

Spent coffee grounds by-products and their influence on soil C–N dynamics

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ABSTRACT

SCG are a bio-waste generated in great amount worldwide which are attractive as soil amendment for their high content of organic matter and nutritive elements. Nevertheless, several studies have shown that soil application of untreated SCG has detrimental agronomic and environmental effects due to their high degradability and content of noxious compounds (phenols, caffeine, and tannins). However, SCG can be valorised, in the frame of circular economy, by extraction of energy and valuable products (carbohydrates, proteins, bio-oil, bio-diesel) and generation of solid by products (biochar, hydrochar, compost) that can be utilized as soil fertilizers and amendments.

Therefore, the aim of this work was the characterization of different solid SCG by-products (as second-generation products) and their assessment as effective organic amendments. The novelty of this study is that for the first time 8 different by-products derived from the same SCG were characterized and comparatively evaluated for their impact on the C and N cycles of soil. SCG was collected and treated to generate 8 different SCG by-products (biochars produced at 270 and 400 °C, hydrochars produced at 160 and 200 °C, vermicompost, defatted SCG and biochars produced from defatted SCG at 270 and 400 °C). SCG and derived by-products were characterized for SEM micromorphology, pH and EC values, and C, N, H, O, volatile matter, fixed C, LOI, carbonates, water soluble C and N, NO₃⁻ and NH₄⁺ content. SCG and SCG by-products assessment as organic amendments was performed with an incubation experiment. The residues were added (2.5%) to a moist Mediterranean agricultural soil and the amended soil samples were placed in mesocosms and incubated at 20 °C for 30 days. During incubation, CO₂ and N₂O emissions were measured every 6 h by means of a gas chromatography automated system for GHG sampling and measurement. The percentage of added C remaining (C_R) in the soil was calculated by fitting the cumulative respiration of amended soil to a two-pool model. After 2, 7 and 30 days of incubation, the control and amended soils were sampled and analyzed for their content of extractable organic C, N, NO₃⁻ and NH₄⁺ and microbial biomass C and N. Results showed that SCG by-products presented a great variability in their properties. SCG and hydrochars presented higher contents in volatile matter and water soluble C and N, and low content of fixed C, while biochars showed an opposite behaviour. SEM images confirmed the different characteristics of the SCG by-products: the biochar presented a porous structure, honeycomb-like form, due to the loss of the more soluble compounds, while the SCG and hydrochars' pores were filled with amorphous carbonaceous materials. Consequently, soil addition of SCG by-products showed a distinct impact on C and N cycle and microbial biomass content. Addition of SCG and hydrochars generated the highest cumulative CO₂-C emissions (2103–2300 μg g⁻¹), the lower amount of C_R (86.8–88.6%), increased the soil extractable organic C and microbial biomass C and N and caused N immobilization. On the other hand, the addition of biochars generated lower CO₂-C emissions (542–1060 μg g⁻¹), higher amounts of C_R (96.3–99.9%) and lower amounts of extractable compounds and microbial biomass C and N, generating also N immobilization, but to a lesser extent. The addition of vermicompost generated 723 μg g⁻¹ of CO₂-C and 98% of C_R remaining. However, this by-product did not generate N immobilization being able to act as N fertilizer. None of the residues generated N₂O emissions. The different properties of the SCG by-products and their impact on C and N cycle indicated that they can be effectively applied to soil to exert different agronomical and environmental functions.

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1. Introduction

Over 120 million Mg of bio-residues are generated annually in Europe, which is landfilled and only a small part is incinerated (Chojnacka et al., 2020) causing several harmful environmental effects and the loss of nutritive elements. One solution to decrease the detrimental side effects of biomass disposal is the so-called circular economy, which is a process that keeps resources within the economy for as long as possible and eliminates wastes; these resources can be used again and again and create further value (COM/2014/398/EC).

In line with the circular economy concept, different biomass valorisation methods have been widely used. The most popular one is composting (within which vermicomposting is particularly significant), but in recent years, other types of techniques have been used for the transformation of raw materials, such as anaerobic digestion, incineration, gasification, pyrolysis and hydrothermal carbonization (HTC) (Chojnacka et al., 2020; Wang et al., 2018). Thermochemical conversion is the most common process for the transformation of agricultural wastes due to their lignocellulosic nature (Cao et al., 2017). The by-products resulting from the pyrolysis and HTC process are known as biochar and hydrochar (Kambo and Dutta, 2015). Both pyrolysis and HTC provoke an increase in fixed carbon, ash and carbon content and a decrease in volatile matter and O content (Azzaz et al., 2020; Yu et al., 2019; Libra et al., 2011). There is much interest in valuing these types of second generation residues from the agro-environmental point of view. For example, the effect of biochars and hydrochars on greenhouse emissions has been reflected in the works of Sri Shalini et al. (2020), Schimmpfennig et al. (2014) or Kammann et al. (2012). The impact of this kind of products on C and N dynamics has been also studied (Cayuela et al., 2010; Song et al., 2020; Bera et al., 2021; Galvez et al., 2012; Nguyen et al., 2017).

Spent coffee grounds (SCG) are a bio-waste, whose annual generation amounts to 15 million tons (Kamil et al., 2019). The utilization of SCG as soil organic amendment has been previously studied by our research group. The addition of SCG improved soil chemical and physical fertility, increasing N, P and K content (Cervera-Mata et al., 2018) and enhancing structural stability of soil aggregates, water holding capacity, soil hydrophobicity and decreasing soil bulk density (Cervera-Mata et al., 2019, 2021a). SCG also improved the content of all fractions of soil organic matter, especially the most labile fractions (Comino et al., 2020) and increased soil microbial diversity and the complexity of microbial interaction networks (Vela-Cano et al., 2019).

The transformation of SCG as waste within a circular economy scheme generates added-value products. For example, pyrolysis generates biogas, bio-oil (Alves et al., 2017), and HTC produces a liquid residue rich in manno-oligosaccharides (Pérez-Burillo et al., 2019) and other second generation solid residues with a high content of C (biochar and hydrochar). The study of the solid bio-amendments derived from SCG (such as biochar, hydrochar, compost, vermicompost) as amendment or fertilizer has been focused on its effect on plant growth, nutrient mobilization, or on a simple characterization of the residue (Afolabi et al., 2020; Cervera-Mata et al., 2020, 2021; Kim et al., 2017; Ronga et al., 2016; Vardon et al., 2013). SCG hydrochar and biochar are characterized by an increase in C, fixed C and by a decrease in volatile matter, O and H/C and O/C molar ratios with respect to SCG (Afolabi et al., 2020; Kim et al., 2017), cause an effect already reported for other residues (Azzaz et al., 2020; Yu et al., 2019; Libra et al., 2011). Such modifications suggest that these bio-products can have a significant effect on the C and N cycles and biological fertility. On the other hand, studies performed on the phytotoxicity of different SCG derived by products (compost, vermicompost, biochar and hydrochar) has shown a different behaviour depending on the treatment undergone by SCG (Cervera-Mata et al., 2020, 2021b). In particular, it has been shown that carbonization at temperatures above 400 °C and vermicomposting are effective in alleviating the toxicity present in the original SCG. Therefore, an extensive study is required before utilization of SCG derived

by-products as organic amendments in order to maximize their beneficial agronomical and environmental functions and decrease negative side effects. To date there are no extensive and systematic studies in the literature about the effect of SCG and SCG solid by-products (including vermicompost) on soil C and N dynamics and biochemical properties. For example, Zhang et al. (2014) reported that the addition of SCG biochar (at 700 °C) did not enhance soil microbial biomass and soil respiration and Cervera-Mata et al. (2021a) found a significant increase in respiration rate with the addition of SCG. Regarding N dynamics, Cruz and Marques dos Santos Cordovil (2015) and Hardgrove and Livesley (2016) found that the addition of SCG caused N immobilization in soil, recorded as reduced soil NO₃⁻ availability. According to these authors, N immobilization is due to the low N mineralization of this waste in soil. They attributed this to the wide C/N ratio of SCG. Beside C/N ratio, also the quality of added C and N can play an important role. SCG presents compounds like lignin, phenols and tannins that for their chemical composition and structure are resistant to microbial decomposition. Moreover, caffeine is present in great amounts in SCG, has a high content of N (C/N of 2) and can inhibit growth of microorganisms (Cruz and Marques dos Santos Cordovil, 2015), therefore acting as N storing molecule.

Despite several researches aimed to evaluate the effect of SCG application to soil, to date there are no extensive and systematic studies in the literature about the effects of SCG and SCG solid by-products (including vermicompost) on soil C and N dynamics, and biochemical properties.

Therefore, the aims of this study were: (i) to characterize the solid SCG by-products generated through pyrolysis, hydrothermal carbonization, vermicomposting, and defatting, and (ii) to evaluate in a soil incubation experiment, the influence of bio-residue properties on C and N dynamics, added C conservation potential, microbial biomass content and nutrients availability.

2. Materials and methods

2.1. Soil and residues used for incubation

The soil used in the incubation assay was sampled from the arable layer (0–20 cm) of an agricultural soil from the Vega of Granada (Andalusia, Southern Spain), typical of the Mediterranean climate. This soil was classified as Cambic Calcisol (Aric, Ochric) (IUSS Working Group WRB, 2014) and presents the following properties: sand 281 g kg⁻¹, clay 58 g kg⁻¹, silt 13.9 g kg⁻¹, moisture 4.1 g kg⁻¹, pH 8.2, OC 1.36 g kg⁻¹, total N 0.105 g kg⁻¹, C/N 13, carbonates as CaCO₃ 39 g kg⁻¹, available K 453 mg kg⁻¹, available P 69 mg kg⁻¹. Soil samples were air-dried and sieved (2 mm) (Cervera-Mata et al., 2021a).

SCG were obtained from the cafeteria of the Faculty of Pharmacy (University of Granada). SCG were spread into a thin layer and dried at room temperature to remove residual moisture. Seven by-products were produced from SCG: biochar produced at 270 °C (B270) and 400 °C (B400), hydrochar produced at 160 °C (H160) and 200 °C (H200), vermicompost (VC), defatted SCG (SCG_d) and two biochar from defatted SCG (produced at 270 °C and 400 °C, B270_d and B400_d, respectively). Biochars (both those from fresh SCG and defatted ones) were produced in a pyrolytic oven (Navertherm GmbH, Germany) in two different ways: 270 °C for 60 min (modified from Comino et al., 2017), and 400 °C for 30 min (Kim et al., 2014). The hydrochars were generated in a laboratory-scale hydrothermal carbonization (HTC) reactor (High-preactor™ BR-300, Berghof Ltd, Germany). The HTC reactor temperature was set to 160 and 200 °C (for each run) during 1 h (heating rate of 12–15 min) and agitation speed of 200 rpm. The vermicompost derived from SCG were supplied by the organic natural fertilizer company AGROHULOVA S.L. (Granada, Spain). The vermicomposting of SCG was performed for 8 months using Californian red earthworm (*Eisenia foetida*). The defatting of SCG was performed by lipids extraction with hexane during 3 h in a Soxhlet apparatus, in order to improve the

performance of the pyrolysis process as indicated by Vardon et al. (2013).

2.2. Soil incubations

The soil was pre-conditioned at 40% of water holding capacity and 20 °C under aerobic conditions for 5 days. Subsequently, the residues were thoroughly added at the dose of 2.5% (w:w) and aerobically incubated in the dark at 20 °C for 30 days. Untreated soil was also included as a control. Samples were incubated in sealed plastic jars for determination of CO₂ and N₂O evolution every 4 h (in triplicate), while an identical parallel incubation was set out for destructive sampling after 2, 7 and 30 days for determination of extractable NH₄⁺, NO₃⁻, organic C (EOC), N (EN) and soil microbial biomass C and N content (in quadruplicate). The moisture levels in the jars were checked weekly by measuring weight loss, and deionised water was added when necessary to maintain constant moisture.

2.3. Analytical methods

2.3.1. SCG and SCG by-products

Organic amendment analyzes were performed on the freeze-dried samples. Elemental analysis (C, H, O and N content) was performed using a CHN analyzer (Thermo ScientificTM Flash 2000). Proximate analysis, i.e. volatile matter (at 950 °C), ash contents (at 750 °C), moisture content (at 105 °C) and fixed carbon (calculated from the above parameters), was performed using the ASTM D1762-84 method. Water soluble carbon (WSC) and N (WSN) were determined in 1:20 (w/v) water extracts using a TOC-TN analyzer (TOC-VCSN Shimadzu). Loss on ignition (LOI) and CaCO₃ were measured with a thermogravimetric analyzer (Leco). Electrical conductivity, measured at 25 °C (EC₂₅), and pH were determined in a 1:5 (w/v) water-soluble extract. N-NH₄⁺ was extracted using a 1:20 (w/v) ratio of amendment to KCl 1M and determined by a modified colorimetric method based on Berthelot's reaction (Sommer et al., 1992). NO₃⁻ was extracted using a 1:20 (w/v) ratio of amendment to H₂O and determined by a modified colorimetric method based on VCl₃-Griess reaction (Miranda et al., 2001).

Scanning electron microscopy (SEM) images were captured from SCG by-products fixed with double-sided adhesive carbon tape, metallized with carbon and analyzed with variable pressure and high-resolution scanning electron microscope (VPSEM-FESEM) SUPRA40VP (ZEISS, Oberkochen, Germany).

2.3.2. Amended soils

CO₂ and N₂O evolution was determined by an automated system for continuous gas sampling and analysis. The system operates as an "open chamber" system in which the sealed plastic jars containing the soil sample are continuously aerated at constant flow rate (15 ml min⁻¹). The output of all jars is vented to the ambient, except for a selected jar of which the output is directed by means of two valves to a gas chromatograph (Agilent 7890A) for GHG content (CO₂ and N₂O) determination. At the end of the measurement period (6 min), the valves automatically direct the output of the following jar to the GC and so on. The system can operate with up to 30 samples and allows the measurement of the evolution rate of greenhouse gases over regular periods.

The percentage of C remaining in soil with respect to the total C added (C_R) was calculated by fitting the cumulative respiration curve of the amended soil minus the cumulative respiration curve of the control soil to a two-pool model according to the following equation (Robertson and Paul, 2000):

$$C_R(t) = f \times \exp(-k_1 t) + (100 - f) \times \exp(-k_2 t). \text{Where,}$$

C_R (%) = fraction of added C remaining in the soil at time t,

t (days) = incubation time,

f (%) = fraction the active or fast turnover pool of added C,

k₁ (days⁻¹) = decomposition rate constant for the active pool,

k₂ (days⁻¹) = rate constant for the slow pool.

The fraction of exogenous organic matter that remains in soil after 1 year (the humification coefficient, *h*), was also calculated based on an average annual temperature of 20 °C (Bradbury et al., 1993). The humification coefficient gives an estimation of the stable organic matter that remains in soil (Janssen, 1984), so it was used as an indicator of C sequestration potential.

Extractable organic C, N, NH₄⁺ and NO₃⁻, were determined following extraction using a 1:4 (w/v) ratio of soil to K₂SO₄ 0.5 M extract. K₂SO₄-extractable organic C (EOC) and N (EN) were measured using a TOC-TN analyzer (TOC-VCSN Shimadzu). Extractable NH₄⁺ was determined by a modified colorimetric method based on Berthelot's reaction and performed in microplate (Sommer et al., 1992). The content of NO₃⁻ was measured by a modified colorimetric method based on VCl₃-Griess reaction (Miranda et al., 2001). Net mineral N was calculated as the difference between NO₃⁻ + NH₄⁺ in the amended soil and NO₃⁻ + NH₄⁺ in the control soil. Soil microbial biomass C (B_C) and N (B_N) were determined by the fumigation-extraction method (Vance et al., 1987).

2.4. Statistical methods

Means between groups were compared by analysis of variance (ANOVA) at *p* < 0.05 confidence level (SNK test). Linear correlations were evaluated by computing the correlation coefficient by Pearson. These statistical procedures were carried out using SPSS 22.0 for Windows (IBM SPSS Inc., New York, USA). Partial least squares regression (PLS-R) analyses were performed to predict dependent variables (X) from a large set of independent variables (Y) using the XLSTAT version 2021.2.1. Principal component analysis (PCA) was performed for clustering samples and relating them to the different parameters used in the study. This statistical treatment was performed in Origin b9.5.5409 (OriginLab Corporation, Northampton, MA, USA).

3. Results

3.1. SCG and SCG by-products properties

The physicochemical properties of SCG and SCG by-products are shown in Table 1. All treatments, except vermicomposting, caused an increase in C content, with pyrolysis and HTC causing the larger and the lower increase, respectively. Defatting appears to increase the efficiency of pyrolysis on the concentration of C. The highest contents of N correspond to VC, followed by both biochars at 400 °C. C/N ratio ranged between 7 (VC) and 25 (H200). Biochars are the residues with the highest content of fixed C and the lowest volatile matter, while hydrochars and both SCG show the opposite behaviour. Fixed C is higher in both biochars at 400 °C and lower in the SCG and H160. The ash ranged between 0.41% and 3.72%, except for the VC which has a content of ashes of about 20%. Due this high ash content, LOI of VC is quite low (80%) in comparison to the other amendments, which is in the range 96–99%.

Regarding pH and electrical conductivity (both important properties for soil nutrients dynamics), hydrochars and SCG presented acid values, while B400 and VC showed basic ones. Furthermore, VC had an extreme value of salinity (48 dS m⁻¹) and the highest content of carbonates (2.3%), which is in agreement with its higher concentration in inorganic compounds. Concerning the soluble forms of C and N, SCG and hydrochars had the highest values. On the contrary, the amount of these forms on biochars was minimum. The residues also differed in the composition of N forms. NH₄⁺-N varied between 3 μg g⁻¹ (for both B400) and 160 μg g⁻¹ (H160). NO₃⁻-N was not detected in biochar samples while VC presented a remarkable high content.

The different treatments applied to SCG (pyrolysis, HTC, vermicomposting and defatting), also modified the physical structure of SCG, which is shown in the SEM images (Fig. 1). Fig. 1a shows a typical SCG's porous structure with the pores (approximately 30 μm) surrounded by

Table 1
Compositional and chemical properties of SCG and SCG by-products.

Residue	Ultimate analysis (%)				Proximate analysis (%)				LOI (%)	pH	EC ₂₅ (dS m ⁻¹)	CaCO ₃ (%)	WSC (µg g ⁻¹)	WSN (µg g ⁻¹)	NH ₄ -N (µg g ⁻¹)	NO ₃ -N (µg g ⁻¹)
	C	N	H	O	C/N	Moisture	Ash	Fixed carbon								
SCG	48.0	2.290	7.58	42.1	21	7.53	1.45	13.97	98.58	5.4	9.00	0.15	25.92	3.74	11.6	2.59
B270	58.1	3.157	6.67	32.1	18	4.06	2.09	29.20	97.91	6.4	3.15	0.18	6.56	0.72	7.64	nd
B400	69.8	4.253	5.78	20.2	16	2.53	3.72	57.21	96.53	8.4	1.78	0.34	0.63	0.5	3.12	nd
H160	52.0	2.210	8.08	37.7	24	3.58	0.41	13.45	99.64	4.6	4.41	0.08	31.36	3.8	160.53	6.37
H200	62.6	2.470	7.62	27.3	25	3.46	0.54	26.02	99.49	3.9	4.25	0.05	37.65	4.72	47.41	1.30
VC	40.6	5.77	5.60	48.0	7	10.38	19.11	18.31	80.09	7.8	48.28	2.34	10.85	2.96	58.39	21.61
SCG _d	48.8	2.60	7.73	40.9	19	8.01	1.60	14.85	98.42	5.4	11.2	0.19	26.46	3.99	20.19	1.07
B270 _d	63.0	4.09	6.15	26.8	15	4.85	3.07	36.59	96.55	5.9	5.60	0.32	4.67	0.58	13.37	nd
B400 _d	72.2	4.46	5.99	17.4	16	4.06	2.85	50.32	97.68	8.6	2.20	0.23	0.94	0.22	3.03	nd

SCG: spent coffee grounds; B270: biochar produced at 270 °C; B400: biochar produced at 400 °C; H160: hydrochar produced at 160 °C; H200: hydrochar produced at 200 °C; VC: vermicompost; SCG_d: defatted SCG; B270_d: biochar from defatted SCG produced at 270 °C; B400_d: biochar from defatted SCG produced at 400 °C; LOI: loss on ignition; EC₂₅: electrical conductivity measured at 25 °C; WSC: water soluble carbon; WSN: water soluble nitrogen; nd, not detected.

the cellulose wall structure. Due to the pyrolysis process, the structure of B400 particle (Fig. 1b), shows a honeycomb-like form, with thinner walls, and with pores that appear to be more tubular. In addition, the HTC process generated a modification of the structure and led to filling the pores with materials (Fig. 1c). The VC particle does not maintain any structural characteristics of the coffee bean. It corresponds to an agglomerated structure typical of the digestion of worms (Fig. 1d).

3.2. CO₂ emissions and C remaining

The dynamics and the total amount of CO₂ emitted during the incubation period are shown in Fig. 2. The addition of H160 and H200 caused a rapid and significant increase of emissions that reached a maximum peak after 2 days, followed by a decreasing trend (Fig. 2a). This fact was reflected by the fact that both hydrochars presented the highest values of cumulative CO₂-C emission (Fig. 2b). The addition of both SCG also generated an increase, but with peaks at different times of incubation: SCG within 2 days and SCG_d after 2 days, but both generating a very similar cumulative emission of CO₂-C at the end of incubation. The addition of B400 and B400_d did not result in significant differences in CO₂ with regards to the control sample. The addition of the rest of by-products (B270, B270_d and VC) resulted in CO₂ emissions with intermediate values.

The amount of C added to soil (Table 2) was lower for VC and higher for biochar and varied between 9.95 and 18.03 (µg g⁻¹) for VC and B400_d, respectively. The C remaining (C_R) in soil estimated by fitting added C decay to a two-compartment model is shown in Table 2 (as g added C kg⁻¹ soil) and Fig. 3 (as % of added C). SCG, SCG_d, H160 and H200 generated the highest rate of mineralization with a high active fraction (f = 4.18, 5.79, 2.98 and 5.72%, respectively) and the maximum k₂ (Table 2). On the contrary, the percentage of C_R in soil for B400 and B400_d is close to 100% (Fig. 3), which is supported by the lowest fraction of C active pool (f = 0.2) and the lowest decomposition rate constant for the slow pool (k₂ close to 0) (Table 2). VC and B270 had similar behaviour to biochars at 400 °C, but less pronounced. The humification coefficient (h, Table 2) indicates the C sequestration potential of the SCG by-products 1 year after the addition. According to this parameter, the residues can be ranked as follows: B400 > B400_d > VC > B270_d > B270 > H200 > SCG_d > H200 > SCG > H160 (Table 2).

3.3. C and N forms

At 2, 7 and 30 days of incubation, the addition of SCG by-products increased significantly (p < 0.05) EOC, except for B400, B270_d and B400_d (Fig. 4a). The highest values of EOC were recorded for H200 reaching the value of 730 µg g⁻¹. EOC decreased significantly during the incubation time, except for H160, which decreased between 2 and 7 days and then increased until day 30. Despite this reduction, the addition of some by-products (SCG, H160, H200, VC and SCG_d) resulted in higher values than the control at the end of the incubation.

At each sampling time, the treatment that increased EN to a larger extent with respect to the control, was VC that reached the highest value at 30 days of incubation (77 µg g⁻¹, Fig. 4b). On the contrary, the addition of SCG, B270, H160, SCG_d caused a significant (p < 0.05) decrease of EN. Addition of the remaining by-products (B400, B270_d and B400_d) did not result in values significantly different from the control. During the incubation period, EN decreased significantly (p < 0.05) in the case of SCG, B270, H200, SCG_d and B270_d, and the rest of by-products had an irregular behaviour.

The addition of SCG by-products, except for both biochar at 400 °C, increased the content of B_C and B_N (Fig. 4c and d). The most significant increases in B_C and B_N were caused by the addition of SCG, H160 and SCG_d at 2 and 7 days. On the whole, all treatments showed a general decreasing trend for B_C and B_N during the incubation period.

The addition of SCG by-products significantly modified (p < 0.05) the content of nitrate and ammonium and consequently the value of net

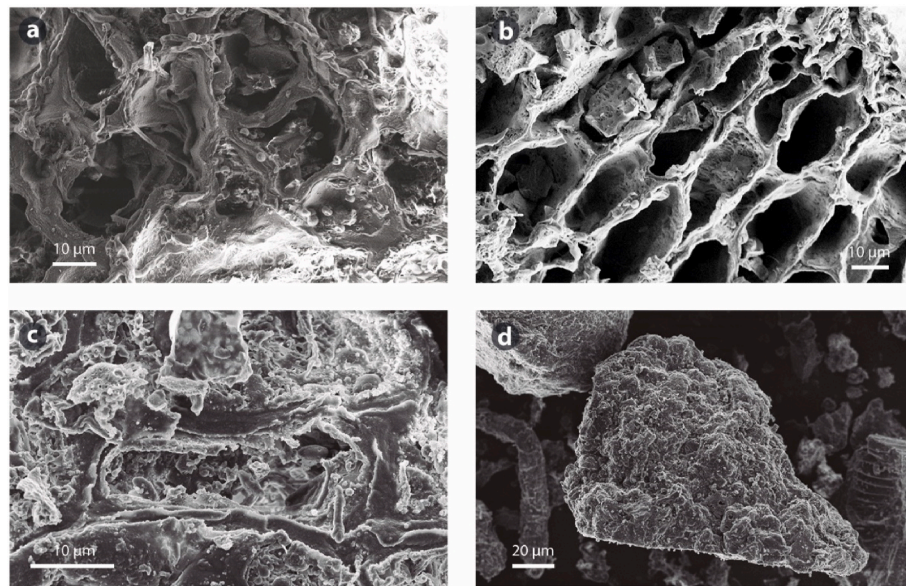


Fig. 1. Scanning electron microscopy images. a) Spent coffee grounds (SCG); b) Biochar at 400 °C (B400); c) Hydrochar at 200 °C (H200); d) Vermicompost (VC).

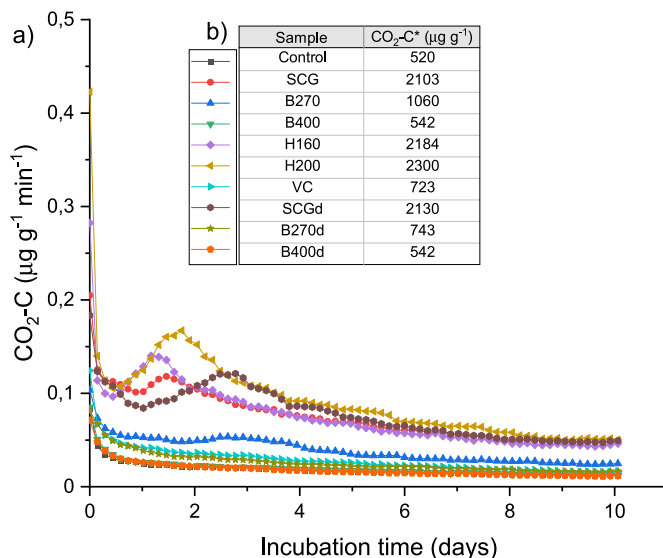


Fig. 2. Dynamics of CO₂ emissions from amended soils during the first 10 days of incubation (a) and cumulative CO₂ emissions after 30 days. Abbreviations as in Materials and methods sections. SCG: spent coffee grounds; B270: biochar produced at 270 °C; B400: biochar produced at 400 °C; H160: hydrochar produced at 160 °C; H200: hydrochar produced at 200 °C; VC: vermicompost, SCG_d: defatted SCG; B270_d: biochar from defatted SCG produced at 270 °C; B400_d: biochar from defatted SCG produced at 400 °C.

mineral N (Table 3). The addition of B270, H160, H200 and SCG_d significantly decreased ($p < 0.05$) soil NO₃-N content compared to the control on the second day of incubation. The only treatment that significantly increased the soil NO₃⁻ was VC. Regarding the incubation time, there is an irregular behaviour among the treatments. For example, control, B400, VC and B400_d tend to increase NO₃⁻ until 30 days of incubation, while the addition of SCG, H160, H200, SCG_d decreased NO₃⁻ between 2 and 7 days and then increased until 30 days. NH₄⁺ values are very low in all cases. The only treatment that significantly increased soil NH₄⁺ content was the addition of VC at 2 days. Net mineral N has a negative balance in all cases, except for VC sample. The most negative balances were recorded for SCG, B270, H160, H200, and SCG_d. The balances closest to 0 correspond to the biochars of 400 °C at 2

Table 2

Equations obtained by fitting a two-pool model to the C decay pattern in soil and C characteristic values.

Sample	C added (g C kg ⁻¹ soil)	f (%)	k ₁ (day ⁻¹)	k ₂ (day ⁻¹)	C _{30d} (g C kg ⁻¹ soil)	h (%) 20 °C
SCG	11.99	4.18	-0.2081	-0.0034	10.41	28.11
B270	14.54	1.81	-0.1565	-0.0007	14.00	77.01
B400	17.46	0.2	-0.1809	-0.0000	17.44	99.80
H160	13.00	2.98	-0.3311	-0.0036	11.34	25.70
H200	15.64	5.72	-0.1939	-0.002	13.86	45.11
VC	10.15	1.25	-0.2267	-0.0003	9.95	88.59
SCG _d	12.20	5.79	-0.1542	-0.0027	10.59	35.42
B270 _d	15.75	0.29	-0.4984	-0.0004	15.53	86.50
B400 _d	18.05	0.09	-0.1683	-0.0000	18.03	99.55

SCG: spent coffee grounds; B270: biochar produced at 270 °C; B400: biochar produced at 400 °C; H160: hydrochar produced at 160 °C; H200: hydrochar produced at 200 °C; VC: vermicompost, SCG_d: defatted SCG produced at 270 °C; B400_d: biochar from defatted SCG produced at 400 °C.

$C_R = f \times e^{(-k_1 t)} + (100-f) \times e^{(-k_2 t)}$; where, f: fraction of C of the active pool; k₁: decomposition rate constant for the active pool; k₂: decomposition rate constant for the slow pool.

C_{30d}: fraction of added C remaining in the soil after 30 days of incubation; h, humification coefficient: fraction of exogenous organic matter that remains in the soil after 1 year based on an average annual temperature of 20 °C.

and 7 days. Negative balances become relatively larger after 30 days.

Soil addition of all SCG by-products did not let N₂O emissions increase throughout the whole incubation period.

4. Discussion

4.1. SCG organic amendments characterization

The treatments applied to SCG (slow pyrolysis, HTC process, vermicomposting and defatting) differently modified the initial physico-chemical characteristics of this raw material. Changes in SCG properties were also affected by process conditions, such as temperature or residence time in the case of pyrolysis.

The results obtained for biochars (Table 1) indicated that the higher the pyrolysis temperature, the higher the C and ash fractions and the lower the volatile matter, which is in agreement with the results of

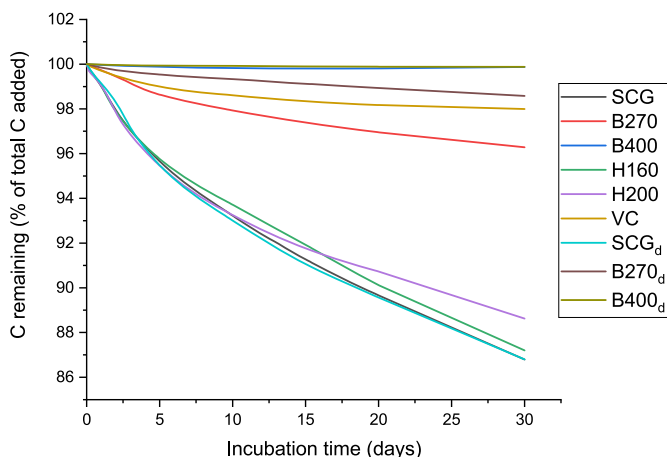


Fig. 3. Remaining fraction of residue organic C in soil over time respect of the total C added. SCG: spent coffee grounds; B270: biochar produced at 270 °C; B400: biochar produced at 400 °C; H160: hydrochar produced at 160 °C; H200: hydrochar produced at 200 °C; VC: vermicompost, SCG_d: defatted SCG; B270_d: biochar from defatted SCG produced at 270 °C; B400_d: biochar from defatted SCG produced at 400 °C.

Chatterjee et al. (2020), Tomczyk et al. (2020) and Kambo and Dutta (2015). An increase in the C and N content due to pyrolysis was also reported by Sri Stylianou et al. (2020) and Tangmankongworakoon (2019) for SCG biochar, and it is related to stable aromatic hydrocarbon formation and thermochemical C–H and C–C rupture (Das et al., 2021). The decrease in O and H content (Table 1) has been attributed to the loss of CO₂, CO, hydrocarbon (Gai et al., 2014). The content of WSC was the lowest in the B400, which could be explained by the fact that at this temperature approximately 80% of bio-residue labile C is transformed into a recalcitrant fraction (Das et al., 2021). In the case of B270, the amount of WSC is higher compared to B400 due to the lower temperature applied.

The hydrothermal carbonization of SCG increased the C and fixed C content (Table 1), which is attributed to dehydration and decarboxylation reactions (Afolabi et al., 2020; Kim et al., 2017), since 60–84% of C may be retained in the hydrochar (Libra et al., 2011). The high amounts of WSC detected in the hydrochars (Table 1) are not in accordance with the thermochemical processes occurring during HTC, as pointed out by other authors. Thus, according to Wang et al. (2018), during the process, the hydrolysis of the molecules occurs, giving rise to shorter fragments and later dehydration, condensation and polymerization reactions to take place. However, these reactions depend on the residence time and the temperature applied (Wang et al., 2018). The HTC process applied in this assay (160 and 200 °C for 1 h), seems not to be sufficient to initiate the condensation and polymerization reactions. In the same line, Song

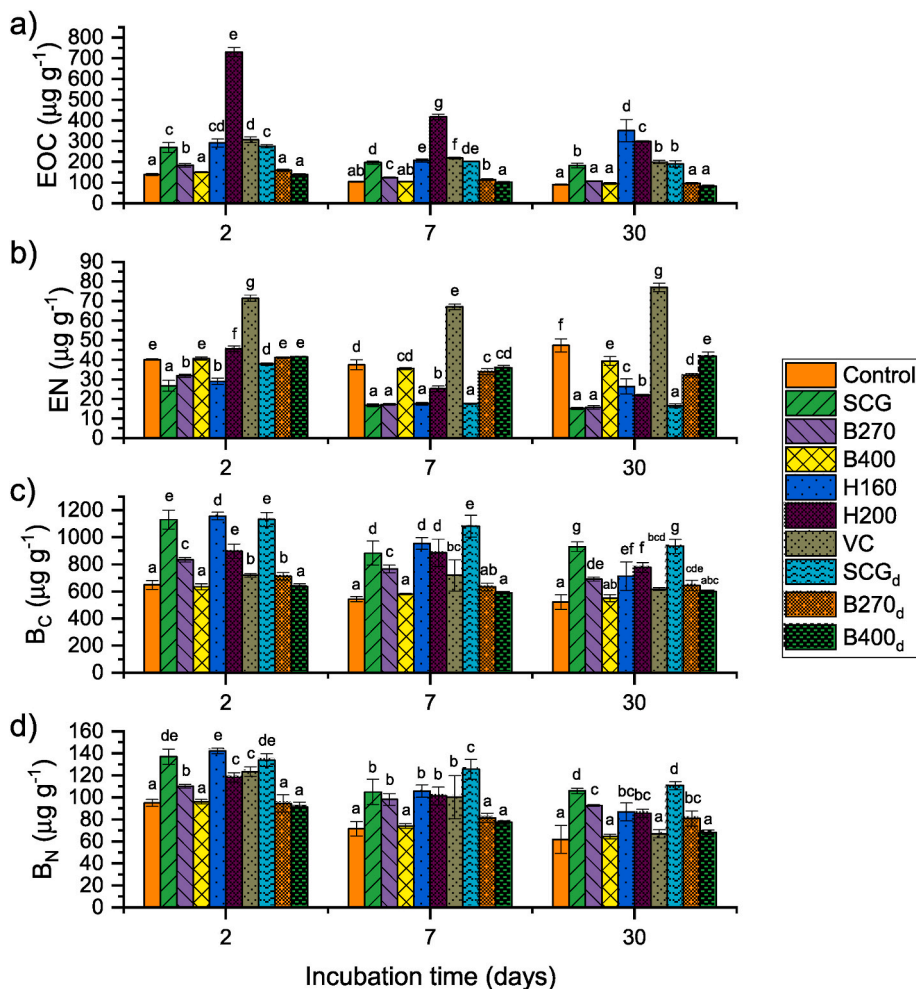


Fig. 4. C and N forms at 2, 7 and 30 days of incubation. SCG: spent coffee grounds; B270: biochar produced at 270 °C; B400: biochar produced at 400 °C; H160: hydrochar produced at 160 °C; H200: hydrochar produced at 200 °C; VC: vermicompost, SCG_d: defatted SCG; B270_d: biochar from defatted SCG produced at 270 °C; B400_d: biochar from defatted SCG produced at 400 °C.

Table 3NO₃⁻, NH₄⁺ and net mineral N after 2, 7 and 30 days of incubation.

Sample	NO ₃ ⁻ (µg N-NO ₃ ⁻ g ⁻¹)			NH ₄ ⁺ (µg N-NH ₄ ⁺ g ⁻¹)			Net mineral N (µg N g ⁻¹)		
	2 days	7 days	30 days	2 days	7 days	30 days	2 days	7 days	30 days
Control	28.59 ^e	27.26 ^e	37.64 ^e	0.28 ^a	0.00 ^a	1.02 ^a	–	–	–
SCG	2.42 ^b	0.15 ^a	0.74 ^a	0.40 ^a	0.66 ^{bc}	1.27 ^a	-26.06 ^a	-26.45 ^a	-36.65 ^a
B270	17.03 ^d	5.17 ^b	6.44 ^b	0.11 ^a	0.08 ^a	1.43 ^a	-11.74 ^a	-22.01 ^a	-30.79 ^a
B400	26.94 ^e	24.59 ^d	31.16 ^d	0.27 ^a	0.56 ^{bc}	1.47 ^a	-1.67 ^a	-2.11 ^a	-6.03 ^a
H160	0.00 ^a	0.00 ^a	0.89 ^a	0.67 ^a	0.00 ^a	2.73 ^b	-28.20 ^c	-27.26 ^b	-35.04 ^b
H200	0.00 ^a	0.08 ^a	0.79 ^a	0.58 ^a	0.47 ^{bc}	1.56 ^a	-28.29 ^d	-26.71 ^d	-36.31 ^d
VC	33.57 ^f	38.48 ^f	46.24 ^f	2.58 ^b	0.26 ^{ab}	1.50 ^a	7.27 ^e	11.48 ^f	9.08 ^f
SCG _d	9.29 ^c	0.06 ^a	0.73 ^a	0.52 ^a	0.87 ^c	1.59 ^a	-19.07 ^b	-26.32 ^a	-36.34 ^a
B270 _d	26.63 ^e	22.84 ^c	20.26 ^c	0.31 ^a	0.00 ^a	1.40 ^a	-1.94 ^d	-4.41 ^c	-17.00 ^c
B400 _d	28.15 ^e	25.06 ^d	28.91 ^d	0.42 ^a	0.51 ^{bc}	1.42 ^a	-0.31 ^d	-1.68 ^d	-8.33 ^d

SCG: spent coffee grounds; B270: biochar produced at 270 °C; B400: biochar produced at 400 °C; H160: hydrochar produced at 160 °C; H200: hydrochar produced at 200 °C; VC: vermicompost, SCG_d: defatted SCG; B270_d: biochar from defatted SCG produced at 270 °C; B400_d: biochar from defatted SCG produced at 400 °C. Significant different are indicated by different letters in the same column ($p < 0.05$).

et al. (2020) indicated that the HTC process is weaker than pyrolysis and a large part of dissolved organic C is not completely polymerized, which leads to higher WSC concentration in these residues.

The vermicomposting of SCG reduced the total C content and enhanced N, which leads to a reduction in the C/N ratio (Table 1), in agreement with the results of Liu and Price (2011). The conservation of N in vermicompost derived from SCG is attributed in part to the higher oil content of the SCG (Liu and Price, 2011) and in part to the N-rich nature of SCG (Adi and Noor, 2009). However, there is a loss of WSN when SCG are vermicomposted, which is in accordance with the findings of Alidadi et al. (2016) for other types of wastes.

On the other hand, the defatting process does not appear to have substantial effects on the physicochemical properties of SCG (Table 1). This is in contrast with other authors (Vardon et al., 2013) who found differences between the defatted SCG and non-defatted SCG in properties related to energy use. In the biochars derived from defatted SCG of the present study, some differences are observed with those derived from non-defatted SCG. The most striking of these differences are the C and N content, somewhat higher in the B270_d and B400_d (Table 1). This fact is consistent with the main defatting objective indicated by Vardon et al. (2013), that is to obtain a better carbonization during the pyrolysis process. However, these differences were not very significant in terms of the influence of these residues on the dynamics of C and N, as will be seen later.

The modifications in the composition of the different SCG by-products with respect to the SCG can also be understood from the van Krevelen diagram (Fig. 5) obtained from the ultimate analysis data (Table 1). The representation of the atomic ratio H/O versus atomic ratio O/C indicates that SCG and SCG_d exhibit higher values of such ratios than hydrochar and biochar samples. The low O/C and O/H values are related to the occurrence of oxidation and dehydration processes, respectively. The HTC and pyrolysis process move the atomic ratios from upper right to lower left. In the case of H200, the H/C and O/C ratios decreased by 30 and 100% with respect to SCG, respectively. The pyrolysis at 400 °C generated by-products with the lowest H/C and O/C ratios. The VC showed a higher O/C ratio. Based on the van Krevelen diagram of D'Andrilli et al. (2013), where they related H/C and O/C ratios with reference source materials, biochars at 400 °C were found close to the black carbon zone, H200, B270 and B270_d in the zone corresponding to lignin, and SCG, SCG_d and H160 in the area of amino sugars. The vermicompost is in the zone corresponding to cellulose. Afolabi et al. (2020) found that, similarly to our results, the H/C and O/C ratios of SCG hydrochar decreased with respect to SCG.

Fig. 1 shows important differences between the SCG particles and those corresponding to B400, H200 and VC. These differences can be explained by the coffee bean structure and by the pyrolytic, hydrothermal carbonization and vermicomposting processes suffered by the SCG particles. According to Fadai et al. (2017), the structure of a green

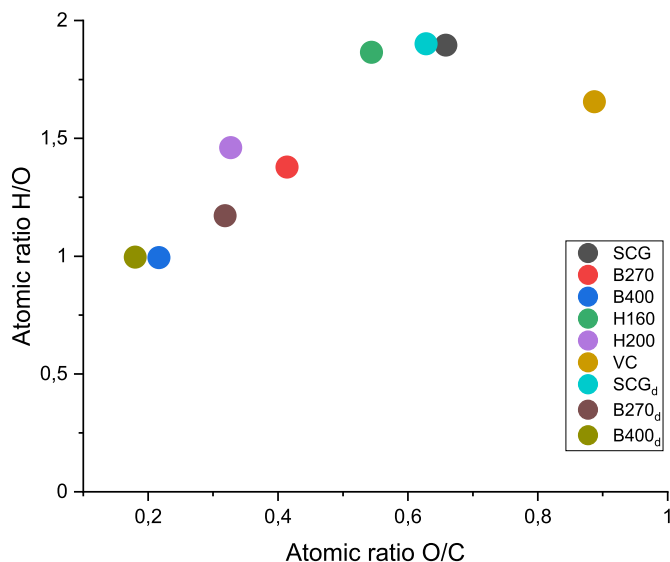


Fig. 5. Van-Krevelen diagram with reference to the data of C, H and O, shown in Table 1. SCG: spent coffee grounds; B270: biochar produced at 270 °C; B400: biochar produced at 400 °C; H160: hydrochar produced at 160 °C; H200: hydrochar produced at 200 °C; VC: vermicompost, SCG_d: defatted SCG; B270_d: biochar from defatted SCG produced at 270 °C; B400_d: biochar from defatted SCG produced at 400 °C.

coffee bean is composed of an intercellular matrix with cellulose, galactomannans, arabinogalactans, lignin, bound water, and structural carbohydrates. This structure contains pockets of biological cells with water, oil protein, sugar, etc. The SCG particles come from the roasted, ground and hydrolyzed seed at low temperature to obtain the coffee beverage. Fig. 1a corresponds to a SCG particle and shows a partial emptying of the pockets, which leads to a certain porosity, also indicated by other authors (Ballesteros et al., 2014). In the B400 sample, a honey-comb type porous structure is observed (Fig. 1b), generated, as indicated by some authors (Sri Shalini et al., 2020; Kambo and Dutta, 2015), by the loss of the more volatile organic compounds. This fact is supported by the decrease in the volatile matter in biochar samples (Table 1). The H200 residue particles (Fig. 1c) show a different morphology than biochars. The pores are filled with materials, which is in agreement with Kambo and Dutta (2015). The clogging of the pores is due to a release of soluble compounds generated during the HTC process as indicated by Song et al. (2020) and is consistent with an increase in the volatile matter in H200 with respect to B400 (Table 1). The morphology of the VC particles reveals the destruction of the SCG residue since no structures from the seed are appreciated (Fig. 1d).

4.2. Soil C dynamics

4.2.1. CO₂ emissions and C remaining

The analysis of CO₂ evolution and C_R, showed two main and very well-differentiated patterns (Figs. 2 and 3): SCG, SCG_d, H160 and H200 generated larger CO₂ fluxes and consequently lower C_R, while biochars and VC did not change or slightly increased the CO₂ emissions. The only exception was represented by B270 that showed a somehow intermediate behaviour between these two general patterns. These results are in agreement with those of Galvez et al. (2012), showing very different C sequestration potential and CO₂ emissions of bioenergy process residues strongly related to their composition and properties.

The behaviour of SCG and hydrochars indicates that they were the most degradable residues tested. Comino et al. (2020) reported that the addition of SCG increased all soil organic matter (SOM) fractions, especially the level of more labile SOM fractions (such as hot water-soluble C) and total extractable C, being, therefore, a not very stable residue in soil. Zhang et al. (2014) stated that addition of SCG increased dissolved organic C concentrations and as a result enhanced soil respiration rates with values of about 0.06 μg CO₂-C g⁻¹ min⁻¹, a very similar result to that of our study (approximately 0.1 μg CO₂-C g⁻¹ min⁻¹, Fig. 2). Regarding hydrochars, our results are in accordance with Bargmann et al. (2014b), Bamminger et al. (2014) and Kammann et al. (2012), who indicated that hydrochars (from beetroot chips, bark chips, maize and spent brewer's grains) exhibited significantly higher CO₂ emissions than biochars. Specifically, Bargmann et al. (2014b) found that the addition of 2% hydrochar generated a maximum peak of 0.17 μg CO₂-C g⁻¹ min⁻¹, similar to SCG hydrochars (Fig. 2). This fact could be attributed to the presence of less polyaromatic C and the predominance of aliphatic compounds (Islam et al., 2021) making the hydrochars less stable than biochars (Islam et al., 2021; Bargmann et al., 2014b; Kammann et al., 2012). According to Eibisch et al. (2013), the properties of the raw material, such as large amount of hydrophilic functional groups, low C/N ratio and low lignin content, are the main factors favouring the degradability of hydrochars. In general, due to their variable composition, SCGs could generate hydrochars with unforeseeable composition and properties, as they present appreciable amounts of lignin, but also significant contents of proteins and sugars (Alves et al., 2017). Results of the present work showed that in the tested hydrochars dominate the labile character of the most degradable compounds (Table 1). According to Schimmelpfennig and Glaser (2012), the values of molar H:C and O:C ratios of the studied hydrochars (Fig. 5), correspond to those of low stability residues.

Regarding the C_R from SCG and hydrochars, values recorded after 30 days in this study are similar to those found by Galvez et al. (2012) for rapeseed meal or bioethanol residue considered as labile residues.

On the other hand, biochars showed low CO₂ emission and high C_R when added to soil (Figs. 2 and 3). The low degradability of these by-products could be explained on the basis of their low amounts of WSC, high quantities of fixed C and low content of volatile matter (Table 1). Bernal et al. (1998) showed that WSC of compost is well correlated with stability index such as cumulative respiration and decomposition parameters. Fixed C and volatile matter are related to biochar stability (Leng et al., 2019). Similarly to our results, Zhang et al. (2014) reported that biochar from SCG did not increase the soil respiration over the incubation significantly. The temperature of pyrolysis influences this behaviour as the lower the temperature, the higher the emissions, with biochar produced at higher temperatures being more stable than B270 and B270_d and the latter less degradable than SCG and hydrochars, in agreement with Ameloot et al. (2013). According to Zhang et al. (2014) biochars produced at low temperatures (250 and 400 °C) increased the soil respiration rates, which could be related to the labile biochar C fractions (unpyrolyzed compounds). This statement partially coincides with the behaviour of the B270, but not with B270_d or with biochars at 400 °C (Figs. 2 and 3). The behaviour of B270_d, closer to B400 and B400_d, could be explained according to Vardon et al. (2013), which

stated that defatting increases the performance of the pyrolysis process. The results of this study are in line with the results of Galvez et al. (2012) which found that biochar obtained from slow pyrolysis resulted in the highest C_R due to a high content of slow degrading C pool. The effect of biochar on CO₂ emissions is controversial in the literature: some studies showed reduced or unaltered CO₂ emissions and others indicated increased CO₂ emissions in the first days of incubation (Sri Shalini et al., 2020). The VC has intermediate concentrations of WSC (10.83 μgg⁻¹, Table 1) and consequently, its addition did not generate high CO₂ emissions, never exceeding the limit of 2 mg g⁻¹ day⁻¹ (threshold established for a "very stable" compost according to Santos et al., 2017). This stability was supported by its low C/N ratio (Table 1). Compared with the respiration generated by other types of compost reported in the bibliography (Galvez et al., 2012), the addition of VC generated 10 times more CO₂ than household waste compost and vine shoot compost, which could be attributed to the different dose added (0.5%).

From all the above and according to the literature we can deduce that WSC and volatile matter seem to be the characteristics of residues that are more correlated with the behaviour of the tested SCG by-products regarding CO₂ emissions and C_R. Thus, the amendments characterized by a high content of WSC and volatile matter (Table 1), produced the large amounts of CO₂ emissions (Fig. 2) and low C_R (Fig. 3), which is corroborated by the significant correlations between WSC and CO₂ ($r = 0.970$; $p < 0.001$), WSC and C_R ($r = -0.937$, $p < 0.001$), volatile matter and CO₂ ($r = 0.863$, $p < 0.01$) and volatile matter and C_R ($r = -0.910$, $p < 0.001$). On the other hand, there are also significant correlations with fixed C that also explain the behaviour of residues: fixed C and CO₂ ($r = -0.732$, $p < 0.05$), fixed C and C_R ($r = 0.790$, $p < 0.05$).

4.2.2. Extractable organic C and microbial biomass C

Extractable organic carbon (EOC) and microbial biomass C (B_C) are two important indicators of C dynamics, as both are closely related to CO₂ emissions and C_R. Soil EOC is positively and significantly correlated with the content of WSC in the residues. The relation occurred at 2 days ($r = 0.775$, $p < 0.05$), 7 days ($r = 0.830$; $p < 0.01$) and 30 days ($r = 0.887$; $p < 0.01$). Therefore, addition of SCG by-products with a higher WSC content (SCG, SCG_d, hydrochars and VC, Table 1), generates higher EOC content in the soil (Fig. 4a). The opposite behaviour was recorded in the case of biochars samples. A higher soil EOC means a greater amount of substrate available for microbial activity (Bargmann et al., 2014b). Consequently, this results in higher CO₂ emissions and lower residual C (Figs. 2 and 3). Thus, the EOC content in soils is significantly correlated with CO₂ emissions (for example, at 30 days, $r = 0.788$; $p < 0.001$) and C_R (for example, at 30 days, $r = -0.718$; $p < 0.001$). This fact agrees with the results of Bera et al. (2021). The increasing in EOC content favoured by the addition of SCG by-products with a higher WSC content, not only stimulated microbial activity, but also favoured the growth of microbial biomass C (Fig. 3) which is confirmed by the positive relationship between EOC and B_C ($r = 0.463$; $p < 0.001$). As a consequence of this relationship with EOC, B_C was also related to the WSC amounts in the residue ($r = 0.507$, $p < 0.01$). Therefore, B_C is higher in SCG, SCG_d, hydrochars and VC amended soil and lower in the case of biochars, except for B270, which confirms its similar behaviour to SCG and hydrochars. Zhang et al. (2014) also reported an increase in B_C (by 110%) when SCG was added to soil. In our case, the increase with respect to the control sample at 2 days of incubation (the maximum value) was 83% (Fig. 4c). The last authors also found that the addition of biochar from SCG did not modify the B_C, which could also be attributed to the presence of toxic organic compounds (Deenik et al., 2010). Afterward, the B_C decreased during incubation time due to the lower availability of EOC (Fig. 4a and c). The decrease in EOC during the decomposition process has been related to the maturity of the residue (slowdown of degradation process) (Mohanty et al., 2013).

4.2.3. Influence of the bio-amendment properties on C cycle. Statistical analysis

To show how the properties of the bio-amendments influence the C cycle parameters, a partial least squares regression (PLS-R) was performed in which the C_R was established as a dependent variable (Fig. 6 a and b). A result of the PLS-R is the variable importance for the projection (VIP) (Fig. 6a). This PLS-R analysis indicates that C_R is highly related to some properties of the residues. The variables with a VIP >1 (which indicate good candidates to explain C_R , Lew et al., 2019) are: H, H/C, C/N, volatile matter, fixed C, pH, WSC and WSN. C and O had a VIP between 0.8 and 1, and therefore, are also good candidates to explain C_R , but to a lesser extent. The negative or positive relationships of C_R with the residue properties (Fig. 6a) can be explained because these properties are related to the greater or lower biodegradability of the residues and therefore to the ability to store C in the soil. Thus: i) high values of H and H/C, and low values of O, are related to a more reduced nature of organic compounds (Das et al., 2021); ii) the highest C and C/N values correspond to organic materials that are relatively rich in C; iii) volatile matter represents the least condensed and most labile fraction (Das et al., 2021); iv) WSC and WSN are related to the presence of smaller and less condensed organic molecules (more aliphatic) (Alidadi et al., 2016); v) fixed C corresponds to the stable fraction of C (Afolabi et al., 2020; Bera et al., 2021) and vi) the most acidic pHs are related to the presence

of aliphatic chains with acidic and hydroxyl functional groups (Alidadi et al., 2016; Das et al., 2021). In the scatter diagram of Fig. 6a, component 2 is represented vs component 1, which explains 96.09% of the variance. The relationships between C_R and the different properties of the amendments are confirmed by considering the position of amendments in the plot space with respect to C_R (Fig. 6b). Thus, a high C_R is associated to B400 and B400_d and to a lesser extent with the B270 and B270_d. The lowest C_R corresponds to SCG, SCG_d, H160 and H200. VC does not appear to have a significant influence on C_R .

4.3. Soil N dynamics

4.3.1. Overall impact of SCG by-products

According to Mohanty et al. (2013), soil N dynamics is related to total N, other forms of N and the C/N ratio of the organic amendments. Other authors (Galvez et al., 2012) consider that N dynamics closely depends on the C labile forms, represented by WSC, and the C/N ratio. The latter globally indicates the stability of the residues (Wilson et al., 2019). The results related to the N cycle (Fig. 4 and Table 3) show that the tested bio-residues can be grouped into three groups according to their effects on soil properties: i) SCG, SCG_d, H160, H200 and B270, ii) B400, B400_d, and B270_d, and iii) VC. The first group generates a significant N immobilization and increase in B_N . The second group have a

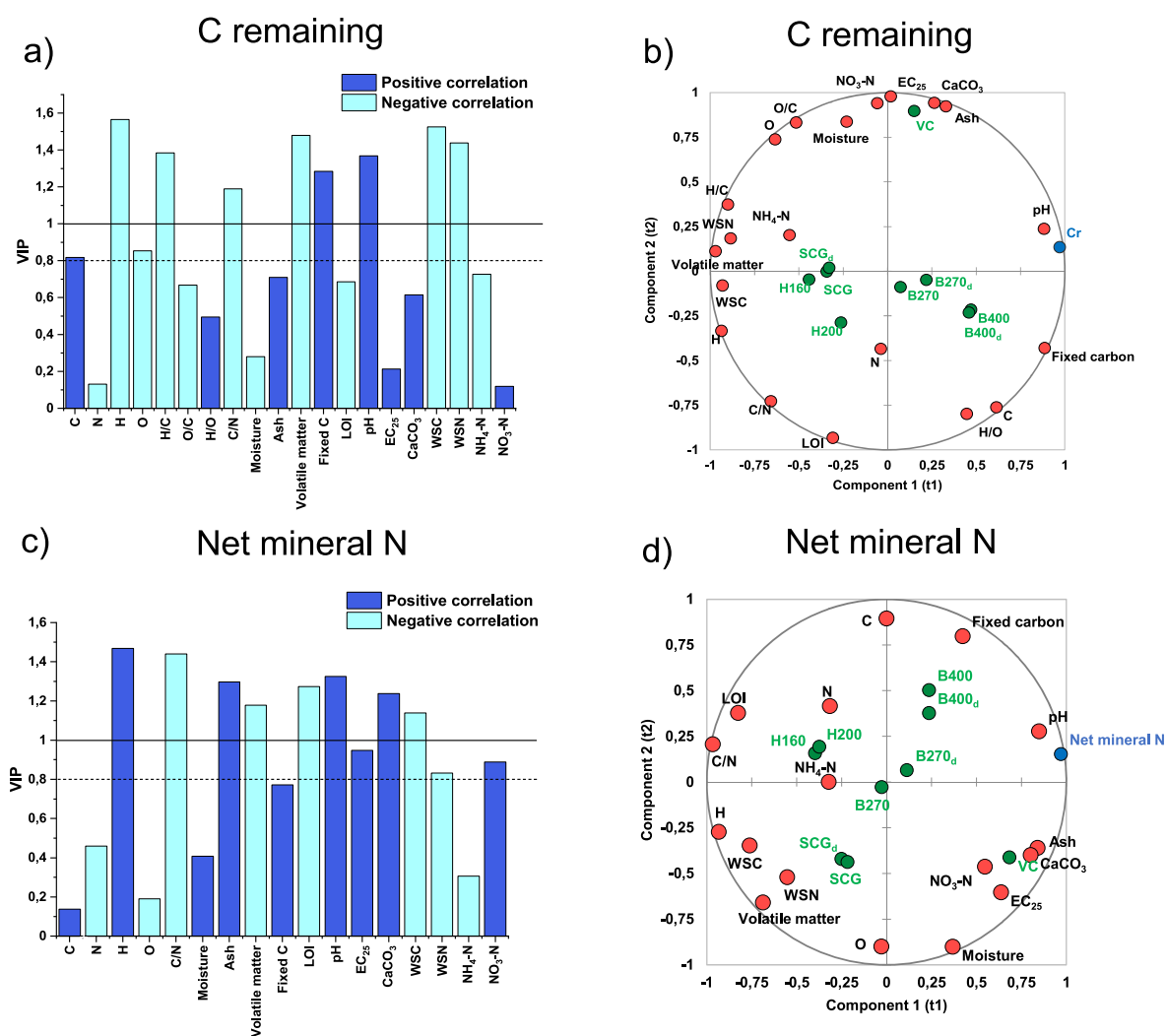


Fig. 6. Partial least squares regression (PLS-R) analysis associated to the first two components. a) and c) The VIPs (Variable Importance for the Projection) for explanatory variables of component 1, with respect to C remaining and net mineral N as dependent variables. VIPs >1 indicate the explanatory variables that contribute the most to the PLS models. VIPs >0.8 indicate an important contribution to the PLS model. b) and d) Scatter plot of component 1 vs component 2, in which correlations with C remaining and net mineral N, for bio-residues properties and the own residues as variables, are shown.

negligible effect on N forms. Only after 30 days B270_d caused a slight increase in N immobilization and B_N. VC addition cause an increase in extractable mineral N and in B_N. From the data reported on Table 1, it can be deduced that there is a clear relationship, as in the case of C, between the composition of these residues and their influence on the N cycle.

Thus, the first group of bio-amendments is characterized by higher WSC, WSN, C/N and lower proportions of total N, NO₃⁻ and NH₄⁺. The second group have a different and opposite composition to the previous one. VC shows moderate amounts of WSC, a very low C/N and high contents of different forms of N. In general, the characteristics of materials with more relation to the effect on soil N cycle were N content and WSC. As a matter of fact, there were significant positive relationships between N content of materials and extractable and mineral N for all the 3 sampling events. In addition, there was a positive correlation between WSC and B_N after 2 days of incubation ($r = 0.80$).

Regarding N₂O emissions all tested residues were shown to be safe products for that concerning possible effects on this harmful gas. These results are in accordance with Zhang et al. (2014) who reported that amending soil with biochar from SCG had no significant effect on N₂O emissions rate. Santos et al. (2017) also reported that during the composting process of the SCG, N₂O emissions were very low.

4.3.2. Effect of SCG, hydrochars and biochar at 270 °C

In the case of SCG, SCG_d, H160, H200 and B270, the high amounts of WSC, positively correlated with WSN ($r = 0.953$; $p < 0.001$), stimulated the activity and the growth of the microorganisms, as seen analysing soil CO₂ and B_C dynamics, and the consequent mineralization of exogenous organic matter. Thus, a B_N increase was observed at 2 days in the first group of the bio-amendments with respect to the control sample (Fig. 4d). These materials present the lower N content and the higher C/N values (18–25) and therefore their mineralization did not provide microorganisms with the entire N required by the growing biomass to incorporate the C derived from the residue. Consequently, microorganisms cause a significant reduction of the extractable and mineral N of soil (N immobilization). Indeed, a decrease of EN was recorded in the first days of incubation. A decrease in soil EN related to simultaneous increases in B_N has been already reported in amended soil (Bargmann et al., 2014b). The above reported evidence could explain the microbial immobilization caused by the addition of SCG, H160, H200, SCG_d and B270 during the 30 days (see net mineral N, Table 3). This fact is consistent with previous findings related to hydrochars (Bargmann et al., 2014a, 2014b). More specifically, Bargmann et al. (2014a) found that the addition of hydrochar (from beet-root chips and spent brewer's grains) reduced the concentration of nitrate within the first week after incorporation. In that study, 4 weeks were needed to detect NO₃⁻, which is in line with the results of this study, since at 30 days small amounts of nitrates were detected in H160 and H200 (Table 3). The N immobilization caused by SCG addition (see net mineral N, Table 3) concurs well with the results of Cruz and Cordovil (2015), who found a reduced N uptake by the plants. These results corroborated the initial findings of our research group (Cervera-Mata et al., 2018): the addition of SCG stimulates microbial growth and inhibited plant growth, which suggested that there was a competition for N between microorganisms and plants.

4.3.3. Effect of biochars

Addition of biochars (with the only exception of B270) did not increase the microbial biomass with respect to the control sample (Fig. 4d), and as a consequence there seems to be no microbial N immobilization with the addition of this SCG by-product. During the incubation period, the values of EN are maintained to values similar to the control (Fig. 4b), except for the case of B270, which has a behaviour more similar to that of the first group. Biochars presents more than 3% of total N (Table 1), resulting in a larger supply of N to soil. From this it could be anticipated that their addition to the soil would increase the

content of available N. However, these substrates are characterized by the high stability of C and low amount of readily available C and N (WSC and WSN) (Table 1). Therefore the microorganisms would be able to degrade and convert into easily extractable N only a limited part of the total N of residue not exceeding the EN concentrations of the control sample.

Considering the inorganic N forms, the use of biochars resulted in slight N immobilization, as shown in the negative values of net mineral N (Table 3), higher in the case of B270. N immobilization was significantly lower with respect to SCG and hydrochars. A meta-analysis study performed by Nguyen et al. (2017) stated that biochar reduced soil inorganic N, however, 95% of cases were observed within one year after biochar application. This delay in the immobilization also coincides with our results, although in our case the trial only lasted 30 days. The N immobilization could be attributed to a microbial one in the case of degradable residues, such as SCG and hydrochars, which is supported by the B_N values (Fig. 4d). However, as stated above, there is not a significant increase of B_N with the addition of biochars, except for B270, which is in line with the findings of Bargmann et al. (2014b) who stated that only a small amount of immobilized N was found in the microbial biomass with the addition of biochars derived from beet-root chips and spent brewer's grains. These authors, in a previous study (Bargmann et al., 2014a), raised a question about the causes of N immobilization in biochar amended soils: this phenomenon could be produced by sorption to inner surface areas of biochar or by microbial immobilization of mineral N. In the conditions of the present study the latter mechanism seems to be more relevant. Dieguez-Alonso et al. (2018) and Bargmann et al. (2014b) conclude that the BET specific surface area is greater in biochars than in hydrochars. In our case, we do not have these data to support the hypothesis of Bargmann et al. (2014a). However, the SEM images (Fig. 1) suggest that B400 has a larger visually estimated surface, due to its greater porosity than hydrochars. Moreover, according to Dieguez-Alonso et al. (2018) the lower the volatile content, the higher the specific surface area, which would support the fact that in our case, biochars have a higher specific surface area than hydrochars. Further research is needed to understand mechanisms leading to N immobilization caused by biochars.

4.3.4. Effect of vermicompost

The VC sample cannot be included in the two groups mentioned above due to its high amount of total N and all forms of N, including WSN (Table 1). As shown in Fig. 4c there is an increase of EN with respect to the control sample in all experiments, which could indicate that there is enough N in the soil solution. The behaviour of B_N is somewhat different. B_N is greater than the control in the first two sampling events (2 and 7 days), but decreases during the incubation time, which may be attributable to the decrease in EOC, as can be seen in Fig. 4a. VC was characterized by higher N content and consequently by the lower C/N value. Consequently, the addition of VC did not induce N immobilization, as corroborated by the positive values of net mineral N (Table 3). Regarding the effect on N immobilization of other compost used in the literature, it depends on the degree of maturity of the compost used: in general, mature compost does not generate immobilization of N, due to its low C/N ratio and a low NH₄-N: NO₃-N ratio (Wilson et al., 2019). On the other hand, in the work of Galvez et al. (2012), the addition of household waste compost and vine shoot compost resulted in N immobilization. Both composts had a quite high C/N ratio (15 and 23, respectively), which could be considered as not completely stable compost.

4.3.5. Influence of the bio-amendments properties on N cycle. Statistical analysis

As with C_R, a PLS-R analysis was carried out, with the mineral net N at 30 days as the dependent variable, to show how the properties of the residues influence the N cycle in the amended soil (Fig. 6c and d). Ash, pH, EC₂₅, CaCO₃ and NO₃⁻ show positive relationships with a VIP > 0.8.

Negative relationships are with H, C/N, volatile matter, LOI, WSC and WSN. Net mineral N could be understood as a final result of biological activity. The residues whose properties lead to an increase of biological activity caused N immobilization and therefore a lower net mineral N (Bargmann et al., 2014a). The relation between net mineral N and EC_{25} and $CaCO_3$, in the residue, could be understood indirectly due to these variables having an unusual value in VC (Table 1). When the bio-amendments are considered as variables in themselves (Fig. 6d), the previous categorization of the amendments in relationship to their impact on mineral N is confirmed. Thus, the residue that in the plot space is closer to net mineral N is VC, as already mentioned, followed by the B400, B400_d, B270 and B270_d and lastly by the most degradable residues (SCG, SCG_d, H160 and H200).

4.4. Global effect of residues on C and N cycles. Soil quality implications

A principal component analysis was performed to analyze the comprehensive response of soil parameters related to C and N cycles to the addition of SCG residues (Fig. 7). A matrix containing the values of EOC, EN, B_C , B_N , $N-NO_3^-$, $N-NH_4^+$, net mineral N, cumulative CO_2 and C_R at 2, 7 and 30 days was selected. Fig. 7 shows the space defined by PC1 and PC2 (which capture 72.7% of variance) with the scores values of the samples. The first component explained the 50.0% of the variance and groups materials according to their effect on soil parameters. The higher values on PC1 correspond to biochar and VC samples, with high values of C_R , EN, $N-NO_3^-$, and net mineral N. On the contrary, the negative values on this PC corresponded to more degradable residues such as SCG, SCG_d, H160 and H200, with high values of B_C , B_N , EOC and CO_2 emissions. PC2, explaining the 22.7% of the variance, groups samples according to the time of incubation. Positive values correspond to 2-day samples close to the variables B_C , B_N , EOC and C_R since the values of these parameters decreased during the incubation (Figs. 3 and 4). Negative values correspond to 30-day samples close to the variable cumulative CO_2 emissions as this variable increases with the incubation time (Fig. 2). The behaviour of N with respect to days is not clear. Results of PCA analysis confirms what has been previously highlighted regarding C and N dynamics.

Also, based on the PCA, we can discuss one of the most interesting

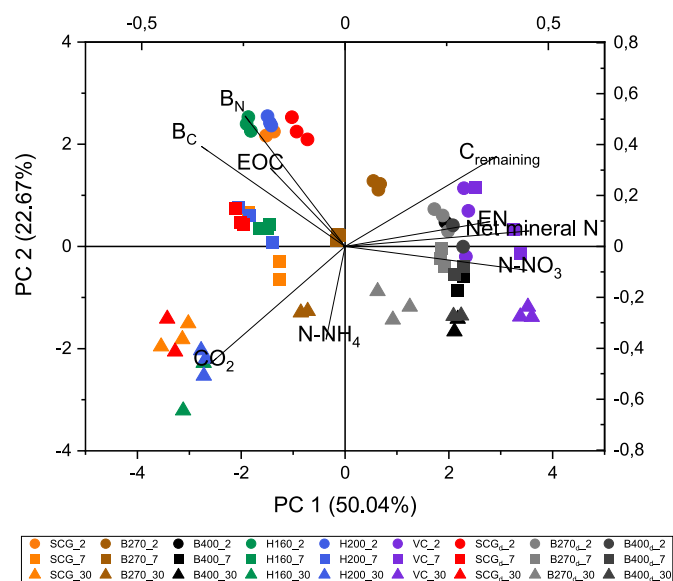


Fig. 7. Superimposed graph of PCA scores obtained for samples (PC2 vs PC1) and loadings of soil parameters at 2, 7 and 30 days. SCG: spent coffee grounds; B270: biochar produced at 270 °C; B400: biochar produced at 400 °C; H160: hydrochar produced at 160 °C; H200: hydrochar produced at 200 °C; VC: vermicompost, SCG_d: defatted SCG; B270_d: biochar from defatted SCG produced at 270 °C; B400_d: biochar from defatted SCG produced at 400 °C.

aspects of the evaluation of organic amendments, which is their effect on soil quality. In a review of Bünemann et al. (2018) about this topic, several soil quality indicators such as N mineralization, microbial biomass, soil respiration, labile C and N, available N and total organic C, were collected. These soil quality indicators (all employed in this paper) were used in more than 20% of the reviewed soil quality assessment approaches. From the point of view of soil quality, the SCG by-products employed in this assay could have different impacts on soil, suggesting they could fulfil specific agronomical and environmental purposes. Thus, for instance, regarding the persistence of added organic C into the soil, the biochars are more effective, but on the other side they do not represent a source of available N and do not improve biological fertility. On the contrary, SCG and hydrochars, characterized by high degradability, promote the development of microbial biomass and therefore can sustain biological fertility of soil. However due to the relatively high C/N ratio they may cause a temporary N immobilization in the soil. VC produced by SCG is a material showing interesting agronomical and environmental properties. It is a good source of available N, but at the same time presents good soil persistence and promotes a limited but significant increase in microbial biomass.

5. Conclusions

All transformations applied to SCG generate by-products that are quite different from the original SCG and with very distinctive chemical, physicochemical and morphological properties. A clear relationship has been demonstrated between the properties of the tested bio-amendments and their effects on the C and N cycles. SCG, SCG_d and hydrochars are bio-residues that stimulate soil biological activity, due to the fact that they contain easily decomposable carbonaceous molecules. The hydrothermal carbonization process (generator of hydrochars) accentuates this characteristic. As a consequence, SCG and hydrochars lead in the short and medium term to N immobilization, lower organic C conservation in the soil and to CO_2 emissions in the atmosphere. The pyrolysis of SCG, which gives rise to biochars, removes much of the easily decomposable C from these residues, leading to less N immobilization and greater fixation of organic C in the soil. Therefore, the two thermal transformation pathways lead to wastes with divergent characteristics and effects on the soil. The vermicomposting of SCG generates a product with stable carbonaceous molecules, but with a high content of different forms of N. It is the only one of the SCG by-products that does not generate N immobilization and can even be considered as a N fertilizer. All tested materials did not cause an increase in N_2O emissions.

The results of the present study showed the potential of SCG by-products as effective organic amendment. Moreover, depending on their properties, they can be used to fulfil specific agronomic and ecosystem service functions.

Further research on the impact of SCG by-products residues on soil quality and fertility and crops are needed to evaluate their safety, trade-off between agronomical and environmental purpose and the identification of the material best suited for a specific aim.

In particular, researches are needed to better understand the relationship between by-products properties and effect on soil functions as this would allow for the full exploitation of SCG potential as soil amendment.

Credit author statement

Ana Cervera-Mata: Investigation, Writing – Original Draft Gabriel Delgado: Conceptualization, Writing Original-Draft, Writing – Review and Editing Alejandro Fernández-Arteaga: Writing – Review and Editing, Funding acquisition Flavio Fornasier: Methodology, Investigation, Resources Claudio Mondini: Conceptualization, Methodology, Resources, Writing – Original Draft, Writing – Review and Editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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