was probably due to the higher pH buffering capacity (pHBC) of the latter. The pHBCs were 32.44 and 25.01 mmol/(kg·pH) for the Ultisols from Anhui and Guangdong, respectively, which were consistent with the CECs of the soils (Table 1) because CEC was the main factor determining the pHBC of these variable charge soils (Xu et al., 2012).

## 2.6. Effects of biomass ashes on soil exchangeable acidity and exchangeable base cations

Table 5 shows that the soil exchangeable acidity was significantly reduced ( $p < 0.05$ ) after the addition of all the five biomass ashes to the two Ultisols. The greatest decrease in soil exchangeable acidity was observed in the BA-1 treatment, which decreased by 97.64% and 97.03% for the two Ultisols, respectively, followed by BA-2. The effectiveness of the other three ashes was similar. This order was in accordance with magnitude of increase in soil pH. Biomass ashes mainly contributed to reductions in soil exchangeable  $\text{Al}^{3+}$ , since the exchangeable acidity in these acid soils mainly existed as exchangeable  $\text{Al}^{3+}$  and the percentage of exchangeable  $\text{H}^+$  in the exchangeable acidity was very low (Table 5). The alkali in the biomass ashes neutralized soil acidity and increased soil pH, which then promoted the hydrolysis and precipitation of soil exchangeable aluminum. As a consequence, the soil exchangeable  $\text{Al}^{3+}$  decreased significantly or even disappeared from these soils (Li et al., 2010).

The total soil exchangeable base cation number increased significantly ( $p < 0.05$ ) in all the treatments compared to the control (Table 5), and exchangeable  $\text{Ca}^{2+}$  made the largest contribution because the five ashes contained more Ca than K, Na, and Mg. BA-1 induced the greatest increases in exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the soils, which rose by 13.4 and 20.5 times, respectively, for  $\text{Ca}^{2+}$  and by 6.6 and 13.5 times, respectively, for  $\text{Mg}^{2+}$  in the two Ultisols compared with controls. This was because BA-1 had the highest Ca and Mg contents. BA-3 induced the largest increases in soil exchangeable  $\text{K}^+$  because it had the highest K content (Table 3). There was a significant positive correlation between the Ca, Mg, and K contents in each ash and the relevant exchangeable base cations of the soils amended with the ashes. This suggested that the improvement to exchangeable base cations was mainly due to the release of Ca, Mg, and K from the ashes. When these biomass ashes were incorporated into acidic soils, the base cations exchanged with soil exchangeable  $\text{Al}^{3+}$  and released some of the exchangeable  $\text{Al}^{3+}$  into the soil solution. The alkali from the ashes promoted the hydrolysis and precipitation of the exchangeable  $\text{Al}^{3+}$ . This was induced by the increase in soil pH, which was the main mechanism underlying the reduction in soil exchangeable  $\text{Al}^{3+}$  caused by the biomass ashes.

Soil exchangeable base cations increased sharply after ash addition, which meant that the effective CEC (ECEC) of the two Ultisols significantly rose despite the decrease in exchangeable  $\text{Al}^{3+}$ . BA-1 induced the largest increase in soil



**Fig. 4 – Soil pH dynamics during the incubation of acid Ultisols from Anhui and Guangdong containing the different biomass ashes.**

**Table 5 – Effect of different biomass ashes on exchangeable base cations and exchangeable acidity of Ultisols from Anhui and Guangdong provinces, China (unit: cmol<sub>(+)</sub>/kg).**

Soil	Treatment	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	H <sup>+</sup>	Al <sup>3+</sup>	ECEC
Ultisol from Anhui	Control	0.36 ± 0.017d <sup>*</sup>	0.07 ± 0.017e	0.76 ± 0.029e	0.28 ± 0.003k	0.32 ± 0.008a	4.35 ± 0.012a	6.14 ± 0.047e
	BA-1	0.94 ± 0.017b	0.63 ± 0.60a	10.95 ± 0.322a	2.13 ± 0.014a	0.07 ± 0.006fg	0.04 ± 0.016hi	14.76 ± 0.369a
	BA-2	0.56 ± 0.017c	0.12 ± 0.017de	4.25 ± 0.082b	1.56 ± 0.029b	0.19 ± 0.034cde	0.72 ± 0.094e	7.39 ± 0.120cd
	BA-3	1.11 ± 0.017a	0.13 ± 0.033de	3.82 ± 0.159b	0.72 ± 0.006g	0.23 ± 0.010bcd	1.79 ± 0.067d	7.80 ± 0.243c
	BA-4	0.58 ± 0.000c	0.28 ± 0.060c	3.30 ± 0.095c	0.63 ± 0.008h	0.29 ± 0.033ab	2.48 ± 0.128b	7.55 ± 0.127cd
	BA-5	0.53 ± 0.000c	0.08 ± 0.017de	2.99 ± 0.200cd	1.01 ± 0.019e	0.27 ± 0.039ab	2.13 ± 0.109c	7.01 ± 0.222d
Ultisol from Guangdong	Control	0.16 ± 0.017f	0.07 ± 0.017e	0.49 ± 0.025e	0.10 ± 0.017l	0.25 ± 0.057abc	2.11 ± 0.049c	3.18 ± 0.031g
	BA-1	0.93 ± 0.029b	0.38 ± 0.044b	10.52 ± 0.306a	1.46 ± 0.017c	0.05 ± 0.000g	0.02 ± 0.016i	13.36 ± 0.378b
	BA-2	0.29 ± 0.017e	0.08 ± 0.017de	3.90 ± 0.154b	1.29 ± 0.018d	0.13 ± 0.006ef	0.18 ± 0.024ghi	5.88 ± 0.178e
	BA-3	0.89 ± 0.017b	0.08 ± 0.017de	2.85 ± 0.191cd	0.49 ± 0.024i	0.16 ± 0.017de	0.24 ± 0.016fgh	4.72 ± 0.201f
	BA-4	0.39 ± 0.017d	0.18 ± 0.017d	3.10 ± 0.043c	0.42 ± 0.004j	0.22 ± 0.003bcd	0.32 ± 0.014fg	4.63 ± 0.062f
	BA-5	0.16 ± 0.017f	0.13 ± 0.033de	2.47 ± 0.068d	0.81 ± 0.000f	0.22 ± 0.012bcd	0.43 ± 0.074f	4.23 ± 0.08f

ECEC: effective cation exchange capacity.

<sup>\*</sup> The different letters within the same column indicated the significant differences between the means for each soils ( $p < 0.05$ ).

ECEC. This increase was 1.4 and 3.2-fold for the two Ultisols, respectively. The increase in soil ECEC will enhance the ability of the soils to retain nutrients. Therefore, the ash from concrete containing materials not only increased soil exchangeable base cations and ECEC, due to the high Ca and Mg contents in the ash, but also considerably reduced the exchangeable Al<sup>3+</sup>.

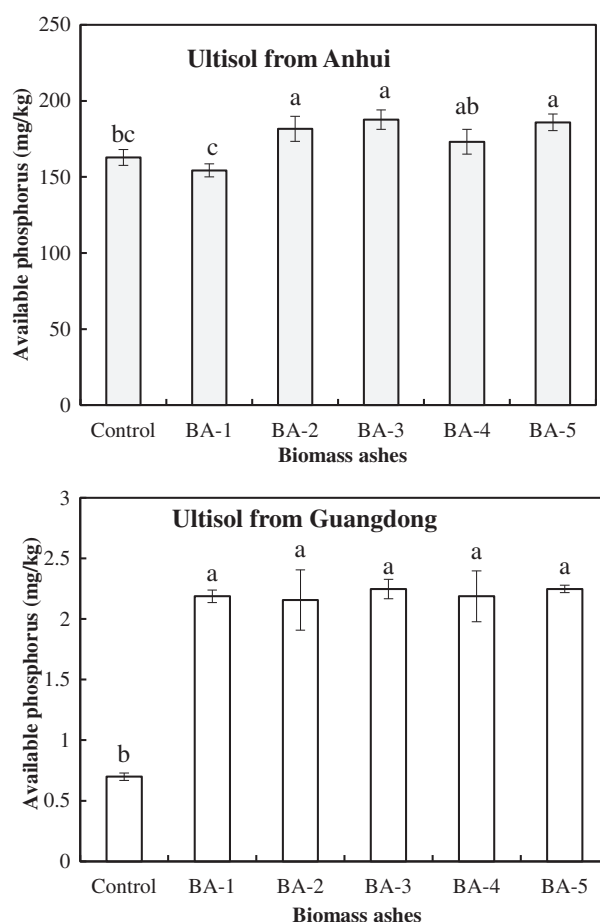
## 2.7. Effects of biomass ashes on soil available P

When BA-2, BA-3, or BA-5 was added to the Ultisol from Anhui, the soil available P content rose significantly compared to the control ( $p < 0.05$ ). However, the differences among these three treatments were not significant (Fig. 5). BA-1 and BA-4 did not increase soil available P significantly. There was even a slight decrease after the BA-1 treatment. The available P in the Ultisol from Guangdong also increased when it was treated with the five biomass ashes compared to the control ( $p < 0.05$ ), and the differences among the treatments were also not significant (Fig. 5). Two possible mechanisms may be responsible for the increase in soil available P induced by biomass ashes. First, the P in ashes is released into soils directly, which would increase available P, and/or the increased soil pH caused by the application of these ashes led to a release of P from Fe-P and Al-P in the acid soils (Arai and Sparks, 2007). The opposite effect of BA-1 on available P in the Anhui Ultisol compared to the Guangdong Ultisol may be due to the higher P content in the Anhui Ultisol. When BA-1 was applied to the Anhui Ultisol, the exchangeable Ca<sup>2+</sup> increased sharply and led to some P being transformed into Ca-P due to the higher P content in Anhui Ultisol, which decreased soil available P, whereas the lower P content in the Guangdong Ultisol did not lead to similar transformations in the soil.

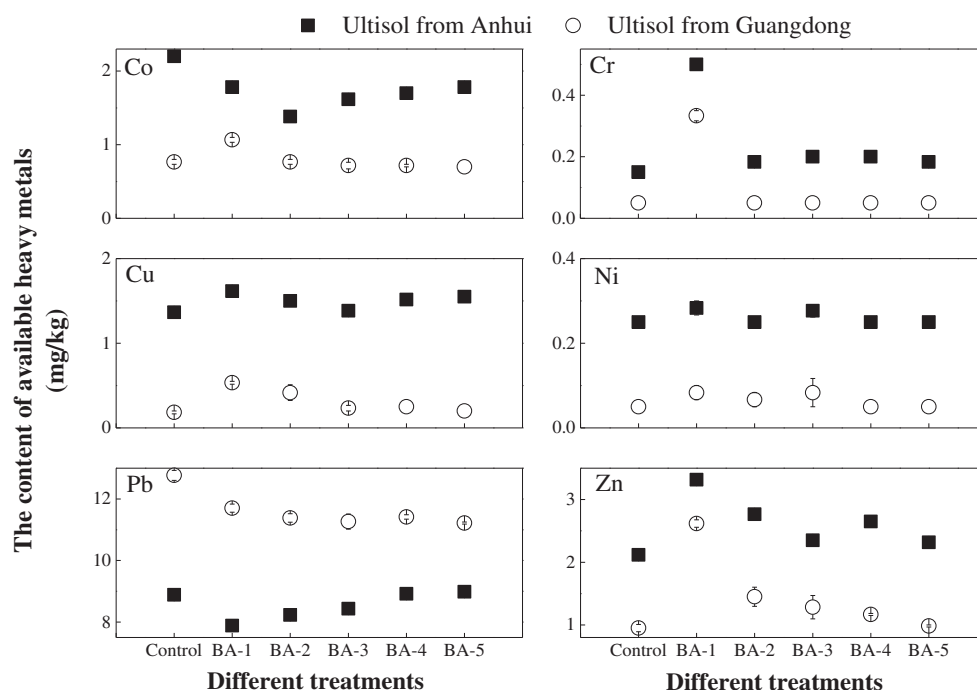
## 2.8. Effects of biomass ashes on available heavy metals

Incorporation of BA-1 clearly increased the available heavy metals levels in the two soils, especially available Cr, Cu, and Zn, because BA-1 contained relatively high amounts of these metals. However, the other four ashes only had a small effect on available heavy metals (Fig. 6). Although all the five ashes

contained a certain amount of Pb, the available Pb in the soils did decrease significantly after these ashes were applied to the two Ultisols. The application of these ashes also decreased the available Co in the Anhui Ultisol, which may be due to the



**Fig. 5 – Effects of incorporating the different biomass ashes on available phosphorus in Ultisols from Anhui and Guangdong. Different letters on pillars indicated significant differences among treatments ( $P < 0.05$ ).**



**Fig. 6 – Effects of incorporating the different biomass ashes on the available heavy metal contents in the two Ultisols from Anhui and Guangdong.**

increased soil pH after ash addition (Sungur et al., 2014). The available Co and Ni in the two soils did not increase significantly after the addition of the ashes because of the low Co and Ni contents in the five ashes.

A comparison of the biomass ashes from the husks of crop and woody byproducts showed that BA-1 considerably increased the available heavy metal levels in the soils, which was probably due to the high heavy metal contents in the ash. This could lead to an increased heavy metal risk if it was used to ameliorate acidic soils.

### 3. Conclusions

The alkali contents, element composition, and mineral components of biomass ashes from five power plants varied depending on biomass materials. Five biomass ashes ameliorated soil acidity and significantly increased the Ca, Mg, K, and P contents in the two acidic Ultisols. The higher residual concrete levels in BA-1 ash led to more alkaline substances, greater ameliorative effects on soil acidity than the other ashes, but it increased the soil available Cr, Cu, and Zn heavy metal contents. Therefore, the ashes from biomass materials containing wood and crop residues with low concrete contents are a better choice for acid soil amendment.

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