Agronomic properties of biochars from different manure wastes

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ABSTRACT

Biochar research has focused in the last years in the use of wood or grass derived materials for carbon sequestration. However, manure derived biochar can provide other benefits after soil addition, including nutrient supply. At present, there is an incomplete understanding of pyrolysis on manures. In order to understand the benefits obtained after addition of these types of materials to the soil, an experiment involving the use of different manures and pyrolysis temperatures was performed. Five manure wastes were selected for this experiment: cattle manure (E); cattle manure mixed with straw (EP), chicken manure (G), chicken manure mixed with sawdust (GS) and pig slurry (PC). Unpyrolyzed samples were compared to biochars prepared at 300 and 500 °C. Relevant properties for agronomic purposes were determined, including pH, electrical conductivity, nutrient content, metal content, proximate analysis and carbon thermostability. Our results show that biochars tailored for different purposes can be prepared after a careful choice of feedstock and pyrolysis temperature.

Keywords:
Biochar
Manure waste
Pyrolysis

1. Introduction

In the last years, intensive animal husbandry production has led to a large concentration of animals in small areas. This has resulted in the production of excessive amounts of manures with insufficient nearby land for application. There are a number of environmental problems associated with these intensive agricultural systems, including N and P pollution of water bodies, methane emissions and odour pollution. These serious environmental threats are called for innovative environmental management approaches. A feasible technology for the managements of manures, offering a potential to valorise these wastes, is pyrolysis, which results in the production of biochar.

Biochar is a carbonaceous material obtained from biomass pyrolysis. For many years now, it has been researched as a significant mean to improve soil productivity and carbon storage [1]. Biochar has also been shown to influence soil physico-chemical properties, such as pH, porosity, bulk density and water holding capacity. However, the usefulness of a specific biochar for any particular application depends on its inherent properties. Biochars with high recalcitrant carbon content may function as carbon fixation materials whereas those rich in available nutrients and minerals or showing high water holding capacity could be used as amendments to improve soil fertility [2,3].

Additionally, biochar production is attracting more attention because it is a safer method of organic waste management with additional advantages such as reduction of waste stream volume and extraction of useful energy from the gas and liquid fractions [4]. Many types of biomass can be transformed into biochar including wood wastes, crop residues, switch grass, wastewater sludges or deinking sludges [5–7]. It has been shown that biochar characteristics are influenced by production variables, especially feedstock and pyrolysis temperature [3,8–10]. Generally, plant-derived biochars like those obtained from woody biomass or grasses are low nutrient materials due to their scarce ash, nitrogen, phosphorous and potassium contents. So, these biochars have disadvantages compared to traditional fertilizers for supplying crop nutrients. However, research to date has focused in these types of materials [11,12]. On the other hand, the soil application of biochars obtained from pyrolysis of ash-rich wastes such as sewage sludges have positive effects on soil agricultural properties as an increment of water holding capacity, improvements on organic carbon content and liming effect [6] or positive effects on soil biochemical properties [13]. Indeed, Liang et al. [14] observed an increment of the resistance of both the bacterial and fungal networks to drought on an Acrisol amended with poultry litter biochar while Lu et al. [15] reported that biochar addition improves soil biochemical properties in a soil polluted with Cd.

In this way, manure wastes are nutrient-rich materials and, consequently, interesting feedstocks for biochar production that can offer additional benefits to soils, not only as soil conditioner, but also as fertilizer [16,17]. Also, manure pyrolysis could reduce the problems of nitrogen leaching from soils compared to when using manures as fertilizers, while the phosphorous and potassium contents of feedstock could almost completely be recovered in the biochar [18]. In fact, manure biochars can be used as slow-release fertilizers [19].

Although there have been some studies using biochars prepared from manures in relation to soil pollution remediation or greenhouse gas emission [15,20], there is a lack of studies characterizing different types of biochar from manure pyrolysis [2]. This is important as manures from cattle, pig or chicken can have different initial properties which would result into different biochars. In particular, manures are often mixed with sawdust and there is a scarcity of articles addressing the pyrolysis products of this type of material.

The main objective of the present work is to study the influence of feedstock properties and pyrolysis temperature on the agronomic properties of biochars from manure wastes. For this purpose, five manure wastes were selected, characterized and pyrolyzed at 300 and 500 °C.

2. Experimental

2.1. Raw materials selection

Five manure wastes from Avila region (Central Spain) were selected: cattle manure (E); cattle manure with straw (EP), chicken manure (G), chicken manure mixed with sawdust (GS) and pig slurry (PC). The five samples were dried at room temperature and then crushed and sieved through a 2 mm mesh prior to analysis.

2.2. Pyrolysis of raw materials

Biochars were prepared as follows [21]: Feedstock (100 g) were placed in a covered steel cup and introduced in an electric furnace where the temperature was increased to 300 °C or 500 °C at a rate of 10 °C min^{-1} and the final temperature was maintained for 1 h.

Biochars prepared from cattle manure (E) were named BE300 (300 °C) and BE500 (500 °C), from cattle manure mixed with straw (EP): BEP300 and BEP500, from chicken manure (G): BG300 and BG500, from chicken manure mixed with sawdust (GS): BGS300 and BGS500 and from pig slurry (PC): BPC300 and BPC500.

2.3. Manure wastes and biochar characterization

Manure and biochar samples were characterized as follows:

The pH and electrical conductivity (EC) were determined using a sample: water ratio of 1:2.5 (g mL^{-1}) using a Crison micro-pH 2000 [22] and a Crison 222 conductivimeter [23], respectively. Cation exchange capacity (CEC) was determined as follows: 5 g biochar were introduced in a volumetric flask. Then, 50 mL 1 M NH_4OAc pH 7 were added and the flask was stirred and allowed to stand overnight. After this period, the suspension was leached and 200 mL 1 M NH_4OAc pH 7 were added and leached. Ca^{2+}, Mg^{2+}, K^+ and Na^+ were determined in this solution using a Perkin Elmer 2280 atomic absorption spectrophotometer. Then, 200 mL of ethanol were added and biochar was stirred and leached. Leachate was discarded and later, the biochar was leached with 200 mL 1 M acidulated NaCl and NH_4^+ in the leachate was determined. The iodine number (mgI_2 g^{-1}) defined as the quantity of iodine adsorbed per gram of activated carbon at an equilibrium concentration of 0.02 N was calculated according to D-4607 standard test method [24]. The iodine number is considered a simple method to evaluate the surface area of activated carbons associated

Table 1
pH, electrical conductivity (EC), cation exchange capacity (CEC) and iodine number of manure wastes and biochar from pyrolysis of manure wastes.

Property	Cattle manure			Cattle–straw manure			Chicken manure			Chicken–sawdust manure			Pig manure		
	E	BE300	BE500	EP	BEP300	BEP500	G	BG300	BG500	GS	BGS300	BGS500	PC	BPC300	BPC500
pH	8.8 ± 0.5	8.0 ± 0.1	10.2 ± 0.1	10.3 ± 0.1	10.1 ± 0.1	10.1 ± 0.1	5.8 ± 0.1	8.1 ± 0.1	10.6 ± 0.1	8.0 ± 0.1	10.6 ± 0.1	10.3 ± 0.1	9.0 ± 0.1	7.8 ± 0.1	8.2 ± 0.1
EC(µS cm^{-1} 20 °C)	265 ± 15	312 ± 12	391 ± 15	600 ± 36	422 ± 21	568 ± 43	430 ± 31	519 ± 36	662 ± 25	350 ± 5	408 ± 10	315 ± 29	124 ± 3	102 ± 11	59 ± 3
CEC($cmol_{(c)}$ kg^{-1})	53.7 ± 4.7	66.3 ± 8.5	70.9 ± 1.5	60.2 ± 0.9	65.5 ± 1.3	58.4 ± 0.7	66.8 ± 1.4	137.6 ± 9.7	81.4 ± 2.0	64.2 ± 0.6	81.7 ± 0.3	65.8 ± 0.7	44.1 ± 0.3	35.6 ± 0.1	32.7 ± 3.6
Iodine number(g iodine 100 g^{-1})	–	19.67 ± 1.47	19.21 ± 1.77	–	21.30 ± 1.04	20.18 ± 3.72	–	20.52 ± 3.75	19.29 ± 3.92	–	15.17 ± 0.58	10.47 ± 1.56	–	9.55 ± 1.04	11.67 ± 1.49

with pores with $d > 1$ nm N was determined by Kjeldahl digestion [25], Phosphorus (P) according to Watanabe and Olsen [26] and organic carbon oxidized with dichromate was determined by the Walkley–Black method [27].

Total metal content in Fe^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} was determined using a Perkin Elmer 2280 atomic absorption spectrophotometer after sample extraction by digestion with concentrated HCl/HNO_3 following the method 3051a [28], while the mobile forms of metals were extracted using 0.1 M $CaCl_2$ [29].

Proximate analysis was determined by thermogravimetry using a Labsys Setaram equipment. The sample was heated to a temperature of 600 °C under N_2 atmosphere and 30 °C min^{-1} heating rate. Humidity was calculated as the weight loss from the initial temperature to 150 °C. The volatile matter (VM) was determined as the weight loss from 150 °C to 600 °C under N_2 atmosphere. At this temperature, air atmosphere was introduced and fixed carbon (FC) was calculated as the weight produced when the final sample was burnt. The ashes were determined as the final weight of the samples [21,30].

Elemental analysis (C, H, N) was performed by combustion of samples at 1000 °C in a Macro-analyser elemental Leco TruSpec CHNS instrument. Oxygen was determined by difference.

Biochar and manure samples were subjected to thermogravimetric (TG), derivative thermogravimetric (dTG) and differential thermal analysis (DTA) in a thermobalance Labsys Setaram. Samples were analysed as follows: about 80 mg of each sample were heated at 15 °C min^{-1} until 850 °C in air atmosphere using a flow rate of 30 mL min^{-1}.

3. Results and discussion

3.1. Chemical characterization

Table 1 shows pH, EC CEC and iodine number of various manure wastes and the corresponding biochar samples obtained by pyrolysis at 300 and 500 °C. Biochar with different agronomic properties could be obtained depending on the feedstock and pyrolysis conditions used.

The pH values of the manure wastes ranged from 5.8 (G) to 10.3 (EP), whereas the pH of biochar samples varied from 7.8 (BPC300) to 10.6 (BGS300). Generally, it is established that pH increases with pyrolysis temperature, but the magnitude of this increment depends on the raw material characteristics [16]. However, for cattle manure (E) and pig (PC) manures, pyrolysis at 300 °C led to lower pH than the corresponding raw materials. Hossain et al. [9] found a similar behaviour after pyrolysis of sewage sludges at lower temperatures (<400 °C). Finally, all biochar samples obtained at 500 °C showed alkaline pH (from 8.2 for BPC500 to 10.6 for BEP500).

Electrical conductivity (EC) was the parameter used to estimate the amount of total dissolved salts. Hossain et al. [9] found that EC of biochars from sewage sludge pyrolysis decreases significantly with pyrolysis temperature in a similar way to the results found in our study for pig slurry (PC) and poultry litter with sawdust (GS). However, for dairy (E), cattle manure-straw manure (EP) and poultry litter (G) the EC increased with pyrolysis temperature indicating that feedstock characteristics influence the EC evolution during pyrolysis.

Cation exchange capacity (CEC) indicates the ability of biochar and manure wastes to adsorb cation nutrients. Mineral soils generally have CEC values lower than 15 $cmol_{(c)}\,kg^{-1}$ while humic substances may have CEC greater than 100 $cmol_{(c)}\,kg^{-1}$ [31]. Soils with high CEC values are able to retain cationic nutrients fertilizers (K^+ and NH_4^+) in the root zone and prevent nutrient leaching. Therefore, the addition of amendments with high CEC improves soil productivity and also can reduce groundwater contamination via

Table 2
$N_{Kjeldhal}$, phosphorous, oxidizable carbon ($C_{Cr_2O_7}$), C/N ratio and Ca^{2+}, Mg^{2+}, Na^+ and K^+ content of manure wastes and corresponding biochar samples.

Property	Cattle manure			Cattle–straw manure			Chicken manure			Chicken–sawdust manure			Pig manure		
	E	BE300	BE500	EP	BEP300	BEP500	G	BG300	BG500	GS	BGS300	BGS500	PC	BPC300	BPC500
$N_{Kjeldhal}$ (%)	1.92 ± 0.13	1.91 ± 0.23	1.29 ± 0.11	1.81 ± 0.17	2.87 ± 0.14	1.43 ± 0.12	3.35 ± 0.17	4.72 ± 0.34	1.52 ± 0.02	3.18 ± 0.03	1.26 ± 0.12	1.41 ± 0. 3	2.51 ± 0.22	2.24 ± 0.04	1.19 ± 0.14
P (g kg^{-1})	3.1 ± 0.2	1.8 ± 0.1	2.3 ± 0.4	3.2 ± 0.1	1.8 ± 0.1	3.6 ± 0.1	3.6 ± 0.1	2.2 ± 0.1	1.4 ± 0.2	3.2 ± 0.2	2.6 ± 0.1	1.3 ± 0.2	2.3 ± 0.2	2.8 ± 0.2	1.2 ± 0.1
$C_{Cr_2O_7}$ (%)	40.2 ± 2.1	35.2 ± 1.8	8.0 ± 0.3	33.0 ± 1.5	21.4 ± 1.9	4.8 ± 0.8	35.8 ± 1.6	13.6 ± 0.9	3.1 ± 0.2	32.6 ± 1.2	4.2 ± 0.6	2.4 ± 0.1	13.5 ± 0.7	7.9 ± 0.4	5.0 ± 0.3
C/N	20.94	18.43	6.17	18.23	7.46	3.35	10.67	2.89	2.06	10.26	3.32	1.69	5.38	3.52	4.15
Ca^{2+} (g kg^{-1})	5.3 ± 0.2	3.7 ± 0.1	10.5 ± 0.8	3.8 ± 0.3	3.2 ± 0.2	1.8 ± 0.2	1.8 ± 0.2	3.4 ± 0.3	2.6 ± 0.1	2.6 ± 0.1	3.0 ± 0.3	2.7 ± 0.1	1.5 ± 0.2	1.3 ± 0.2	0.8 ± 0.1
Mg^{2+} (mg kg^{-1})	2270 ± 140	3289 ± 481	2053 ± 160	1430 ± 140	2208 ± 160	2126 ± 220	203 ± 32	119 ± 24	55 ± 11	193 ± 32	52 ± 10	59 ± 12	732 ± 123	897 ± 128	863 ± 107
Na^+ (g kg^{-1})	8.2 ± 0.1	2.7 ± 0.1	2.7 ± 0.1	17.3 ± 0.8	4.3 ± 0.2	2.8 ± 0.1	7.7 ± 0.1	13.3 ± 1.4	13.7 ± 0.9	8.7 ± 0.1	12.2 ± 0.7	11.5 ± 0.4	0.6 ± 0.1	0.6 ± 0.1	0.6 ± 0.1
K^+ (g kg^{-1})	12.9 ± 0.6	3.3 ± 0.3	3.4 ± 0.2	3.5 ± 0.1	3.5 ± 0.3	3.5 ± 0.4	29.7 ± 0.8	50.7 ± 0.9	56.5 ± 0.9	31.0 ± 0.9	53.6 ± 0.9	51.8 ± 0.9	0.7 ± 0.1	0.8 ± 0.1	0.8 ± 0.1

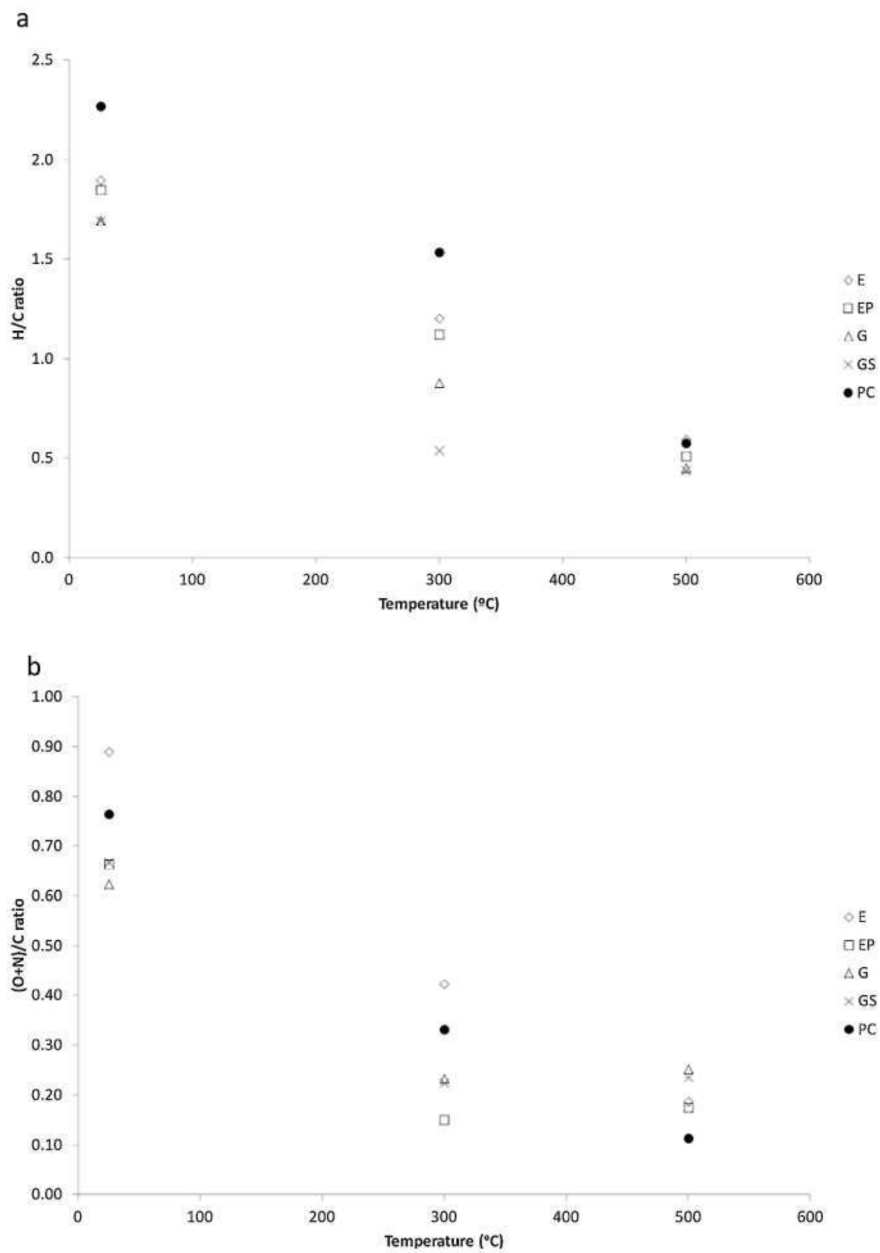

Fig. 1. H/C and (N + O)/C molar ratios of manure wastes and corresponding biochars at 300 and 500 °C.

minimizing the leaching of nutrients and trace metals and thus, enhances nutrient cycling [32]. Table 1 shows that, for manure wastes, the CEC ranged from 44.1 $cmol_{(+)}\,kg^{-1}$ to 66.8 $cmol_{(+)}\,kg^{-1}$ for PC and G, respectively. For biochar samples, CEC varies greatly among biochars produced from different manure feedstock's and pyrolysis temperatures. The highest value of CEC was obtained for BG300 (137.6 $cmol_{(+)}\,kg^{-1}$) indicating that this material could be an interesting soil amendment for agronomic purposes. This value was similar to that obtained by Zhao et al. [8] after pyrolysis of pig manure at 650 °C. The lowest CEC values were measured in BPC300 and BPC500. In this case, and in accordance with Song and Guo [2], the CEC decreases with pyrolysis temperature. Meszaros et al. [33] hypothesized that K, Ca, Mg, Na and P in the biomass promote the formation of O-containing groups on biochar surface during pyrolysis, resulting in higher CEC. Table 2 shows the K, Ca, Mg, Na and P contents for different manure wastes. The lowest CEC values for BPC300 and BPC500 could be related with the lowest K, Mg, Na, K and P contents of PC feedstock. CEC of cattle manure (E) biochars increased with temperature, in agreement with the results obtained by Zhao et al. [8]. Finally, for biochar obtained after pyrolysis of EP, G and GS a different behaviour was observed as CEC increased following pyrolysis at 300 °C, while decreasing in treatments prepared at 500 °C.

Iodine number of biochar was determined. Table 1 shows that all biochar, obtained by pyrolysis without any activation step, have low iodine number values following next sequence: BEP ≈ BG ≈ BE > BGS ≈ BPC.

Table 2 shows $N_{Kjeldhal}$, $C_{Cr_2O_7}$ and C/N ratio of manure wastes and corresponding biochar samples. $N_{Kjeldhal}$ includes the organic and ammonium nitrogen but not the inorganic forms. For manure waste, the $N_{Kjeldhal}$ content ranged from 1.81% for EP to 3.35% for G. $N_{Kjeldhal}$ content was reduced for E, GS and PC manures with increasing pyrolysis temperature. These results were in accordance with those obtained by Wang et al. [18] who studied nitrogen availability in biochar produced from cattle manure and found that nitrogen in biochar became more stable as pyrolysis temperature increased. For EP and G, the $N_{Kjeldhal}$ content increases with pyrolysis at 300 °C (the high biochar $N_{Kjeldhal}$ content corresponds to BG300) decreasing at higher temperatures. Therefore, in both waste materials, pyrolysis at low temperatures made N more labile, whereas at higher temperatures it became more stable.

Calvelo Pereira et al. [34] found that, in general, wet oxidation with potassium dichromate reflected the degree of biomass carbonization and could therefore be used to estimate the labile fraction of C in biochar. Wang et al. [18] found that $C_{Cr_2O_7}$ decreased as pyrolysis temperature increased whereas elemental C followed the opposite trend. Song and Guo [2] studied the variation in the quality of poultry litter biochar generated at different pyrolysis temperatures and found that the recalcitrant portion of poultry litter biochar resistant to oxidation with dichromate to increase with pyrolysis temperature. In a similar way, Table 2 shows a decrease of $C_{Cr_2O_7}$ with pyrolysis temperature, which is indicative of the increment in biochar stability caused by a progressive rearrangement of organic structures in newly synthesized structures of high stability during pyrolysis. The reduction in $C_{Cr_2O_7}$ content was more important for chicken manure based biochars (G and GS) which lead to very stable biochar samples at only 300 °C. The values of C/N ratio for different feedstocks are in agreement with the mean values found in the literature for this type of manure [35,36], i.e., the mean values for cattle manure are generally between 15 and 20 (*E* value is 20.94 and EP is 18.23), for chicken manure between 10 and 15 (G value is 10.67 and GS is 10.26) and for pig manure should be around 4–5 (PC value: 5.38). For biochar samples, the C/N ratio decreased with pyrolysis temperature as a consequence of the changes on $N_{Kjeldhal}$ and $C_{Cr_2O_7}$ contents.

The soluble P content of manures decreased with pyrolysis at 300 °C (Table 2). However, from 300 to 500 °C there was not a clear trend in the variation of soluble P value increasing for cattle manure and cattle–straw manure and decreasing for the pig and chicken manure based biochars. With respect to the exchangeable and soluble content in Ca, Mg, Na and K, the concentrations were in the same range of values found by other authors [16] but enrichment with pyrolysis temperature was not observed. This fact could be due to cation enrichment due to weight reduction during pyrolysis being counteracted by the decrease in cation leaching with temperature.

Fig. 1 shows elemental analysis results of manure wastes and their corresponding biochar samples. The H/C and (N + O)/C molar ratios are routine measurement for biochar characterization. The molar H/C ratio (Fig. 1a) was used as an indicator of the degree of aromatization because the proportion of carbon in a sample increases and hydrogen decreases as dehydration, polymerization and volatilization of light organic structures take place. At 300 °C, the H/C ratio of biochar was highly dependent on the characteristics of the raw materials. Biochar samples containing chicken manure (G and GS) showed H/C ratio $\leq$0.7, similar to those obtained for other manure wastes at 500 °C. At 500 °C, the H/C ratio achieved was similar for all biochar samples. Fig. 1b shows (O + N)/C molar ratio for manure wastes and their corresponding biochar samples. This ratio was related to the polarity of the samples and decreased with pyrolysis at 300 °C. From 300 to 500 °C, for G, GS and EP manure, this ratio increased slightly probably due to some oxidation of the samples.

Table 3 shows proximate analysis of manure wastes and their corresponding biochar samples. Enders et al. [37] mapped on a triangular diagram the ash, fixed carbon and volatile matter content of several biochars and found that areas of the triangle remained unpopulated despite the large number of samples characterized. Specifically, they found that fixed carbon contents of biochars with ash content over 35% were limited to below 30%. In addition, fixed carbon contents increased with pyrolysis temperature when the biochars contained less than 20% ash, but decreased for biochars

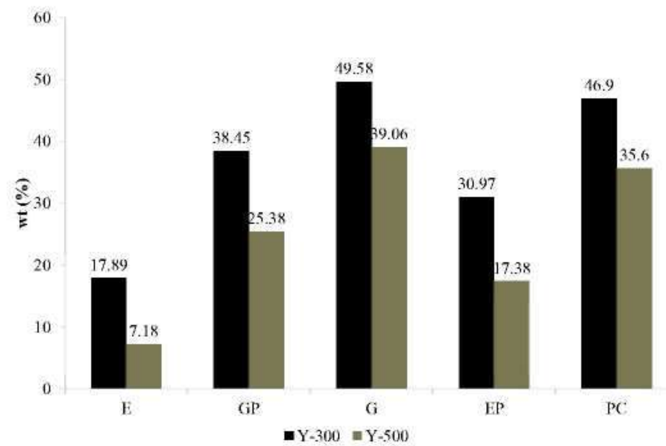

Fig. 2. Pyrolysis yields at 300 (Y-300) and 500 °C (Y-500).

having over 20% ash. In order to avoid decomposition of some clays and carbonates in ash rich organic wastes, we calculated the fixed carbon content by combustion at 600 °C and not at 800–900 °C [20,30,38]. Table 3 shows that for the samples with the highest ash content (PC and EP), the fixed carbon increased with pyrolysis temperature. However, the increases were less pronounced than for manure wastes with lower ash content (E, G and GS). Ash compounds hinder the formation of aromatic structures that contribute greatly to fixed carbon content. The FC/(VM + FC) ratio, named thermostability index, was previously identified as a reliable parameter to evaluate the level of stability of organic matter in biochar and other organic wastes [21,34]. This parameter indicates the relative amount of the most thermally stable fraction of organic matter with respect to less stable one. In our study, the thermostability index, FC/(VM + FC), increased with pyrolysis temperature and the increases were higher for G and GS samples, even at low temperatures, indicating the synthesis of structures with high stability at lower temperatures (300 °C). This result was congruent with the values of $C_{Cr_2O_7}$ evolution and the H/C molar ratio during pyrolysis of G and GS manures.

Generally, pyrolysis yield was positively correlated with the ash content of the feedstock. Comparing ash content of manure wastes (Table 3) with pyrolysis yield at 300 and 500 °C (Fig. 2), it could be observed that G and GS show a pyrolysis yield higher than that expected from their ash content (Table 3). This result was in agreement to the high fixed carbon of the corresponding biochar obtained at 300 °C.

3.2. Thermal analysis

Fig. 3 shows differential thermogravimetry (dTG) in air atmosphere of manure wastes and their corresponding biochar samples. Thermal analysis has been extensively used for the study of organic matter stabilization during composting [39–41]. Weight loss at temperatures below 150 °C was related to water release. From 200 to 550 °C oxidation of labile organic matter took place. Then, at temperatures higher than 550 °C weight loss could be attributed to refractory carbon and clays decomposition and finally, between 700 and 800 °C, carbonates decomposition was observed. Otero et al. [40] monitored the stabilization progress of sewage sludge from wastewater treatment plants by means of differential thermogravimetry and found that advanced sludge stabilization due to aerobic digestion was related to a shift to higher combustion temperature. So, it is established that the higher the temperature at which weight loss occurs, the more resistant and structurally ordered the organic fraction which is burning is. Generally, from our experimental results, it could be observed that combustion

Table 3
Proximate analysis of manure wastes and corresponding biochar samples.

Property	Cattle manure			Cattle–straw manure			Chicken manure			Chicken–sawdust manure			Pig manure		
	E	BE300	BE500	EP	BEP300	BEP500	G	BG300	BG500	GS	BGS300	BGS500	PC	BPC300	BPC500
VM (wt%)	64.66	47.31	13.20	56.56	24.91	11.95	64.85	23.87	11.96	59.80	13.01	8.28	41.72	31.25	6.50
FC (wt%)	20.67	32.50	43.15	16.97	36.75	36.73	14.92	41.38	50.01	22.79	52.44	55.77	11.06	18.50	19.62
Ash (wt%)	14.66	20.20	43.65	26.46	38.34	51.32	20.24	34.75	38.03	17.40	34.55	35.95	47.22	50.25	73.88
FC/(VM + FC)	0.24	0.41	0.77	0.23	0.60	0.75	0.19	0.63	0.81	0.28	0.80	0.87	0.21	0.37	0.75

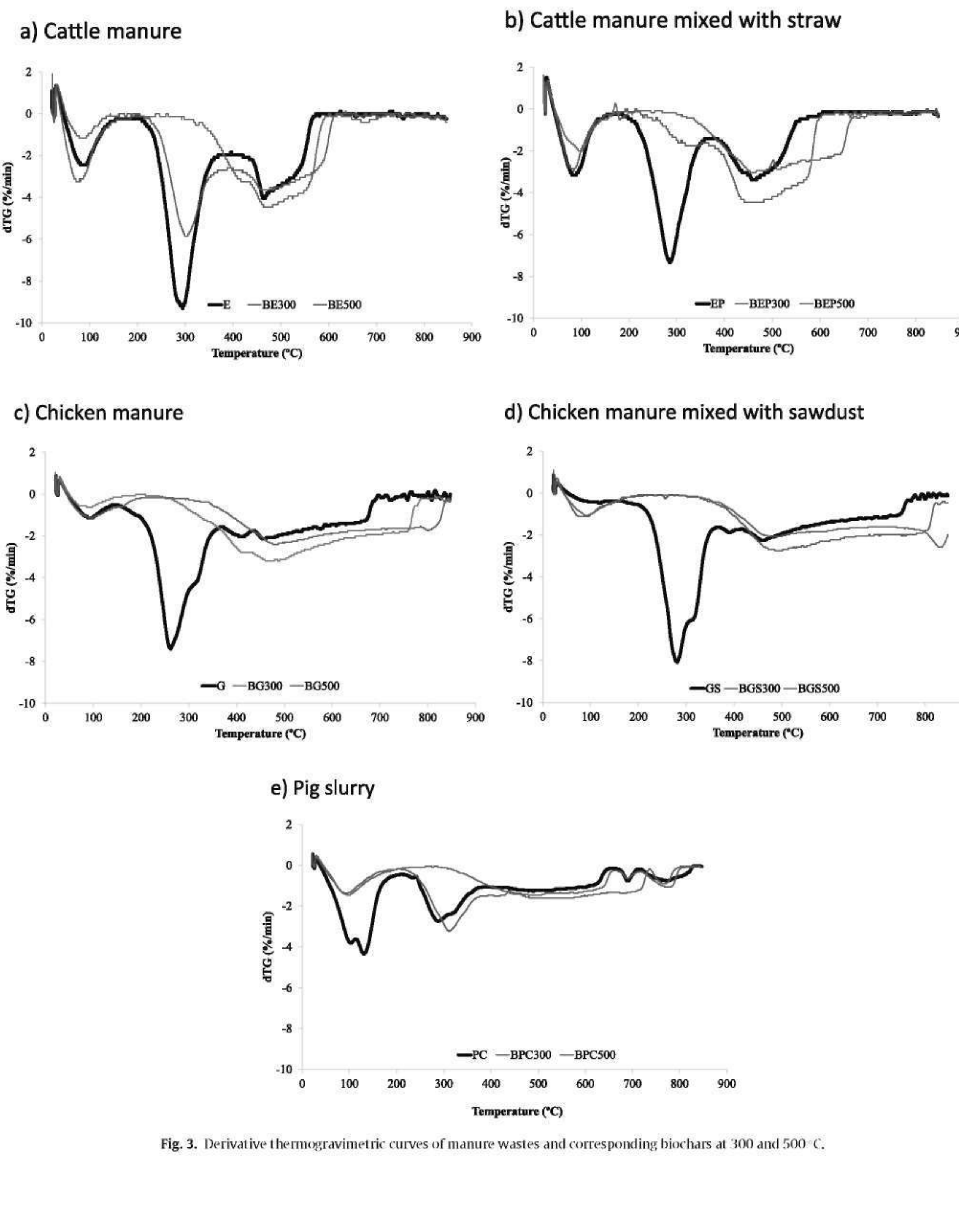

Fig. 3. Derivative thermogravimetric curves of manure wastes and corresponding biochars at 300 and 500 °C.

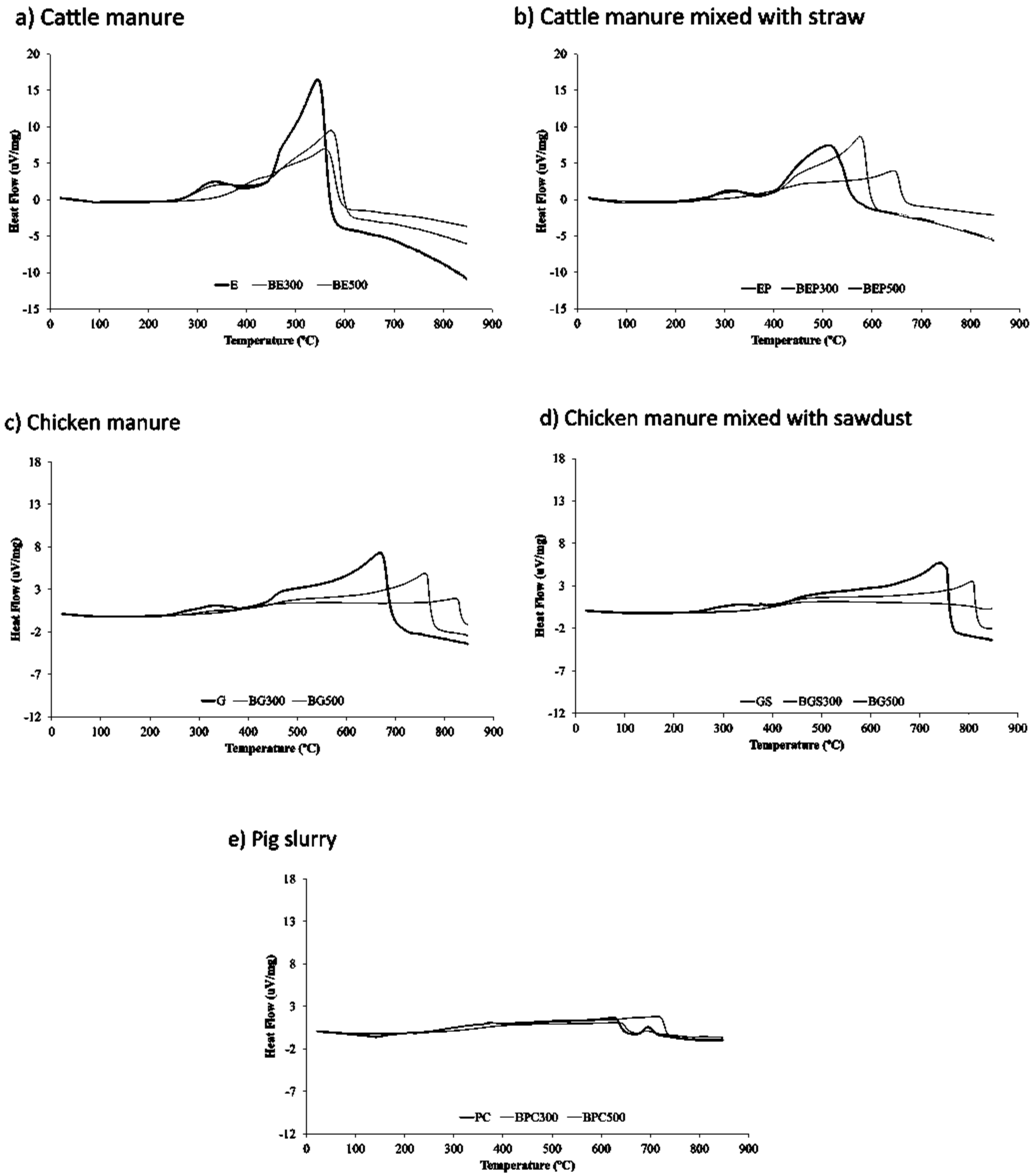

Fig. 4. Differential thermal analysis of manure wastes and corresponding biochars at 300 and 500 °C.

of samples shifted towards higher temperatures when the pyrolysis temperature for biochar preparation increased, reducing the organic matter content and leading to more stable carbon, which oxidizes at higher temperatures. This effect was more important for G and GS manures, as temperature pyroysis of 300 °C led to biochar samples (BG300 and BGS300) that started their combustion at higher temperatures, indicating the presence of stable carbon. This result was in agreement with $C_{Cr_2O_7}$ content (Table 2), fixed carbon (Table 3) and H/C ratio (Fig. 1a).

Finally, Fig. 4 shows the results from differential thermal analysis (DTA) of manure wastes and their corresponding biochar samples. It is established that energy release during organic matter combustion shifts to higher temperatures with advancing stability, in association with the combustion of an organic fraction increasingly difficult to oxidize. Fig. 4 shows different thermal behaviour of feedstock wastes. Cattle manure showed higher amount of less stabilized organic matter whereas poultry and poultry mixed with sawdust showed higher amount of more stabilized organic

Table 4
Total metal content of manure wastes and corresponding biochar samples (mg kg^{-1}).

Metal	Cattle manure			Cattle–straw manure			Chicken manure			Chicken–sawdust manure			Pig manure		
	E	BE300	BE500	EP	BEP300	BEP500	G	BG300	BG500	GS	BGS300	BGS500	PC	BPC300	BPC500
Fe	453 ± 35	528 ± 40	480 ± 36	266 ± 15	346 ± 22	300 ± 19	75 ± 7	105 ± 9	103 ± 8	80 ± 5	110 ± 10	100 ± 6	4146 ± 180	6094 ± 212	5597 ± 198
Zn	200 ± 7	234 ± 8	272 ± 7	117 ± 5	314 ± 13	477 ± 18	336 ± 15	520 ± 23	649 ± 33	315 ± 18	610 ± 25	609 ± 20	988 ± 96	1213 ± 101	1318 ± 107
Ni	7 ± 1	10 ± 1	10 ± 1	2 ± 1	3 ± 1	3 ± 1	7 ± 1	11 ± 1	10 ± 1	14 ± 1	18 ± 1	16 ± 1	11 ± 1	17 ± 1	15 ± 1
Cu	22 ± 1	28 ± 4	24 ± 8	14 ± 4	20 ± 2	16 ± 3	22 ± 4	33 ± 6	28 ± 7	51 ± 6	65 ± 14	62 ± 10	227 ± 6	348 ± 8	310 ± 12
Cd	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

Table 5
Bioavailable metal content of manure wastes and corresponding biochar samples (mg kg^{-1}).

Metal	Cattle manure			Cattle–straw manure			Chicken manure			Chicken–sawdust manure			Pig manure		
	E	BE300	BE500	EP	BEP300	BEP500	G	BG300	BG500	GS	BGS300	BGS500	PC	BPC300	BPC500
Zn	1.52 ± 0.04	0.70 ± 0.03	–	0.23 ± 0.03	–	–	18.75 ± 1.25	0.23 ± 0.05	–	9.44 ± 1.52	–	–	0.23 ± 0.02	–	–
Ni	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cu	0.53 ± 0.04	–	–	–	–	–	–	–	–	11.65 ± 1.34	3.02 ± 0.17	2.97 ± 0.08	4.84 ± 0.39	3.87 ± 0.21	1.54 ± 0.08
Cd	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

matter that combusts at very high temperature. In all cases, it could be observed the shift towards higher temperatures with increasing pyrolysis temperature. This effect was more relevant for G and GS manures, probably due to their high initial stabilization.

3.3. *Trace metals*

Table 4 shows the total trace metal content on the raw materials and biochars. Pyrolysis produced an increment in the nutrient content of the biochars [6], including Fe and other trace metals such as Zn, Ni and Cu which are essential to plant growth. Also, biochar metal content did not exceed the threshold values for concentrations of metals in soil set up by the European Union [42] and were below the limits recommended by Cely et al. [30] for agricultural use of biochar. Moreover, bioavailable forms of Zn and Cu (Table 5) decreased after pyrolysis process, in accordance with previous works that have showed that metal lixiviation decreases after pyrolysis [6].

4. Conclusions

Biochar properties were strongly influenced by manure source and pyrolysis temperature. Thus, it is possible to prepare biochars with different agronomic properties depending on the feedstock and pyrolysis conditions.

Biochars with high cation exchange capacity and elevated stability could be obtained from pyrolysis of chicken manure at 300 °C. This type of biochar has the potential to be used when the main purpose is an increase in crop yields, in particular in nutrient poor soils.

The highest biochar yields were obtained after pyrolysis of pig slurry, due to its high ash content, and chicken manure, as a consequence of its high carbonization at low temperatures.

Fixed carbon increased with pyrolysis temperature. However, this increase was more important for chicken manure and chicken manure mixed with sawdust. Biochar from chicken manure and chicken manure mixed with sawdust show high thermostability at 300 °C. In all cases, the thermostability index increased with pyrolysis temperature, indicating the presence of stable carbon and biochar as a soil amendment could be a way to enhance carbon storage in soils.

Finally, mobile forms of Zn and Cu decreased after the pyrolysis process, reducing the risk of groundwater contamination in comparison to the direct application of raw materials.

References

[1] J. Lehmann, S. Joseph, Biochar for environmental management: an introduction, in: J. Lehmann, S. Joseph (Eds.), Biochar for Environmental Management, Earthscan, London, 2009, pp. 1–9.

[2] W. Song, M. Guo, Quality variations of poultry litter biochar generated at different pyrolysis temperatures, J. Anal. Appl. Pyrolysis 94 (2012) 138–145.

[3] J.H. Yuan, R. Xu, H. Zhang, The forms of alkalis in the biochar produced from crop residues at different temperatures, Bioresour. Technol. 102 (2011) 3488–3497.

[4] R. Omar, J.P. Robinson, Conventional and microwave-assisted pyrolysis of rapeseed oil for bio-fuel production, J. Anal. Appl. Pyrolysis 105 (2014) 131–142.

[5] O. Mašek, P. Brownsort, A. Cross, S. Sohi, Influence of production conditions on the yield and environmental stability of biochar, Fuel 103 (2013) 151–155.

[6] A. Méndez, A. Gómez, J. Paz-Ferreiro, G. Gascó, Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil, Chemosphere 89 (2012) 1354–1359.

[7] A. Méndez, M. Terradillos, G. Gascó, Physicochemical and agronomic properties of biochar from sewage sludge pyrolysed at different temperatures, J. Anal. Appl. Pyrolysis 102 (2013) 124–130.

[8] L. Zhao, X. Cao, O. Masek, A. Zimmerman, Heterogeneity of biochar properties as a function of feedstock sources and production temperatures, J. Hazard. Mater. 256-257 (2013) 1–9.

[9] M.K. Hossain, V.S. Strezov, K.Y. Chan, A. Ziolkowski, P.F. Nelson, Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar, J. Environ. Manage. 92 (2011) 223–228.

[10] A. Mukherjee, A.R. Zimmerman, W. Harris, Surface chemistry variations among a series of laboratory-produced biochars, Geoderma 163 (2011) 247–255.

[11] D. Fabbri, C. Torri, K.A. Spokas, Analytical pyrolysis of synthetic chars derived from biomass with potential agronomic application (biochar). Relationships with impacts on microbial carbon dioxide production, J. Anal. Appl. Pyrolysis 93 (2012) 77–84.

[12] J. Kaal, A. Martínez Cortizas, O. Reyes, M. Soliño, Molecular characterization of Ulex europaeus biochar obtained from laboratory heat treatment experiments—a pyrolysis—GC/MS study, J. Anal. Appl. Pyrolysis 95 (2012) 205–212.

[13] J. Paz-Ferreiro, G. Gascó, B. Gutiérrez, A. Méndez, Soil activities and the geometric mean of enzyme activities after application of sewage sludge and sewage sludge biochar to soil, Biol. Fertil. Soils 48 (2012) 511–517.

[14] C. Liang, S. Fu, A. Méndez, G. Gascó, J. Paz-Ferreiro, Biochar alters the resistance and resilience to drought in a tropical soil, Environ. Res. Lett. 9 (2014) 064013.

[15] H. Lu, Z. Li, S. Fu, A. Méndez, G. Gascó, J. Paz-Ferreiro, Combining phytoextraction and biochar addition improves soil biochemical properties in a soil contaminated with Cd, Chemosphere 119 (2014) 209–216.

[16] K.B. Cantrell, P.G. Hunt, M. Uchimiya, J.M. Novak, K.S. Ro, Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar, Bioresour. Technol. 107 (2012) 419–428.

[17] W.T. Tsai, S.C. Liu, H.R. Chen, Y.M. Chang, Y.L. Tsai, Textural and chemical properties of swine-manure-derived biochar pertinent to its potential use as soil amendment, Chemosphere 89 (2012) 198–203.

[18] T. Wang, M. Camps Arbestain, M. Hedley, P. Bishop, Chemical and bioassay characterisation of nitrogen availability in biochar produced from dairy manure and biosolids, Org. Geochem. (2012) 45–54.

[19] T. Wang, M. Camps-Arbestain, M. Hedley, The fate of phosphorus of ash-rich biochars in a soil-plant system, Plant Soil 375 (2014) 61–74.

[20] H. Lu, Z. Li, S. Fu, A. Méndez, G. Gascó, J. Paz-Ferreiro, Can biochar and phytoextractors be jointly used for cadmium remediation? PLoS One 9 (4) (2014) e95218.

[21] G. Gascó, J. Paz-Ferreiro, A. Méndez, Thermal analysis of soil amended with sewage sludge and biochar from sewage sludge pyrolysis, J. Therm. Anal. Calorim. 108 (2012) 769–775.

[22] G.W. Thomas, Soil pH and soil acidity, in: J.M. Bigham (Ed.), Methods of Soil Analysis. Part 3. Chemical Methods, SSSA, Madison, 1996, pp. 417–435.

[23] J.D. Rhoades, Salinity electrical conductivity and total dissolved solids, in: J.M. Bigham (Ed.), Methods of Soil Analysis. Part 3. Chemical Methods, SSSA, Madison, 1996, pp. 417–435.

[24] ASTM, D 4607-94, Standard Test Method for Determination of Iodine Number of Activated Carbon, ASTM, Philadelphia, PA, 1995.

[25] J.M. Bremmer, C.S. Mulvaney, Nitrogen-total, in: A.L. Page, R.H. Miller, D.R. Keeney (Eds.), Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties, ASA, SSSA, Madison, 1982, pp. 595–624.

[26] F.S. Watanabe, S.R. Olsen, Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soils, Soil Sci. Soc. Am. Proc. 29 (1965) 677–678.

[27] D. Nelson, L. Sommers, Total carbon, organic carbon and organic matter, in: J.M. Bigham (Ed.), Methods of Soil Analysis. Part 3. Chemical Methods, SSSA, Madison, 1996, pp. 961–1010.

[28] USEPA, Method 3051: Microwave Assisted Acid Dissolution of Sediments, Sludges, Soils, and Oils, USDA, Washington, 1997.

[29] A.M. Ure, C.M. Davidson, R.P. Thomas, Single and sequential extraction schemes for trace metal speciation in soil and sediment, in: Quality Assurance for Environmental Analysis, Elsevier Science B.V., Amsterdam, 1965, pp. 505–523.

[30] P. Cely, A.M. Tarquis, J. Paz-Ferreiro, A. Méndez, G. Gascó, Factors driving carbon mineralization priming effect in a soil amended with different types of biochar, Solid Earth 5 (2014) 585–594.

[31] G. Sposito, The Chemistry of Soils, Oxford University Press, New York, NY, 1989.

[32] S.P. Sohi, E. Krull, E. Lopez-Capel, R. Bol, A review of biochar and its use and function in soil, Adv. Agron. 105 (2010) 47–82.

[33] E. Mészáros, E. Jakab, G. Várhegyi, J. Bourke, M. Manley-Harris, T. Nunoura, M.J. Antal, Do all carbonized charcoals have the same chemical structure? Implications of thermogravimetry–mass spectrometry measurements, Ind. Eng. Chem. Res. 46 (2007) 5943–5953.

[34] R. Calvelo Pereira, J. Kaal, M. Camps Arbestain, M. Pardo Lorenzo, R. Aitkenhead, W.W. Hedley, F. Macías, J. Hindmarsh, J.A. Maciá-Agulló, Contribution to characterisation of biochar to estimate the labile fraction of carbon, Org. Geochem 42 (2011) 1331–1342.

[35] M. Mustin, Le compost—gestion de la matière organique, Editions François, Dubusc, Paris, 1987.

[36] T. María, S. Muñoz, R. Zúñiga, Valorización Agrícola de Purines Porcinos Procesados con Aserrín de Pino, Inf. Tecnol. 20 (2009) 85–92.

[37] A. Enders, K. Hanley, T. Whitman, S. Joseph, J. Lehmann, Characterization of biochars to evaluate recalcitrance and agronomic performance, Bioresour. Technol. 114 (2012) 644–653.

[38] D. Kalderis, M.S. Kotti, A. Méndez, G. Gascó, Characterization of hydrochars produced by hydrothermal carbonization of rice husk, Solid Earth 5 (2014) 477–483.

[39] E. Smidt, P. Lechner, Study on the degradation and stabilization of organic matter in waste by means of thermal analysis, Thermochim. Acta 438 (2005) 22–28.
[40] M. Otero, L.F. Calvo, B. Estrada, A.I. García, A. Morán, Thermogravimetry as a technique for establishing the stabilization progress of sludge from wastewater treatment plants, Thermochim. Acta 389 (2002) 121–132.
[41] M.T. Dell'Abate, A. Benedetti, P. Sequi, Thermal methods of organic matter maturation monitoring during a composting process, J. Therm. Anal. Calorim. 61 (2000) 389–396.
[42] European Community, Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, Directive 86/276/EEC, Off. J. Eur. Commun. L. 181 (1986) 6–12.