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Thermal analysis of soil amended with sewage sludge and biochar from sewage sludge pyrolysis

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Abstract The main objective of the present study is to study the behaviour of sewage sludge and biochar from sewage sludge pyrolysis after addition to soil in a context of a temperate agricultural soil. For this, an incubation experiment was designed during 200 days. Carbon mineralization of soil amended with sewage sludge and biochar at two different rates (4 and 8 wt%) was evaluated. Differential thermal analysis, thermogravimetry and the first derivate of the TG were performed in oxidizing conditions on soil samples before and after incubation. Biochar obtained from sewage sludge pyrolysis at 500 °C was more stable in soil than original sewage sludge. After incubation experiment, the reduction of soil organic matter content was significantly lower in soil amended with biochar than in soil amended with sewage sludge. The thermostability index WL_3/WL_2 decreases after incubation in soil amended with biochar, however it increases in case of soil treated with sewage sludge.

Keywords Biochar · Sewage sludge · Thermal analysis · Soil

Introduction

In the last years it has been an upsurge in the use of pyrolysis as an alternative in the managing of organic wastes. During pyrolysis three fractions are generated: liquid, gas and solid. Liquid and gas fractions can be used as fuels whereas the solid fraction has been tested as cost-competitive carbon-based adsorbents [1–3]. Other uses of solid fraction could be their direct addition to soils as biochar [4–6]. Obtention of biochar has two main advantages, first, it removes pathogens from organic wastes like in sewage sludges and, second, biochar can improve the structure of soil, increase agricultural output and at the same time contribute to carbon sequestration due to carbon stability of biochar materials [7, 8]. In addition, conversion of organic wastes to biochar has the advantage of reducing the volume, which can improve their management, reducing transport costs. In spite of the high stability of carbon materials like biochar, few studies have quantified the behaviour and potential transformation in temperate agricultural soils.

Thermal analysis (DTA, DSC, TG and dTG) has been used for decades to characterize carbonaceous materials used as fuels (oil, coal). In the last years, these techniques has been applied to soil characterization to assess proportions of labile and recalcitrant organic matter [9] and to study the evolution of organic matter in amended soils [10]. These techniques have the advantage to provide information about the chemical characteristics of soil organic matter without any extraction step. So, the main objective of the present study is to study the behaviour of sewage sludge and biochar from sewage sludge pyrolysis after addition to soil in a context of a temperate climate using thermal analysis (DTA, TG and dTG). For this, one biochar was prepared by pyrolysis at 500 °C during 2 h of sewage sludge from Madrid region (Spain). Biochar was added to one selected soil from the northwest of Madrid region in two dosages (4 and 8 wt%). Experimental results were compared with unamended and amended soil with sewage sludge in the same ratios (4 and 8 wt%).

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Experimental

Soil characterization

The selected soil (S) was sampled in central Spain area (Madrid). Soil was air-dried, crushed and sieved through a 2-mm mesh. Initial pH and electrical conductivity (EC) were determined in a ratio soil:water 1:2.5 (g/mL) using a Crison micro-pH 2000 [11] and a Crison 222 conductivimeter [12], respectively. Cation exchange capacity (CEC) was determined with $NH_4OAc/HOAc$ at pH 7.0 [13]. Total organic matter (TOM) and total organic carbon (TOC) were measured by the dry combustion method at 540 °C [14]. Total humic substances (THS) of soil sample after incubation were extracted with a mixture of 1 M $Na_4P_2O_7$ and 0.1 M NaOH, centrifugated at 3,000 rpm and filtered. An aliquot of this extract was acidified with concentrated H_2SO_4 to pH 1 and centrifugated to separate coagulated humic acids (HA). The non-coagulated fraction with H_2SO_4 is referred as fulvic acids (FA). The C contents of the THS (C_{THS}), HA (C_{HA}) and FA (C_{FA}) were determined by the Walkley–Black method [14].

Soil metal content was determined using a Perkin Elmer 2280 atomic absorption spectrophotometer after sample extraction by digestion with 3:1 (v/v) concentrated HCl/HNO_3 following 3051a method [15].

Finally, soil texture was determined following Bouyoucos methodology [16].

Organic wastes characterization

Sewage sludge (SL) was obtained after aerobic treatment of sludge from one wastewater treatment plant in Madrid region. SL was air-dried, crushed, and passed through a 2-mm sieve. pH, EC, CEC, TOM, TOC, THS, FA, HA and heavy metal content in the sludge were determined, as was described for the soil (Soil characterization).

Preparation and characterization of biochar

Biochar was prepared as follows: 20 g of SL were placed in a ceramic cup placed in an electric tubular furnace Carbolite. Samples were pyrolysed using 50 mL/min N_2 flow rate by increasing the temperature to 500 °C at a rate of 3 °C/min. Final temperature was maintained for 2 h. pH, EC, CEC, TOM and heavy metal content in the biochar were determined, as was described for the soil (Soil characterization).

Treatments

Selected soil (T) was amended with the SL (SL) and the biochar (B) at two different rates: 4 and 8 wt% leading to SL4, SL8, B4 and B8 treatments. All the treatments were replicated three times.

Incubation procedure

The biological activity of non-amended and amended soils was evaluated by soil respiration (cumulative CO_2 evolution) and total mineralization coefficient (TMC). 200 g of each sample were put in a glass vessel and the CO_2 evolved was evaluated during 200 days at a temperature of 28 ± 2 °C. The decomposition rate was determined by passing CO_2 and NH_3 free air through the respiration vessels, trapping the evolving CO_2 in 50 mL of 1 M NaOH. Titration of trapped CO_2 was performed with 1 M HCl after $BaCl_2$ precipitation of carbonates. Triplicate CO_2 measurements of each soil were taken periodically. Another three vessels without soil sample were used as blanks for each measure of evolving CO_2 [17]. TMC was calculated according to [18] as follows:

$$\mathrm{TMC}\ (\mathrm{mg\ C-CO_2/g\ C}) = \mathrm{C-CO_2\ evolved/initial\ TOC}$$

where $C - CO_2$ evolved is expressed as mg $C - CO_2$/100 g soil and initial TOC is expressed as g C/100 g soil.

Organic matter characterization of soils after incubation experiment

The degree of humification was determined according to Zbytniewski and Buszewski [19]. One gram of each sample was weighted into a 250 mL polyethylene flask and extracted with 50 mL of 0.5 M NaOH by shaking for 2 h. Absorption was measured at 280, 472 and 664 nm using a UV–Vis Shimazu UV-1203. The following absorption rates were calculated as follows: $Q_{2/6} = A_{280}/A_{664}$, $Q_{4/6} = A_{472}/A_{664}$, $Q_{2/4} = A_{280}/A_{472}$, according to Zbytniewski and Buszewski [19]. $Q_{2/6}$ represents the relationship between non-humified and strongly humified material; $Q_{4/6}$ is often called the humification index being the most often calculated ratio. Typical values of the $Q_{4/6}$ ratio for humified material were lower than 5 [20]. $Q_{2/4}$ represents the proportion between lignins and other materials at the beginning of humification. Low $Q_{2/6}$ or $Q_{4/6}$ ratios reflect a high degree of aromatic condensation and indicate a higher level of organic material humification [19].

Thermal study of samples

The selected soil, SL, biochar and amended soils 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 until 850 °C in air atmosphere using a flow rate of 40 mL/min.

Thermogravimetric results were quantified as the weight loss of samples attributed to different temperature ranges: WL_1 from 25 to 150 °C; WL_2 from 200 to 400 °C and WL_3 from 400 to 600 °C [9, 21]. WL_1 was related to water release from sample, whereas WL_2 and WL_3 correspond to weight loss associated to organic matter combustion ($W_{org} = WL_2 + WL_3$). It is established that first peak was associated with combustion of less humified organic matter, whilst the second one was related to the more humified [21, 22]. The WL_3/WL_2 ratio, named thermostability index, was previously identified as a reliable parameter for evaluating the level of stability of organic matter in composts and other organic wastes [21, 23, 24] that indicated the relative amount of the thermally more stable fraction of organic matter with respect to less stable one.

Results and discussion

Initial amendment characterization

Table 1 summarizes the main properties of soil, SL and biochar selected for this study. The soil was classified as a Haplic Cambisol [25] and it has a sandy-loam texture, basic pH (8.63) and low organic carbon content (1.16%). It could be observed that pyrolysis process affected the agronomic properties of SL with pH increasing from 6.98 in the SL to 9.54 in the biochar, whilst EC decreased from 1,055/µS/cm for SL to 49.3/µS/cm for biochar. CEC was almost four times higher in the SL than in the biochar (9.16 and 2.36 $cmol_+$/kg, respectively). Both, SL and biochar exhibited high contents for all the heavy metals studied. The copper content increased by 80%, when comparing the biochar with the SL, and by 40% for other heavy metals. Finally, the organic matter content decreases after pyrolysis of SL as a result of polymerisation/condensation reactions produced during pyrolysis process.

Table 1 Main properties for soil, sewage sludge and biochar

Properties	Soil	Sewage sludge	Biochar
pH	8.63	6.98	9.54
EC (1:2.5)/µS/cm	71.6	1055	49.3
TOM/%	1.16	60.4	29.85
C_{THS}/%	0.56	2.25	–
C_{AH}/%	0.21	1.82	–
C_{AF}/%	0.35	0.43	–
$N_{Kjeldahl}$/%	0.02	–	–
CEC/$cmol_{(+)}$/kg	6.6	9.16	2.36
Soil moisture at 33 kPa/%	7.62	–	–
Soil moisture at 1500 kPa/%	4.55	–	–
Cu/mg/kg	7.60	151	276
Ni/mg/kg	13.35	25	35
Cd/mg/kg	4.35	1.28	1.79
Zn/mg/kg	48.45	900	1250
Pb/mg/kg	26.80	136	196
Clay (<0.002 mm)/%	10.0	–	–
Silt (0.002–0.05 mm)/%	12.5	–	–
Sand (0.05–2 mm)/%	77.5	–	–
Texture	Sandy-loam	–	–
Pyrolysis yield/%			45

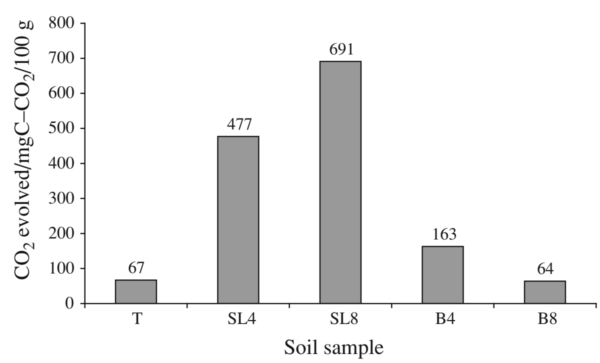

Fig. 1 Cumulative CO_2 evolved during the incubation experiments

Effect of SL and biochar on soil respiration

Cumulative CO_2 evolved during incubation process of control and amended soils is showed in Fig. 1. Previous studies have showed contradictory results in the effect of biochar addition on soil respiration, as some studies have found that young biochar increases soil respiration [26] whilst other studies [27, 28] have found that soil respiration decreases with increasing doses of biochar. Diminishing of soil respiration values have been attributed to chemisorptions of respired CO_2 to the biochar surface, to an increase of C-use efficiency, to a decrease of population abundance or to a combination of these factors [29]. On the other hand, soil respiration increases have been attributed to biochar being not inert in the short-term providing significant amounts of labile C, mainly condensates from the bio-oil formed during pyrolysis that were absorbed to the biochar during cooling [26]. In this study, soil respiration follows the order C < B8 < B4 < SL4 < SL8. Highest respiration values correspond to soil amended with SL. Addition of biochar increases soil respiration with respect to control soil. However, B8 showed lower respiration than B4.

Effect of SL and biochar on soil organic matter

UV–Vis analysis of alkali extracts is generally based on the assumption that the absorbance at 260–280 nm is due to lignin and quinone moieties (i.e. the material at the very beginning of transformation). The absorbance at 460–480 nm reflects the organic material at the beginning of humification and the absorbance at 600–670 nm is said to be indicative of strongly humified material with a high degree of aromatic and condensed groups [20]. With respect to the indices obtained by UV–Vis absorption of NaOH solutions, Table 2 summarizes the $Q_{2/6}$, $Q_{4/6}$ and $Q_{2/6}$ ratios of soil samples after incubation experiment. In soil amended with SL, $Q_{2/6}$ and $Q_{2/4}$ decreases and $Q_{4/6}$ increase with respect to control soil, especially as highest is the SL addition, indicating higher organic matter humification. On the other hand, soil samples amended with biochar show similar $Q_{2/6}$, $Q_{4/6}$ and $Q_{2/4}$ ratios than control soil. Only B8 shows higher $Q_{2/6}$ which was indicative of more content of organic matter less humified after incubation process.

Figure 2 shows DTA of initial control soil (T). First endothermic peak at temperatures lower than 150 °C was due to moisture release from soil sample. Then, two small exothermic peaks could be observed between 200 and 500 °C due to combustion reactions of soil organic matter. It is established that first peak was associated with combustion of less humified organic matter, whilst the second one was related to the more humified [9]. Finally, at 573 °C the endothermic small peak was due to the quartz α–β inversion.

Figure 3 shows TG and dTG curves of SL and biochar. At temperatures from 200 to 550 °C oxidation of organic matter takes place. At temperatures higher than 550 °C weight loss could be attributed to refractory carbon and clays decomposition. Finally, between 700 and 800 °C, carbonates decomposition was observed. It could be observed that pyrolysis of SL reduces their organic matter content. In addition, biochar shows more thermally stable organic matter that oxidizes at higher temperatures. So, carbonates were more abundant in biochar than in SL.

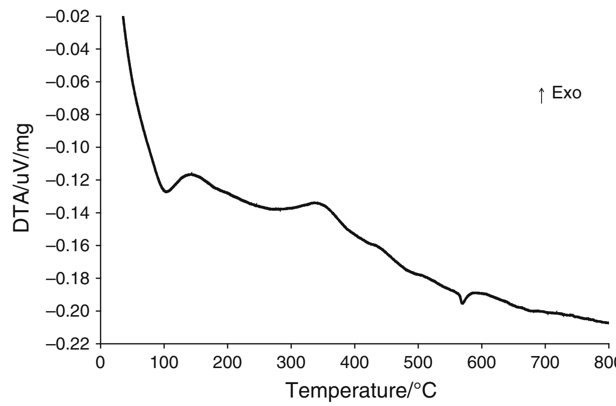

Fig. 2 DTA of selected soil

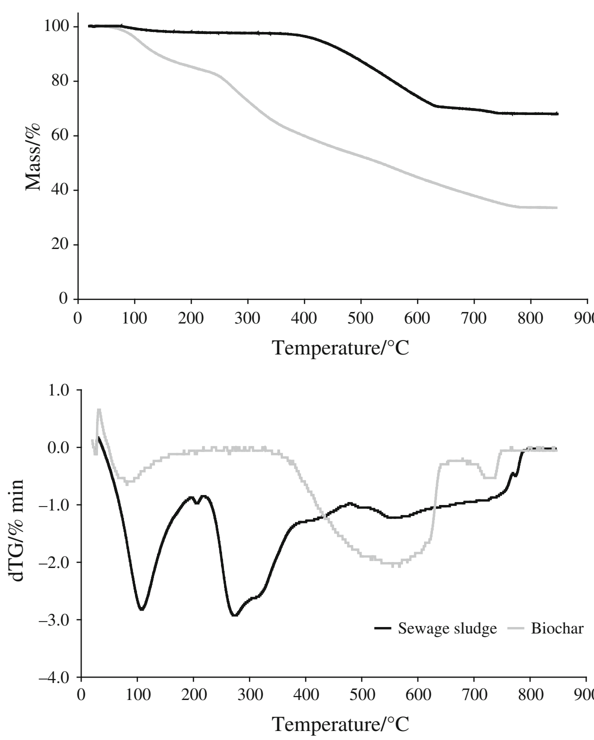

Fig. 3 TG and dTG of sewage sludge and biochar from sewage sludge pyrolysis

Table 2 UV–Visible absorbance ratios of 0.5 NaOH solutions for raw materials (sewage sludge, biochar and soil) and control and amended soils after incubation experiment

	$Q_{2/6}$	$Q_{4/6}$	$Q_{2/4}$
Raw materials			
Sewage sludge	5.75	3.02	1.90
Biochar	20.46	0.82	24.84
T_0	18.48	0.93	19.79
Final day/200 days			
T	16.66 ± 0.10 c	0.78 ± 0.02 a	21.39 ± 0.40 c
SL4	14.66 ± 0.08 b	1.58 ± 003 b	9.26 ± 0.07 b
SL8	10.92 ± 0.03 a	2.01 ± 0.04 c	5.42 ± 0.07 a
B4	16.51 ± 0.03 c	0.77 ± 0.02 a	21.42 ± 0.16 c
B8	17.05 ± 0.09 d	0.78 ± 0.04 a	21.79 ± 0.44 c

Values in a given column followed by the same letter are not significantly different ($P = 0.05$) using Duncan method

Table 3 summarizes thermal parameters obtained by thermogravimetric curves of control and amended soil before (*i*) and after (*f*) incubation experiment. In addition, Fig. 4 shows DTA curves of SL4 (Fig. 4a) and SL8 (Fig. 4b), before (*i*) and after (f) incubation experiment

Table 3 Thermal parameters of control and amended soil before (*i*) and after (*f*) incubation experiment

Soil sample	Mass loss/%			$WL_2 + WL_3$	WL_3/WL_2
	WL_1/25–150/°C	WL_2/200–400/°C	WL_3/400–600/°C		
Ti	2.02	0.41	0.64	1.05	1.56
Tf	0.63	0.30	0.49	0.79	1.63
SL4i	1.46	1.74	2.10	3.84	1.21
SL4f	0.76	1.05	1.38	2.43	1.31
SL8i	1.64	2.43	2.72	5.15	1.12
SL8f	0.83	1.17	1.78	2.96	1.53
B4i	0.92	0.55	2.02	2.57	3.67
B4f	0.93	0.50	1.77	2.26	3.61
B8i	0.86	0.53	2.74	3.27	5.19
B8f	0.90	0.82	2.38	3.20	2.90

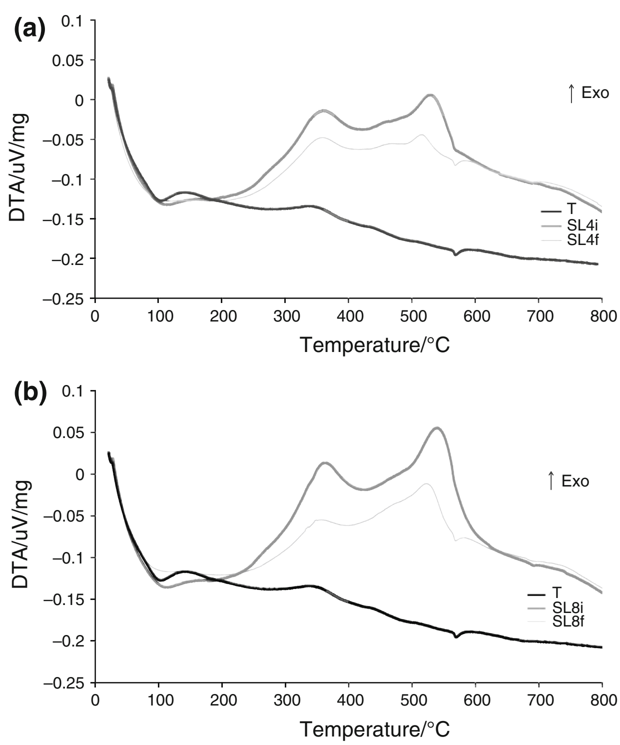

Fig. 4 DTA of sewage sludge-amended soils before and after incubation experiment

compared to control soil (*T*). SL has 60.4 wt% of TOM (Table 1) and consequently, their addition significantly increases the organic matter content of soil ($WL_2 + WL_3$ from Table 3) and the intensity of two exothermic peaks between 250 and 550 °C related to organic matter combustion (Fig. 4). After incubation experiment of SL4 (Fig. 4a), the intensity of both peaks significantly decreases due to carbon mineralization and organic matter transformation. In case of SL8 (Fig. 4b), the first peak related to combustion of less humified organic matter significantly decreases during incubation. However, the reduction of the second peak was lower than that of SL4. This result indicates that more organic matter humification was produced in the sample amended with highest SL content (SL8). This result was in accordance with the important decreases of $Q_{2/6}$ and $Q_{2/4}$ and highest $Q_{4/6}$ for SL8 sample after their incubation.

The thermostability index, WL_3/WL_2, was determined to complete the thermal study of SL-amended soils (Table 3). Initially, WL_3/WL_2 index of soil decreases with the addition of SL, from 1.56 to 1.21 and 1.12 for SL4 and SL8, respectively, due to fresh organic matter addition from SL. However, the $WL_2 + WL_3$ decreases and WL_3/WL_2 index increases after incubation experiment, especially for SL8, due to organic matter mineralization and humification.

Figure 5 shows DTA of B4 (Fig. 5a) and B8 (Fig. 5b) before (*i*) and after (*f*) incubation experiment. In soil amended with 4 wt% of biochar, the second peak slightly decreases after the incubation indicating a little degradation of biochar in soil after the 200 days incubation experiment. In the B8 sample, decrease of second peak intensity was associated with the increase of the first one related to combustion of less thermally stable organic matter. This result was according to the slight increment of $Q_{2/6}$ absorbance ratio being indicative that slight biochar degradation leads to less humified organic structures.

Finally, thermogravimetric results summarized in Table 3 showed that initial addition of biochar to soil increases the WL_3/WL_2 ratio from 1.56 to 3.67 and 5.19 for B4 and B8, respectively due to the addition of more thermally stable organic matter from biochar (Fig. 3). The incubation process during 200 days slightly reduces the $WL_2 + WL_3$ value for B4 and B8, indicating the highest stability of biochar from SL pyrolysis in this soil. However, the WL_3/WL_2 of biochar-amended soils (B4 and specially B8) decreases after incubation indicating that more complex organic structures lead to less thermally stable ones.

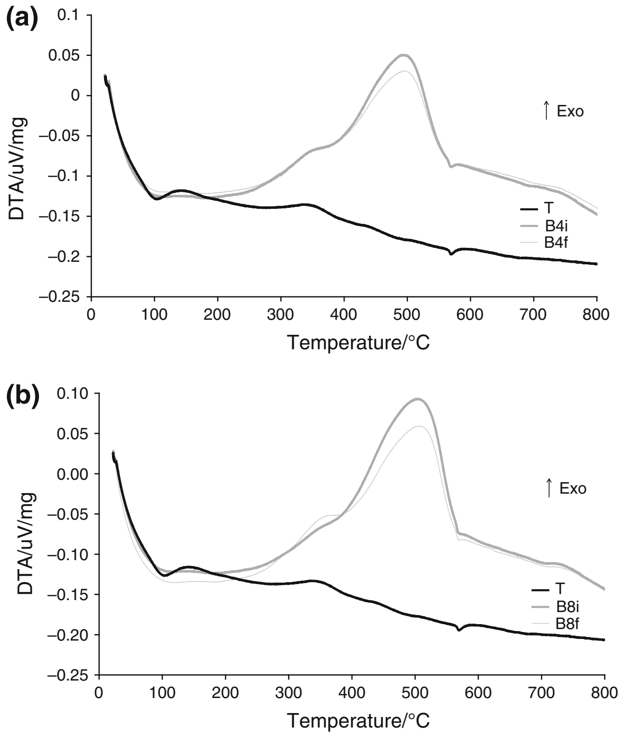

Fig. 5 DTA of biochar-amended soil before and after incubation experiment

Conclusions

– Thermal analysis is an interesting tool to evaluate the organic matter evolution of soils amended with SL and biochar from SL pyrolysis.
– Biochar was more stable in soil than original SL. After 200 days of incubation experiment, the reduction of soil organic matter content was significantly lower in soil amended with biochar than in soil amended with SL.
– The thermostability index WL_3/WL_2 decreases after incubation experiment in soil amended with biochar, however it increases after incubation in soil treated with SL but these values are lower than the obtained after incubation of control soil.

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