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

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43 Introduction

ABSTRACT

The chemical characteristics, element contents, mineral compositions, and the ameliorative 17 effects on acid soils of five biomass ashes from different materials were analyzed. The 18 chemical properties of the ashes varied depending on the source biomass material. An 19 increase in the concrete shuttering contents in the biomass materials led to higher alkalinity, 20 and higher Ca and Mg levels in biomass ashes, which made them particularly good at 21 ameliorating effects on soil acidity. However, heavy metal contents, such as Cr, Cu, and Zn in 22 the ashes, were relatively high. The incorporation of all ashes increased soil pH, exchangeable 30 base cations, and available phosphorus, but decreased soil exchangeable acidity. The 31 application of the ashes from biomass materials with a high concrete shuttering content 32 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. 34

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The increase in CO₂ 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 CO₂ 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 56 of different biomass ashes produced. Hence, there is a need to 57 reuse and manage biomass ash if the benefits to the economy, 58 environment, and society brought about by biomass power 59 generation are to be realized. 60

Previous studies have shown that biomass ashes from 61 wood and crop straw not only contain some alkaline 62 substances, but also contain high levels of nutrients, such as 63 K, Ca, Mg, P, and trace elements (Etiegni and Campbell, 1991; 64 Mozaffari et al., 2000). They could therefore be used to 65 ameliorate soil acidity and increase soil nutrient contents 66 (Muse and Mitchell, 1995; Nkana et al., 1998; Demeyer et al., 67 2001; Mozaffari et al., 2002; Park et al., 2005). However, these 68 investigations just focused on the biomass ashes from single 69

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biomass fuel, such as wood ash, rather than from co-firing 70 different bio-waste materials in biomass power plants. 71 72Biomass ashes showed clear variations in properties and composition due to the differences in the raw biomass 73 materials (Werkelin et al., 2005, 2010; Vassilev et al., 2010). 74 Thus, it is needed to study the various properties and com-75 position of ashes how to affect their amelioration on acidic 76 soils. 77

78 In the subtropical area of China, there is about 2.03 million km² of land covered in acid soils, which accounts 79 for 22% of the total arable soil. Over recent decades, the 80 acidification rate of the soil has been accelerated due to acid 81 precipitation (Reuss and Johnson, 1986; Hu et al., 2007) and 82 excess applications of NH⁺₄ and R-NH₂ fertilizers to farmland 83 (Bolan et al., 1991; Zhang et al., 2009; Guo et al., 2010). 84 Aluminum (Al) toxicity and deficiencies of nutrients induced 85 by soil acidification limit the growth of crops in acidic soils 86 (Von Uexküll and Mutert, 1995). So, it would be a valuable and 87 sustainable way if the plant ashes could be used as ameliorant 88 for acid soils in southern China. On the other hand, it has also 89 been reported that biomass ashes contain heavy metals to 90 varying extents (Pastircakova, 2004; Wang et al., 2011; 91 Williams et al., 2012; Vassilev et al., 2014; Saqib and 92 93 Backstrom, 2015). To ensure environmental security of the ashes, the potential risk from these heavy metals has to be 94 95 considered well when ashes were returned back to soils.

96 This study was designed to (1) examine the physicochem-97 ical properties of biomass ashes produced from different mixed biomass materials; (2) investigate the ameliorative 98 effects of various biomass ashes on acid soils; and (3) evaluate 99 the potential environmental risk of heavy metals in biomass 100 ashes when they are applied as soil amendments. The results 101 obtained in this study can provide practical, technical support 102for appropriate management programs, and will improve and 103 increase the use of biomass ashes derived from the co-firing 104 of mixed biofuels in power plants to ameliorate acidic soils. 105

106 1. Materials and methods

108 **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^+ and Al^{3+} 116 were extracted with 1.0 mol/L KCl and then titrated with 117 0.01 mol/L NaOH. Soil exchangeable base cations were ex- 118 tracted with 1.0 mol/L ammonium acetate. Ca^{2+} and Mg^{2+} in 119 the extractants were measured with atomic absorption 120 spectrophotometry (nov AA350, Analytik, Jena AG, Germany), 121 and K⁺ and Na⁺ were measured using flame photometry 122 (FP640, Aopu, Shanghai, China). 123

The ash samples were obtained from five power plants 124 with circulating fluidized bed belonging to Sunshine Kaidi 125 New Energy Group Co., Ltd. in China. Biomass ash-1 (BA-1), 126 biomass ash-3 (BA-3) and biomass ash-5 (BA-5) were collected 127 from power plants located in Chongqing, Hunan, and Hubei 128 provinces, respectively, and biomass ash-2 (BA-2) and bio-129 mass ash-4 (BA-4) were collected from power plants located in 130 Anhui Province. All samples are bottom ash, which were 131 collected from ash pits. Each ash sample was collected from 132 ten sites in the pit and mixed thoroughly. The biofuels burned 133 were mainly a mixture of crop husks, woody byproducts 134 and concrete shuttering. The same mixed waste biofuels 135 were used during the total combustion process. The specific 136 compositions of the ashes are shown in Table 2.

1.2. Analyses of the properties and compositions of the138biomass ashes139

The pH and electrical conductivity (EC) of the biomass ashes 140 (BA) were measured in suspensions with a solid:water ratio of 141 1:5 by an Orion 720 pH meter (Orion Research Incorporated, 142 Boston, Massachusetts, USA) and an EC 215 conductivity meter 143 (Hanna instruments, Padova, Italy), respectively. The acid-base 144 titration curves of the biomass ashes were measured using 145 an automatic titrator (T50 Titrator, Mettler Toledo, Urdorf, 146 Switzerland), which titrated a 60 mL suspension containing 147 0.250 g biomass ashes to pH 2.5 using 0.2 mol/L HNO₃. The acid 148 consumptions down to pH 5.0 were regarded as the acid 149 neutralization capacities (ANC) of the biomass ashes (Wong 150 et al., 1998). The biomass ashes were digested in a mixture of 151 HF-HClO₄-HNO₃ and dissolved by HNO₃ to determine the K, 152 Na, Ca, Mg, Fe, Mn and P contents using inductively coupled 153 plasma-atomic emission spectroscopy (ICP-AES, VISTA-MPX, 154 Varian, Palo Alto, California, USA), and Cr, Pb, Ni, Cu, Zn, Co, Mo 155 and Cd were analyzed by ICP-mass spectrometry (VGPQII 156 Agilent 7500a, Agilent, California, USA). Mercury, arsenic and 157 selenium levels in the biomass ashes were measured by atomic 158 fluorescence spectrometry (AFS3300, Beijing Titan Instruments 159 Co. Ltd., Beijing, China) after microwave digestion with HNO₃. 160 To evaluate the solubility of nutritional ions in the biomass 161 ashes, 0.200 g biomass ash was leached with 20 mL distilled 162

t1.1	Table 1 – Basic properties of Ultisols used.											
t1.3 t1.4	Location	Utilization	рН	OM (g/kg)	CEC	Exchangeable acidity	Exchangeable base cations (cmol ₍₊₎ /kg)				BS (%)	
							K+	Na+	Ca ²⁺	Mg ²⁺		t1.5
t1.6	Anhui	Farmland	4.6	18	14.3	4.59	0.31	0.34	3.16	0.63	49.17	
t1.7	Guangdong	Forest	4.56	11.9	8.1	3.19	0.02	0.17	0.15	0.1	12.12	
t1.9	OM: organic matter; CEC: cation exchange capacity; BS: base saturation.											

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