



## Biochar produced from mineral salt-impregnated chicken manure: Fertility properties and potential for carbon sequestration



Ran Xiao <sup>a,b</sup>, Jim J. Wang <sup>b,\*</sup>, Lewis A. Gaston <sup>b</sup>, Baoyue Zhou <sup>b</sup>, Jong-Hwan Park <sup>b</sup>, Ronghua Li <sup>a</sup>, Syam K. Dodla <sup>c</sup>, Zengqiang Zhang <sup>a,\*</sup>

<sup>a</sup> College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi 712100, China

<sup>b</sup> School of Plant, Environment & Soil Sciences, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, USA

<sup>c</sup> Red River Research Station, Louisiana State University Agricultural Center, Bossier City, LA 71112, USA

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### ABSTRACT

In this study, nutrient properties and carbon sequestration potential of biochars derived from chicken manure (CM) impregnated with mineral salts (calcium chloride, magnesium chloride, ferric chloride) were evaluated. Pretreatment with mineral salts reduced phosphorus (P) availability via the formation of insoluble metal phosphate minerals. Less carbon was lost during the pyrolysis of pretreated CM, and the produced biochars (BC<sub>Ca</sub>, BC<sub>Mg</sub>, and BC<sub>Fe</sub>) were more stable (i.e., reduced C loss during chemical oxidation and less CO<sub>2</sub> release during incubation) than pristine biochars. Spectroscopic evidence indicated that enhanced biochar stability via metal salt pretreatment before pyrolysis was related to increased aromatization and enhanced physical protection due to the metal-oxygen interaction, together with the formation of metal mineral phases on biochar surfaces. Moreover, ferric chloride was the optimal additive, as it significantly decreased biochar P leachability and increased carbon sequestration potential.

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### 1. Introduction

Animal manure is an abundant fertilizer source of plant nutrients and tends to increase soil organic matter (Zhang and Schroder, 2014). Balanced land application of manure serves two purposes, nutrient cycling and waste disposal (Wang and Gaston, 2014). However, repeated and/or excessive application of manure can cause serious environmental problems. Negative impacts include deteriorated water quality and eutrophication due to nutrient leaching/runoff, heavy metal/antibiotic accumulation in the terrestrial environment, and impaired air quality associated with greenhouse gases emission, odor, smog, and dust (USEPA, 2004). For these reasons, continuous land application of manure as a fertilizer has been strictly (USEPA, 2017).

As one of the cheapest sources of animal protein, chicken production has been steadily increasing to meet the demand of a growing world population (Lee et al., 2017). Production of chicken manure (CM) has proportionally increased, posing a strain on the local environment. According to a USEPA report, approximately

44.4 million tons of CM were generated in the US in 2008 (MacDonald, 2009). Globally, annual production of CM may range from 625 to 938 million tons (Mau and Cross, 2018). Therefore, environmentally sustainable management of CM is a critical issue.

Conventional CM management includes composting and anaerobic digestion. However, these practices are time-consuming and their efficiencies are restricted by operational and environmental conditions (Lee et al., 2017). Recently, thermal conversion of biomass into biochar by pyrolysis has proved to be an alternative strategy for organic waste management (Cantrell et al., 2012; Song and Guo, 2012; Das et al., 2016; Jin et al., 2016). Pyrolysis reduces waste volume (Cantrell et al., 2012; Wang et al., 2015) and eliminates accompanying nuisances such as residual antibiotics (Xiao et al., 2015; Zhu et al., 2016) and pathogens (Yin et al., 2018). Additionally, pyrolysis yields potentially useful products such as biogas, bio-oil, and biochar (Tripathi et al., 2016; Mau and Cross, 2018). Moreover, manure generated biochars are rich in plant nutrients, therefore have high agronomic value (Wang et al., 2015; Subedi et al., 2016; Domingues et al., 2017). Hence, production of biochar from CM and its use as a fertilizer for cropland elsewhere in the vicinity could help achieve a regional nutrient balance (Wang et al., 2015; USEPA, 2017).

\* Corresponding authors.

E-mail addresses: [jjwang@agcenter.lsu.edu](mailto:jjwang@agcenter.lsu.edu) (J.J. Wang), [zqzhang@nwafu.edu.cn](mailto:zqzhang@nwafu.edu.cn) (Z. Zhang).

Apart from soil fertility, another incentive for production and land-application of biochar is carbon sequestration (Nguyen et al., 2009; Harvey et al., 2012; Zhao et al., 2014; Brassard et al., 2016). Due to its high recalcitrance to abiotic/biotic degradation, biochar has a much longer residence time (from the decadal to millennial timescales) than its precursor materials (Zimmerman, 2010; Harvey et al., 2012). However, up to 50% of the feedstock C may be lost during pyrolysis (Zhao et al., 2013; Zhao et al., 2014; Lehmann and Joseph, 2015). Moreover, fresh biochars are partly degraded and oxidized to CO<sub>2</sub> when incorporated into soils (Cross and Sohi, 2013; Zimmerman, 2010). Therefore, reducing C loss during biochar production and increasing the stability of fresh biochar would favor the C sequestration potential of biochar.

Studies have shown that impregnating feedstock with certain chemical agents reduces C loss during biochar production. For example, Zhao et al. (2014) found that phosphorus-bearing materials (H<sub>3</sub>PO<sub>4</sub>, phosphate rock tailings, and triple superphosphate) reduced C loss by 5–15%. Additionally, mineral salts, such as ammonium phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) and iron sulfate clay, increase the thermal stability of biomass (Das and Sarmah, 2015; Rawal et al., 2016). Once biochar is incorporated into the soil, its rate of degradation is affected by interaction with soil constituents (Rawal et al., 2016; Yang et al., 2016; Archanjo et al., 2017). Soil mineral elements such as Al, Si, and Fe can accumulate on the exterior surface of biochars, thereby physically limiting oxidation (Nguyen et al., 2009; Archanjo et al., 2017). Additionally, such surface accumulation can be fast, occurring within the first three months of contact with soil (Lin et al., 2012). Furthermore, since mineral ions such as exchangeable calcium can bind with soil organic matter and increase its resistance to oxidation (Clough and Skjemstad, 2000), divalent bases may have a similar effect with biochar in soil. Accordingly, we hypothesized that impregnation of CM with certain mineral salts before pyrolysis would increase the C sequestration potential of biochar by reducing C loss during production and subsequent loss by oxidation in the soil. Moreover, the added minerals may indirectly as well as directly affected biochar nutrient fertilities. For example, studies have shown that metal-biochar composites increase the adsorption of plant nutrient ions such as NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> (Rajapaksha et al., 2016; Li et al., 2018). To our knowledge, however, no studies have investigated the nutrient dynamics of biochar produced from nutrient-rich manure materials that have been impregnated with mineral salts.

In the presented study, twelve different biochars were produced from CMs, with and without mineral salts-impregnation, at different pyrolysis temperatures. The mineral salts used (i.e., CaCl<sub>2</sub>, MgCl<sub>2</sub>·6H<sub>2</sub>O, and FeCl<sub>3</sub>·6H<sub>2</sub>O) are common in soil and have low toxicity to a living organism. A range of pyrolysis temperature (i.e., 250 °C, 350 °C, and 550 °C) was employed because production temperature greatly affects biochar properties. The specific objectives of this study were to evaluate the effect of adding mineral salts to CM before pyrolysis on: (1) the availability of nutrients in the resulting biochar and (2) conservation of C during and after pyrolysis, thus the C sequestration potential of biochar.

## 2. Materials and methods

### 2.1. Feedstock materials

The CM used in this study was obtained from a commercial poultry production farm in northern Louisiana. It was a pure manure, i.e. without feathers and bedding materials. Manure samples were air-dried and ground, sieved to <2 mm before further analysis and utilization. Chemical characteristics of the manure are presented in Table 1.

**Table 1**  
The chemical characteristics of CM and biochars produced from different treatments.

Samples	pH	Ash content (%)	Total C content (%)	Total N content (%)	Available NH <sub>4</sub> <sup>+</sup> -N (g kg <sup>-1</sup> )		Total P content (g kg <sup>-1</sup> )		Soluble P (g kg <sup>-1</sup> )		K (g kg <sup>-1</sup> )	Ca (g kg <sup>-1</sup> )	Mg (g kg <sup>-1</sup> )
					Water extractable	KCl extractable	Water extractable	Olsen-P	Water extractable				
CM	6.59 ± 0.03 Ad	25.0 ± 2.2 Cd	29.33	2.57	4.21 ± 0.07 a	7.26 ± 0.39 ABa	12.80 ± 1.36 d	5.84 ± 0.14 Aa	6.10 ± 0.11 Ad	33.23 ± 2.80 d	13.09 ± 1.56 c	13.06 ± 1.3 d	
BC-250	7.66 ± 0.06 Ac	36.08 ± 0.83 Cc	34.55	2.79	0.07 ± 0.02 Db	0.16 ± 0.15 Cb	19.09 ± 0.25 c	5.08 ± 0.02 Bb	6.76 ± 0.01 Bc	41.55 ± 0.43 c	19.84 ± 1.00 b	21.43 ± 0.74 c	
BC-350	8.95 ± 0.12 Bb	49.17 ± 0.31 Bd	29.21	2.45	0.07 ± 0.01 Bb	0 Bb	21.50 ± 3.23 b	4.57 ± 0.11 Ac	8.42 ± 0.24 Ab	49.28 ± 0.48 b	21.71 ± 3.46 b	28.39 ± 0.42 b	
BC-550	10.24 ± 0.01 Ba	54.08 ± 0.08 Ca	23.65	1.81	-	-	29.60 ± 0.34 a	2.93 ± 0.00 Ad	8.74 ± 0.16 Aa	59.30 ± 0.37 a	30.25 ± 1.15 a	37.80 ± 1.15 a	
BC <sub>Ca</sub> -0	6.50 ± 0.00 Ba	32.13 ± 0.76 Ad	28.79	2.5	4.62 ± 0.27 a	7.73 ± 0.05 Aa	11.29 ± 0.34 c	3.84 ± 0.02 Ca	4.82 ± 0.01 Bd	31.61 ± 0.08 d	36.7 ± 3.13 c	13.66 ± 1.33 d	
BC <sub>Ca</sub> -250	7.84 ± 0.03 Ab	47.02 ± 0.37 Ac	30.00	2.85	0.27 ± 0.01 Cb	0.48 ± 0.02 Ab	18.28 ± 1.51 b	2.49 ± 0.05 Cb	3.17 ± 0.09 Cc	41.44 ± 0.23 c	40.5 ± 1.82 b	16.72 ± 0.20 c	
BC <sub>Ca</sub> -350	9.32 ± 0.02 Ac	53.77 ± 1.11 Ab	26.68	2.44	0.01 ± 0.01 Ab	0.031 ± 0.01 Ab	22.13 ± 0.35 b	1.23 ± 0.03 Cc	8.68 ± 0.37 Ab	48.68 ± 0.91 b	49.1 ± 3.77 b	21.80 ± 0.14 b	
BC <sub>Ca</sub> -550	10.61 ± 0.04 Ad	61.44 ± 0.37 Aa	24.73	1.96	-	-	30.60 ± 0.35 a	-	1.22 ± 0.63 Ca	60.25 ± 0.11 a	59.1 ± 0.32 a	26.70 ± 0.40 a	
BC <sub>Mg</sub> -0	6.49 ± 0.01 Bd	24.57 ± 0.37 Cd	28.36	2.43	4.39 ± 0.61 a	6.84 ± 0.09 Ba	11.05 ± 0.25 d	4.27 ± 0.01 Ba	6.98 ± 0.08 Cc	31.17 ± 0.11 d	9.32 ± 1.67 d	36.41 ± 0.21 d	
BC <sub>Mg</sub> -250	7.35 ± 0.15 Bc	45.18 ± 1.30 ABc	26.40	2.43	0.40 ± 0.06 Bb	0.30 ± 0.05 Bb	20.47 ± 1.65 c	5.65 ± 0 Ab	6.39 ± 0.35 Ab	39.23 ± 0.49 c	22.37 ± 2.30 c	41.70 ± 0.22 Ac	
BC <sub>Mg</sub> -350	9.17 ± 0.06 Ab	49.71 ± 2.28 Bb	26.22	2.42	-	-	26.65 ± 1.10 b	3.33 ± 0.17 Cc	8.36 ± 0.25 Aa	50.30 ± 0.13 b	28.09 ± 5.99 b	47.30 ± 0.23 Ab	
BC <sub>Mg</sub> -550	10.32 ± 0.01 Ca	58.53 ± 1.27 Ba	27.04	2.06	-	-	30.28 ± 5.14 a	0.05 ± 0 Cd	1.27 ± 0.06 Ba	58.82 ± 1.34 a	30.94 ± 5.99 a	52.24 ± 0.20 Aa	
BC <sub>Fe</sub> -0	5.02 ± 0.01 Ca	28.66 ± 0.65 Bd	27.89	2.53	4.85 ± 0.12 a	7.52 ± 0.19 Aa	12.32 ± 1.23 a	1.05 ± 0.04 Db	1.23 ± 0.02 Da	31.80 ± 0.05 d	13.44 ± 3.12 d	14.66 ± 0.35 d	
BC <sub>Fe</sub> -250	5.75 ± 0.06 Cb	43.96 ± 0.26 Bc	28.26	2.91	0.44 ± 0.02 Ab	0.17 ± 0.02 Cb	20.06 ± 3.07 b	1.27 ± 0.02 Da	1.23 ± 0.11 Da	39.21 ± 0.50 c	20.32 ± 2.89 c	20.26 ± 0.54 c	
BC <sub>Fe</sub> -350	5.72 ± 0.03 Cc	52.04 ± 1.06 ABb	26.44	2.45	0.02 ± 0.00 Bc	-	24.37 ± 1.82 c	1.24 ± 0.04 Ca	1.23 ± 0.08 Ba	50.61 ± 0.48 b	25.30 ± 2.24 b	28.81 ± 3.08 b	
BC <sub>Fe</sub> -550	6.68 ± 0.08 Cc	58.13 ± 0.51 Ba	27.13	2.17	-	-	31.00 ± 0.35 c	0.09 ± 0.01 Bc	0.51 ± 0.06 Db	59.54 ± 1.37 a	31.80 ± 1.21 a	38.65 ± 0.35 a	

Note: Different letter showing the significantly different (*p* < 0.05) existed as determined by the LSD test. The difference among different temperature treatments are represented by small letters, and difference among different mineral salt treatments are represented by big letters.

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