ARTICLE IN PRESS

Waste Management xxx (2016) xxx-xxx





Waste Management



journal homepage: www.elsevier.com/locate/wasman

Influence of biochar addition on the humic substances of composting manures

Keiji Jindo^{a,b,*}, Tomonori Sonoki^c, Kazuhiro Matsumoto^c, Luciano Canellas^b, Asunción Roig^a. Miguel A. Sanchez-Monedero^a

^a Centro de Edafología y Biología Aplicada del Segura (CEBAS-CSIC), Department of Soil Conservation and Waste Management, Campus Universitario de Espinardo, 30100 Murcia, Spain

^b NUDIBA-Universidade Estadual Norte Fulminense, Av. Alberto Lamego 2000, Campos Dos Goytacazes, Rio de Janeiro, Brazil ^c Faculty of Agriculture and Life-Sciences, Hirosaki University, Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan

ARTICLE INFO

Article history: Received 14 July 2015 Revised 5 January 2016 Accepted 7 January 2016 Available online xxxx

Keywords: Charcoal Fulvic acid Compost Humic acid Organic waste

ABSTRACT

Application of biochar (10% v/v) to a manure composting matrix was investigated to evaluate its effect on the chemical composition of humic substances during the composting process. The characteristics of the humic acid (HA) and fulvic acid (FA) fractions were analyzed in compost mixtures originating from two different manures (poultry manure (PM) and cow manure (CM)). The C contents of HA and FA from the manure compost/biochar blends (PM+B and CM+B) were higher than those from PM and CM, with an enhanced recalcitrant fraction, as determined by thermogravimetric analysis. Spectroscopic analysis showed that enrichment of aromatic-C and carboxylic-C occurred in the FA fractions of PM+B and CM +B to a greater extent than in PM and CM. Biochar addition into the composting mixture improved the final compost quality, especially for the light humified fraction (FA).

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1. Introduction

Biochar has a high content of stable C, which resists decay and remains in soils for long periods, and contributes to C sequestration. Its use has other benefits also, such as improving water retention, plant growth, and soil organic C stabilization (Cross and Sohi, 2011; Kimetu and Lehmann, 2010; Sohi et al., 2010). A large number of studies have reported that application of biochar as a bulking agent for composting, provides positive effects such as an increase in aeration, reduction of ammonia volatilization, and improvement of the final product (Dias et al., 2010; Hua et al., 2009; Steiner et al., 2010). However, little information is available about the effect of biochar on the chemical composition of humic substances, which are considered to be the more stable and recalcitrant C fraction

* Corresponding author at: Centro de Edafología y Biología Aplicada del Segura (CEBAS-CSIC), Department of Soil Conservation and Waste Management, Campus Universitario de Espinardo, 30100 Murcia, Spain,

E-mail address: keijindo@hotmail.com (K. Jindo).

http://dx.doi.org/10.1016/j.wasman.2016.01.007 0956-053X/© 2016 Elsevier Ltd. All rights reserved. in organic matter that could contribute to the soil C stock when the compost is applied to soil.

Humic substances, mainly composed of humic acid (HA) and fulvic acid (FA) fractions, are heterogeneous complexes consisting of large macromolecules with functional groups formed by biochemical and chemical reactions. They play a great role not only in increasing soil fertility such as micronutrient uptake and phyto-hormones effect, but also contributing to C sequestration (Spaccini et al., 2002). The degree of humification, described as the transformation process of the easily decomposable organic matter into stabilized and polymerized material, is widely used for monitoring the progress of biodegradation during composting (Sánchez-Monedero et al., 2002). Recently, it has been reported that the humification process during composting can be improved by the addition of biochar into the composting mixture (Dias et al., 2010; Zhang et al., 2014). However, the number of reports on the influence of biochar on the chemical composition of humic substances is still limited, especially regarding FA. Prost et al. (2013) reported increasing contents of water-extractable organic C in biochar blended composts by absorption of organic matter on the biochar and they posed the question of how this water-extractable organic matter could persist in the soil under field conditions. Thus, it is important to study the chemical composition of FA

Please cite this article in press as: Jindo, K., et al. Influence of biochar addition on the humic substances of composting manures. Waste Management (2016), http://dx.doi.org/10.1016/j.wasman.2016.01.007

Abbreviations: CM, cow manure; CM+B, cow manure with biochar; CPMAS ¹³C NMR, cross-polarization magic angle spinning ¹³C nuclear magnetic resonance; FA, fulvic acid; FT-IR, fourier-transform infrared; HA, humic acid; MB, methylene blue MB; OM, organic matter; PM, poultry manure; PM+B, poultry manure with biochar; SOM, soil organic matter; W_1 , mass loss at 110-350 °C in thermal analysis; W_2 , mass loss at 350-550 °C in thermal analysis.

K. Jindo et al./Waste Management xxx (2016) xxx-xxx



Fig. 1. Degree of polymerization (humic acid (HA)/fulvic acid (FA)) during the composting process: poultry manure (PM), poultry manure with biochar (PM+B), cow manure (CM), and poultry manure with biochar (CM+B). The dotted lines exhibit the compost without biochar, while the continuous lines exhibit the compost with biochar.

fraction that is a part of water-extractable organic C before utilization of biochar blended compost as soil amendment.

The aim of the present work is to obtain information on the alteration of the chemical structure of different humic fractions (HA and FA) by the addition of biochar during co-composting of two different types of manure composts (poultry manure (PM) and cow manure (CM)), using thermogravimetric analysis,

fourier-transform infrared (FT-IR), and cross-polarization magic angle spinning ¹³C nuclear magnetic resonance (CPMAS ¹³C NMR).

2. Material and methods

2.1. Biochar preparation

Hard-wood biochar originated from the broad-leaved tree, *Quercus serrata*, was prepared by slow pyrolysis using a traditional Japanese kiln under atmospheric pressure at 550 °C. To analyze the properties of the biochar, we ground and sieved the biochar until it was less than 0.5 mm in diameter. The main characteristics of the obtained biochar are: pH = 7.23; C = 791.5 g kg⁻¹; O = 91.5 g kg⁻¹; N = 37.6 g kg⁻¹; H = 18.9 g kg⁻¹; K = 14.1 g kg⁻¹; P = 2.3 g kg⁻¹. The physical property of biochar was characterized by large surface area (255.0 m²), methylene blue (MB) absorption capacity (8.3 mg g⁻¹) and iodine adsorption capacity (100 mg g⁻¹). The methods of MB number and iodine number were used for the characterization of micro- and mesoporosity of pyrogenic material, respectively.

2.2. Raw materials and composting process

The composting was carried out at the Kanagi experimental farm of Hirosaki University during summer and autumn seasons. Two mixtures consisting of CM and PM (100.9 kg) were prepared with apple pomace (76.8 kg), rice straw (9.7 kg), and rice bran (12.7 kg). Biochar (20 kg) was added to each mixture (CM+B and PM+B). Composting mixtures without biochar addition (CM and PM) were prepared as control treatments. The organic waste mixtures were composted in cone-shaped windrows (0.7065 m³). To aerate and homogenize the organic materials, the mixtures were turned twice a week during the first week and once a week from the second week onwards. The temperature of each pile was continuously monitored during the process using a thermo-recorder (T & D Co., Ltd., Nagano, Japan) and is reported in Supplementary information (Fig. S1). The moisture level of the material was kept at around 60% by adding water. The composting process lasted approximately 3 months for each pile. A representative sample of each organic material was taken at two different stages of the composting process: I (from the initial mixture at thermophilic phase, 1 week of composting) and M (mature compost, 12 weeks). These were collected as composite samples, randomly taken from different subsamples of five different spots in the piles from the top down to the bottom, and then were air-dried and ground to 0.5 mm in order to homogenize the material.

Table 1

Selected chemical and physical properties of poultry manure compost (PM), poultry manure blended with biochar (PM+B), cow manure compost (CM), and cow manure blended with biochar (CM+B).

Origin	Initial phase						Final phase					
	pН	N (%)	C (%)	C/N	O.M. ¹ (%)	B.D. ² (g cm ⁻³)	pН	N (%)	C (%)	C/N	O.M. (%)	B.D. (g cm ⁻³)
PM	5.8 (0.0)	1.7 (0.0)	36.9 (0.3)	22.1	79.9 (0.1)	0.49 (0.0)	8.2 (0.0)	2.9 (0.1)	27.9 (0.2)	9.7	55.2 (0.4)	0.81 (0.0)
PM+B	5.8 (0.1)	1.7 (0.0)	39.9 (0.3)	23.4	84.9 (0.5)	0.40 (0.0)	7.8 (0.0)	2.0 (0.1)	33.6 (0.3)	16.5	73.0 (0.4)	0.57 (0.0)
Significance	ns	ns	**	-	**	**	**	**	**	-	**	**
CM	6.6	1.7	35.6	21.3	75.9 (0.2)	0.47	7.7 (0.0)	2.4	29.8	12.4	59.7 (0.5)	0.66
CM+B	(0.0) 7.0 (0.1)	1.3	(0.5) 37.1 (0.1)	29.1	(0.2) 79.7 (0.3)	0.43	(0.0) 7.6 (0.0)	1.8	31.5 (0.1)	17.9	68.8 (0.3)	0.56
Significance	**	**	**	-	**	**	*	**	**	-	**	**

Standard deviations in parentheses (n = 3 replicates).

For each column, means were subjected to statistical analysis by the *t*-student test. NS, *, and ** indicate non-significant and significant differences at the 5% and 1% levels respectively.

¹ O.M. = Organic matter.

² B.D. = Bulk density.

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