Catena 196 (2021) 104826

Contents lists available at ScienceDirect

Catena

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

Hydrophobicity and surface free energy to assess spent coffee grounds as soil amendment. Relationships with soil quality

A. Cervera-Mata[a,*], V. Aranda[b], A. Ontiveros-Ortega[c], F. Comino[d], J.M. Martín-García[a], M. Vela-Cano[e], G. Delgado[a]

[a] *Department of Soil Science and Agricultural Chemistry, University of Granada, Spain*
[b] *Department of Geology, Soil Science Section, University of Jaén, Spain*
[c] *Andalusian Institute of Geophysics, University of Granada, Spain*
[d] *Department of Physical and Analytical Chemistry, University of Jaén, Spain*
[e] *Institute of Water Research, University of Granada, Spain*

ARTICLE INFO

Keywords:
Soil hydrophobicity
Surface free energy
Organic amendments
Waste management
Organic raw material

ABSTRACT

The aim of this work was to evaluate the effects of spent coffee grounds (SCG), a highly hydrophobic raw material, on the hydrophobicity of two Mediterranean agricultural soils. Physical, chemical, mineralogical and biological soil properties, most of them used to evaluate soil quality, were studied and related to the main hydrophobicity parameters. The in vitro assay was performed with two SCG doses (2.5 and 10%), two soils and two incubation times (30 and 60 days). Hydrophobicity was determined by the water drop penetration time test (WDPT), the contact angle (CA) with H_2O, formamide and diiodomethane, and the surface free energy components (SFE) calculated using the Van Oss model. The addition of SCG increased the WDPT, CA and SFE, being the latter which was related to a greater number of soil quality variables. Hydrophobicity was related to lower humus quality index (HQI), and a higher proportion of labile organic matter, as shown by Infrared and UV–vis spectroscopy. An increase in hydrophobicity was related to an improvement of soil physical quality: a high aggregate stability index, saturated hydraulic conductivity, porosity (total and macro), water retention, and a less bulk density. The most critical effect related to the increase in hydrophobicity was the significant decrease in the available water content. The SEM images showed a greater occlusion and stabilization mechanism of the SCG particles incorporated in Vega soil, probably due to its higher content of smectite and carbonates. The appearance of fungal biomineralizations of calcium carbonate is associated with SCG addition and could be considered as an interesting and little studied process of inorganic carbon fixation and secuestration. These results showed that hydrophobicity can afford relevant information that can help to asses soil quality status after an amendment with SCG.

1. Introduction

Given the alarming deterioration in the quality of agricultural soils in the Mediterranean area (Rodríguez-Entrena et al., 2014), one of the main objectives of conservation agriculture is the increase of soil organic matter, which also favours its physical, chemical and biological properties. Hence, it is mandatory to study in depth the use of biological residues, raw or transformed, of a very different nature (such as ground coffee, SCG) as organic amendments and their effects on the soil physical, chemical and biological soil properties and in general on its quality. The latter includes possible negative effects, such as changes or decreases in biological activity, or alterations in soil water dynamics, as some authors have described (Aranda et al., 2016; Hardgrove and Livesley, 2016). Water holding capacity and water retention characteristics, structural type and aggregate stability, hydraulic conductivity, bulk density, organic matter, CEC, pH and EC can be used to assess soil quality as key attributes (Arshad and Coen, 1992). Soil biological parameters, have been shown to be especially useful to detect small changes in soil conditions, thus providing information regarding subtle alterations of soil quality (García-Ruiz et al., 2008).

Raw bio-residues and inadequate composted by-products, present inconveniences like the more labile and less stable organic matter, although its most critical effect could be its water repellence or hydrophobicity (Comino et al., 2017). Soil hydrophobicity is generated by the accumulation of hydrophobic compounds, originated from vegetation (de Blas et al., 2010) or microorganisms (Schaumann et al., 2007) or

---

[*] Corresponding author.
E-mail address: anacervera@ugr.es (A. Cervera-Mata).

https://doi.org/10.1016/j.catena.2020.104826
Received 17 April 2020; Received in revised form 26 June 2020; Accepted 2 August 2020

produced by the decomposition of fresh organic matter with a low degree of alteration and/or humification (Comino et al., 2017). This hydrophobicity could have a negative impact on soil water regime, infiltration capacity (Mohawesh et al., 2014), hydraulic conductivity and water availability for the plant (Doerr and Thomas, 2000). Furthermore, some authors have reported that hydrophobicity reduces the accessibility of microorganisms to organic matter, decreasing their rate of decomposition, due to the lack of water that restricts their favorable life conditions (Goebel et al., 2005; Leelamanie, 2016). At the same time, hydrophobicity increases the stability of soil aggregates and consequently contributing to the occlusion of organic matter as a stabilization mechanism (Lützow et al., 2006). In this way, moderate hydrophobicity is considered common in soil, and its positive influence on soil structure and quality has begun to be recognized (Goebel et al., 2005; Mataix-Solera et al., 2011; Aranda et al., 2016). These aspects are essential in relation to the conservation of organic matter in the soil and the extension of the concept of soil as a carbon sink. More empirical data on these effects in the soil and their properties are necessary and it is important to properly evaluate hydrophobicity, especially in agricultural soils. Some authors have suggested that hydrophobicity should be included as indicator of soil physical quality due to its relationship with other soil properties and its easy determination (Jordán et al., 2013).

There are several ways to determine hydrophobicity, the most usual but with notable limitations being the water drop penetration time (WDPT) test (Chau et al., 2014). Another widely used measure is the contact angle (CA) (Goebel et al., 2005; Diehl and Schaumann, 2007), which shows some physical meaning and enables the study of water repellency (SWR) in a wide soil range from wettable to extremely repellent. However, these methods estimate only persistence and intensity, respectively between water drops and the soil surface, without providing a comprehensive thermodynamic characterization of the solid surface alone. Many phenomena that take place at the solid-liquid interface, including wettability, adsorption, and aggregation, depend largely on changes involved the surface free energy (SFE) (van Oss, 1994). Hence, a complete determination of SFE components according to the Van Oss et al. (1988) approach for acid-base and Lifshitz-Van der Waals interactions would be recommendable.

The SCG is a bio-residue generated in large amounts (15 million tons annually, according to Kamil et al., 2019), characterized by its high amounts of polysaccharides, lignin and protein (Ballesteros et al., 2014). Previous studies on the effect of SCG on agricultural soils, have concluded that their addition to Mediterranean soils has clear agronomic benefits, in terms of improving soil physical, chemical and biological soil properties (Cervera-Mata et al., 2018, 2019a; Comino et al., 2020; Vela-Cano et al., 2019). The composition of SCG is also characterized by high amounts of lipids, 13–18% (Al-Hamamre et al., 2012; Petrik et al., 2014), which are retained in the SCG after the preparation of coffee beverage, which would justify the hydrophobic nature of this bio-residue (Gross et al., 1997). The positive effects of the SCG on the soil structural stability in the short term could be attributed to this hydrophobic character (Cervera-Mata et al., 2019a). However, there is still insufficient knowledge about their influence on soil hydrophobicity. In this field, new knowledge can be generated as a result of a more exhaustive investigation given that the soil hydrophobicity as a result of the organic amendments in agricultural soils is a problem that has hardly been addressed until now (Aranda et al., 2016; Jiménez-de-Santiago et al., 2019). Together with hydrophobicity, SCG have other limitations for their use as soil organic amendment, such as their phytotoxicity (Cervera-Mata et al., 2018, 2019b). Therefore, the transformation and stabilization of SCG through composting or biocharization could be considered an alternative for the use of these wastes (Liu and Price, 2011; Vardon et al., 2013). However, the time, cost and other environmental consequences of these treatments make it advisable to investigate the possibilities of their reuse as raw material, although taking into account their limitations.

Considering this, we can hypothesize that the addition of untransformed SCG (raw material) as an organic amendment in intensive agriculture as greenhouse crops (very widespread in the southeast of Spain), will effect soil hydrophobicity, and in particular, surface free energy components, which are decisive in the processes of adsorption and absorption in the soil. The main aim of this work is to know these effects in two Mediterranean agricultural soils with contrasted mineralogical properties. Moreover, the relationships between hydrophobicity and other physical, chemical, compositional (organic and mineral) and biological properties, many of them essential to evaluate soil quality, will be measured. Therefore, the changes generated by SCG from the point of view of soil quality will be discussed, an issue that has been little studied in relation to hydrophobicity.

2. Materials and methods

2.1. Soil sampling and spent coffee grounds

Two Mediterranean agricultural soils from Granada province (Andalusia, Southern Spain) were selected: Vega soil (SV) and Red soil (SR). SV was classified as Cambic Calcisol (Aric, Ochric) and SR was classified as Chromic Luvisol (Cutanic, Differentic, Hypereutric, Ochric) respectively (IUSS Working Group WRB, 2015). The sampling of soils consisted of a random selection of three locations within each soil type. In each location, a soil sample that is composed of four sub-samples (from the surface 0–20 cm layer) was randomly taken within a 5 m radius. 12 sub-samples were obtained for each soil type and a total of 24 kg of soil was sampled. These samples were mixed, homogenized, air-dried and sieved (< 2 mm) for further analysis and to constitute the soil substrate for the incubation assay.

The SCG was the solid residue obtained by mixing 50 g of ground coffee (100% Arabica, supplied by Café Cumbal S.A) with 1 L of boiled distilled water followed by filtration and air drying (Cervera-Mata et al., 2018). The particle size distribution (by sieving) of SCG was heterogeneous: 21% between 1000 and 500 µm, 60% between 500 and 250 µm, 12% between 250 and 200 µm and 7% less than 200 µm (Comino et al., 2020).

2.2. Experimental design: soil microcosms

Microcosms were prepared using sieved air-dried soil samples (< 2 mm), and mixing them with 0, 2.5 and 10% w:w of SCG (0, 60 and 240 Mg ha^{-1}) with a rotating shaker in order to obtain 400 g of the soil-SCG mixtures. The soil-SCG mixtures were transferred to PVC pots of 300 mL capacity and each PVC pot was closed with a mesh of fiberglass at the base and covered with a dish to avoid the entrance of light but not of air. The assay was performed in a growth chamber under controlled conditions with a relative humidity of 60–80% and temperature of 22/18 °C (day/night). To prevent leaching and water stress, the moisture of the pots was maintained between field capacity and permanent wilting point. The microcosms were irrigated once a week with distilled water (mean value of added water: 35 mL/week). The irrigation requirements were calculated by weighting (Dumroese et al., 2015). A total of 90 samples were obtained. 18 of them corresponding to initial control samples: 2 soil types (Red and Vega), 3 SCG dose (0, 2.5 and 10%), and 3 replicates (2 × 3 × 3 = 18). These samples were not incubated in the climatic chamber. The other 72 corresponding to incubated samples: 2 soil types (Red and Vega), 3 SCG dose (0, 2.5 and 10%), 2 incubation times (30 and 60 days) and 6 replicates (2 × 3 × 2 × 6 = 72). New samples were composed by mixing an equal weight of three of each case replicates, for a total of 30 composed samples which included each combination of the type of soil and SCG amount. The microcosm samples were air-dried and stored in a sterile bag and kept in a refrigerator at 5 °C.

2.3. Physical, chemical and mineralogical soil analyses

Organic carbon (OC) was determined by wet digestion with $K_2Cr_2O_7$ and H_2SO_4 at 155 °C for 30 min (Mingorance et al., 2007), and further determination by measuring absorbance at 600 nm in a Spectrophotometer BOECO-S200. Carbonates as $CaCO_3$ (CO_3^{2-}) were determined by Bernard's calcimeter method (Soil Survey Staff, 2014). Cation exchange capacity (CEC) was obtained by the ammonium acetate method (pH 7) and the sodium chloride method (Soil Survey Staff, 2014), and then the concentrations of Na were determined using a PFP7 flame photometer (JENWAY, Staffordshire, UK). Granulometry analysis was determined by Bouyoucos's method (Spanish MAPA, 1994). Bulk density was determined by the weight of the dry air sample contained in a cylinder of known volume (Bourger's method, Soil Survey Staff, 2014). Particle density was determined by the pycnometer method (Soil Survey Staff, 2014). Water retention at −33 kPa (field capacity, WR −33 kPa) and −1500 kPa (permanent wilting point, WR −1500 kPa) was calculated by the Richards membrane method, and plant available water content (AWC) from the difference between water retention at −33 and −1500 kPa, employing the Cm coefficient (Soil Survey Staff, 2014). Total porosity was estimated from the particle and bulk density, and macroporosity from total porosity less microporosity, the latter was measured as the water content at field capacity (Sánchez-Marañón et al., 2002). Saturated hydraulic conductivity (Ks, cm h^{-1}) was measured by a constant-head permeameter (Eijkelkamp Agrisearch Equipment, Giesbeek, NL) using sample unaltered cores (Spanish MAPA, 1994). The structural stabilities of aggregates (2000–250 µm) were determined by Kemper and Rosenau (1986) method, using an Eijkelkamp Agrisearch Equipment (Giesbeek, NL) for wet sieving.

Humus quality index (HQI), calculated as the CEC/OC ratio, could be regarded as an index of the quality of humus, considering that SOM accounts for most (> 70%) of the soil exchange capacity (Stevenson, 1982). Although mainly used for the assessment of compost quality, a high CEC/OC ratio could be considered a good indicator of well-humified SOM, as opposed to the less evolved types of humus, where the contribution to the CEC by C unit is much less (Tinoco et al., 2010).

Fractionation of soil organic matter was done by following the IHSS procedure (Swift, 1996): total extractable carbon (TEC); humic and fulvic acids (HA, FA). Hot water soluble carbon (HWSC) was extracted in distilled water (1:10, w/v) for 18 h at 80 °C (Ghani et al., 2003). The C content in these fractions, and total organic carbon (OC), was determined by wet digestion with $K_2Cr_2O_7$ and H_2SO_4 at 155 °C for 30 min (Mingorance et al., 2007), and further determination by measuring absorbance at 600 nm in a Spectrophotometer BOECO-S200.

2.4. Hydrophobicity parameters determination

The water drop penetration time test (WDPT) was performed following Bisdom et al. (1993) and employing the repellency classes: wettable (WDTP ≤ 5 s), slightly water repellent (5–60 s), strongly water repellent (60–600 s), severely water repellent (600–3600 s), and extremely water repellent (> 3600 s). Data (x) from WDPT, were also normalized using the log(x + 1) transformation. The technique used to estimate the SFE of soils in our experiments was advancing contact angles (CA) of three probe liquids (water, formamide and diiodomethane) onto dry soil pellets. Soil water repellence occurs if CA > 0°; soils with 0° < CA < 90° show reduced wettability and values of CA > 90° indicate extreme soil water repellence (Goebel et al., 2011). In this wide, a Ramé-Hart Inc., NRL C.A. goniometer (USA) was used. According to van Oss et al. (1988), the total SFE of a solid is described as a sum of two terms, the Lifshitz-van der Waals component γ_S^{LW} (dispersion component) and the acid-base interaction γ_S^{AB}, which is mainly due to the hydrogen bonding. In general, the polar γ^{AB} interaction is due to the electron-donor, γ^-, and electron-acceptor, γ^+, contributions. The relation among the contact angle θ and both the Lifshitz-van der Waals and Acid-Base components of the SFE of the solid (subscript 1) and the surface tension of the liquid can be written in the sense of the van Oss model as:

$$2\sqrt{\gamma_1^{LW}\gamma_{Li}^{LW}} + 2\sqrt{\gamma_1^{+}\gamma_{Li}^{-}} + 2\sqrt{\gamma_1^{-}\gamma_{Li}^{+}} = \gamma_{Li}(1+\cos\theta) \quad (1)$$

where γ_{Li} is the surface tension of liquid i forming a contact angle θ on the solid and γ_{Li}^{LW}, γ_{Li}^{+}, and γ_{Li}^{-} are the surface tension components of the liquid.

2.5. Phytotoxicity, dehydrogenase enzyme activity and soil respiration rate

Phytotoxicity was determined following the method of Alburquerque et al. (2006) adapted from Zucconi et al. (1981). This method combines the measurements of seed germination and root elongation of cress (*Lepidium sativum* L.). The results were expressed as a percentage of germination and root elongation of control as follows: % GI = (%germination × %root elongation)/100.

Dehydrogenase activity (DHase) was determined following the method of Casida et al. (1964) by the reduction of 2,3,5-triphenyl tetrazolium chloride (TTC). Soil (10 g) was incubated for 24 h with TTC at 27 °C in duplicates. The triphenyl formazan (TPF) formed was extracted with acetone and measured spectrophotometrically at 546 nm. Dehydrogenase activity was expressed as µg $TPFg^{-1}$ dry soil h^{-1}.

The respiration rate (RR), expressed as amount of CO_2-C emitted from carbon mineralization of six selected samples (by triplicate) after SCG amendments with SCG (0, 2.5, 10%) in both soils (SR and SV), was measured continuously during 30 days of incubation (60% water holding capacity, 25 °C and darkness) using the alkaline trap method (Anderson, 1982).

2.6. ATR-FTIR and UV–vis spectroscopy

Mid-IR spectra of bulk soil samples were recorded using a Bruker Tensor 27 FTIR spectrometer, equipped with an attenuated total reflection accessory (ATR, Pike Technologies) with a three-reflection diamond crystal. Soil samples were finely ground in an agate mortar. Samples were placed directly on the ATR crystal. Controlled pressure was applied to ensure good contact between the sample and the ATR element. The spectra ranged from 700 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and 128 accumulations. The spectra of air on the clean dry ATR crystal was used as background. The potential wettability of soil organic matter (PWSOM) (CH/C = O ratio, Ellerbrock et al., 2005) from Mid-IR spectra of bulk soil samples was also calculated using the area under the 3000–2800 cm^{-1} band corresponding to aliphatic C—H bonds as a measure of hydrophobic functional groups, and the total area of the 1740–1600 cm^{-1} band, corresponding to the C═O of aromatic functional groups, as a measure of hydrophilicity (Comino et al., 2017). Areas were calculated using OPUS 7.0 spectroscopy software (Bruker Optics).

UV–Vis spectra of 0.2 mg C mL^{-1} HA solutions in 0.1 M $NaHCO_3$ (Senesi et al., 2003) were recorded from 200 to 800 nm in a computer controlled Varian Cary 50 spectrophotometer with the Varian spectroscopy software, WIN-UV, obtaining the A4/A6 ratio (472 nm/680 nm).

2.7. Scanning electron microscopy (SEM)

SEM images were captured from soil macro-aggregates (1–2 mm) fixed with carbon double-sided adhesive tape, metalized with carbon and analyzed with variable pressure and high resolution scanning electron microscope (VPESEM-FESEM) SUPRA40VP (ZEISS, Oberkochen, Germany), equipped with an energy dispersive X-ray (EDX) elemental analyser.

2.8. Statistical analysis

Data analysis included correlations of variables (Pearson's

Table 1

Soils and Spent Coffee Ground properties before incubation (mean values ± SD; n = 3).

Sample	Dry color (Munsell)	CF (%)	Clay (%)	Silt (%)	pH	EC_{25} (dS m^{-1})	OC (%)	N (%)
Spent Coffee Ground	–	–	–	–	5.76 ± 0.26	4.5 ± 0.5	59.38 ± 0.62	1.87 ± 0.10
Vega Soil	10YR 5.5/2	2.0 ± 0.3^a	58.0 ± 1.7^b	29.9 ± 0.9^b	8.2 ± 0.17^b	1.3 ± 0.2^b	1.36 ± 0.08^a	0.11 ± 0.05^a
Red Soil	2.5YR 4/6	6.0 ± 0.2^b	43.2 ± 0.9^a	18.0 ± 1.2^a	7.2 ± 0.15^a	0.6 ± 0.1^a	1.16 ± 0.11^a	0.11 ± 0.03^a

Sample	C/N	CO_3^{2-} (%)	CEC ($cmol_+$ kg^{-1})	BD (g cm^{-3})	WR −33 kPa (%)	WR −1500 kPa (%)	AWC (mm cm^{-1})
Spent Coffee Ground	32 ± 1	nd	58.28 ± 1.6	0.49 ± 0.01	118.3 ± 3.7	110.4 ± 6.1	0.39 ± 0.02
Vega Soil	13 ± 1^b	39.0 ± 3.2^b	26.61 ± 0.5^b	1.20 ± 0.04^a	26.4 ± 0.4^b	15.6 ± 0.7^b	1.30 ± 0.07^b
Red Soil	10 ± 1^a	1.6 ± 0.5^a	23.73 ± 0.7^a	1.27 ± 0.04^a	20.0 ± 0.6^a	11.7 ± 0.6^a	1.05 ± 0.03^a

CF: coarse fragment; $EC_{25:}$ electrical conductivity at 25 °C; OC: organic carbon; N: total nitrogen; CO_3^{2-}: carbonates as $CaCO_3$; CEC: cation exchange capacity; BD: bulk density; WR-33 and WR-1500: water retention at −33 and −1500 kPa, respectively; AWC: available water content; nd: not detected. Different letters in the same column indicate statistically significant differences between Vega soil and Red soil ($p < 0.05$; *t*-test).

correlation coefficient) and ANOVA. Normality assumptions were tested using the Saphiro-Wilk test. The F-test (ANOVA) was applied to variables fitting a normal distribution, while an alternative nonparametric test (Kruskal-Wallis ANOVA) was applied to the rest. T-student test, Fisher Least Significant Difference and Turkeýs Honestly Significant were used in the appropriate case for search differences between means. Multifactor analysis of variance (multifactor ANOVA) was used to verify the influence of interaction among the main assay factors considered. All statistical procedures were carried out using Statgraphics Centurion XVI software (Stat Point Technologies, Inc.). Principal component analysis (PCA) was used 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 and discussion

3.1. Characterization of soils and spent coffee grounds

The properties of the sampled soils and SCG are reflected in Table 1. SV had higher values of OC, CEC, WR −33 kPa and WR −1500 kPa and AWC, as well as lower values of BD than SR. However, the main difference between both soils was the carbonate content: 39% in the case of SV and 1% in the case of SR. According to Comino et al. (2020), the fine earth of SV was rich in phyllosilicates (47%), quartz (11%) and carbonates (34% calcite and 8% dolomite), whereas SR had more phyllosilicates (63%), quartz (33%) and does not contain appreciable amounts of carbonates. According to the same authors, the clay fraction of SV had a marked smectitic character (17%), illite (29%) and calcite (14%), whereas SR had more kaolinite (27%), illite (33%) and iron oxides (5%) (Comino et al., 2020). In comparison with the soils, SCG has a more acidic character and far higher levels of OC, N, C/N, CEC and water retention at both potentials. These properties were very similar to other SCG used in previous studies (Cruz et al., 2012; Hardgrove and Livesley, 2016), except for C/N ratio, that was higher in this study, which could be due to the form of extraction of coffee beverage (infusion in our case and espresso extraction in the case of references).

3.2. Effects of assay variables on soil quality indicators

Table 2 shows the influence of SCG dose, soil type and incubation time on hydrophobicity, chemical, biological and physical parameters. Most of soil properties were significantly affected by the addition of SCG. Statistically significant differences were found between 0, 2.5 and 10% SCG in hydrophobicity parameters (e.g.: WDPT, CA H_2O and γ^-), chemical parameters (e.g.: OC or TEC), biological parameters (e.g.: RR and DHase) and physical parameters (except total porosity). It is important to highlight that SCG addition is the factor that affects almost all hydrophobicity related properties, whereas the type of soil and the incubation time have no significant effect on most properties. However, they affect some other properties: the type of soil affects potential wettability of SOM, total porosity, WR −33 kPa and AWC, as well as A4/A6 ratio, DHase, BD and macroporosity. Days of incubation only show some significant differences for WDTP, γ^+, BD, total porosity and AWC. All that appears to indicate that the main factor for this assay is the SCG addition, which corroborates the initial hypothesis of this work.

3.3. Soil water repellency and hydrophobicity

Thermodynamic characterization of the soils was carried out in order to estimate their degree of hydrophobicity and measure their wetting and water retention properties. Table 3 shows the advancing contact angles obtained with water, formamide and diiodomethane of known surface tension components (van Oss, 1994), the SFE

Table 2

Mean values of soil quality indicators and surface free energy components for soil type and treatments; statistical tests for differences between means; n = 30.

Indicator	%SCG				Soil			Incubation days			
	0	2.5	10	Sig.	SV	SR	Sig.	0	30	60	Sig.
WDPT (s)	0.23	1.26	4.06	***	1.71	1.98	n.s.	13.64	1.95	1.75	*
logWDPT + 1	0.28	1.04	1.59	***	0.99	0.94	n.s.	1.46	0.99	0.95	n.s.
CA (H_2O)	16.63	20.5	29.00	**	21.50	22.58	n.s.	20.67	23.00	21.08	n.s.
CA (formamide)	12.75	16.88	22.25	n.s.	19.83	14.75	n.s.	12.50	20.42	14.17	n.s.
CA (diiodomethane)	22.38	22.63	35.50	*	28.17	25.50	n.s.	37.17	24.00	29.67	n.s.
γ^{LW} SFE (mJ m^{-2})	45.82	45.12	40.59	**	43.15	44.53	n.s.	40.51	43.62	44.06	n.s.
γ^{+} SFE (mJ m^{-2})	0.54	0.58	1.06	*	0.65	0.80	n.s.	1.38	0.77	0.68	*
γ^{-} SFE (mJ m^{-2})	51.23	48.36	38.85	***	46.27	46.03	n.s.	47.98	46.69	45.60	n.s.
Total SFE (mJ m^{-2})	56.10	55.60	53.40	n.s.	53.98	56.09	n.s.	56.21	55.05	55.02	n.s.
PWSOM	1.92	1.92	2.27	n.s.	2.73	1.34	***	2.09	2.04	2.03	n.s.
OC (%)	1.37	2.43	5.17	***	3.19	2.79	n.s.	3.33	3.01	2.97	n.s.
CEC ($cmol_+$ kg^{-1})	23.72	24.06	27.43	n.s.	27.81	22.33	***	25.52	25.06	25.09	n.s.
HQI	17.46	9.95	5.33	***	11.34	10.49	n.s.	11.24	10.97	10.85	n.s.
CO_3^{2-} (%)	20.67	20.51	19.09	n.s.	39.12	1.07	***	19.23	20.06	20.13	n.s.
TEC (mg C kg^{-1})	5038	8062	17,611	***	10,180	10,293	n.s.	11,289	11,248	92,227	n.s.
HA/FA ratio	11.34	12.47	11.97	n.s.	12.91	10.93	n.s.	12.46	12.26	11.59	n.s.
HWSC (mg C kg^{-1})	198	581	1405	***	698	758	n.s.	904	693	763	n.s.
A4/A6 ratio	4.29	4.63	4.74	n.s.	4.14	4.96	***	4.54	4.54	4.57	n.s.
RR (mg CO_2-C g^{-1} day^{-1})	0.22	1.46	3.82	***	1.52	1.54	n.s.	Not viable			
GI (%)	102.62	98.46	86.16	n.s.	95.61	95.90	n.s.	100.03	95.24	96.26	n.s.
DHase (μg TPF g^{-1} h^{-1})	26.00	49.01	33.33	*	24.86	47.37	***	23.88	34.09	38.13	n.s.
ASI	0.76	0.86	0.94	***	0.87	0.84	n.s.	0.83	0.84	0.86	n.s.
Ks (cm h^{-1})	7.14	11.56	23.03	***	14.73	13.09	n.s.	15.33	14.00	13.81	n.s.
BD (g cm^{-3})	0.97	0.93	0.90	*	0.91	0.96	**	1.10	0.94	0.93	***
PD (g cm^{-3})	2.49	2.44	2.29	***	2.39	2.42	n.s.	2.41	2.39	2.42	n.s.
Total porosity (%)	60.98	61.86	60.56	n.s.	62.05	60.21	*	54.40	60.51	61.76	***
Macroporosity (%)	35.52	35.71	28.30	**	30.52	35.82	**	27.30	32.83	33.52	n.s.
WR −33 kPa (%)	25.46	26.16	32.26	**	31.53	24.39	***	27.09	27.68	28.24	n.s.
WR −1500 kPa (%)	13.99	17.23	26.84	***	21.10	17.60	n.s.	16.14	18.72	20.00	n.s.
AWC (mm cm^{-1})	1.11	0.83	0.49	***	0.95	0.66	*	1.20	0.85	0.77	*

SV: Vega soil: SR: Red soil; WDPT: water drop penetration time; CA: contact angle (°); SFE: surface free energy component; PWSOM: potential wettability of soil organic matter; OC: organic carbon; CEC: cation exchange capacity; HQI: Humus quality index (CEC/OC); CO_3^{2-}: carbonates; TEC: total extractable carbon; HA: humic acids; FA: fulvic acids; HWSC: hot water soluble carbon; A4/A6 ratio: 472 nm/680 nm UV–Vis spectra humic acids; RR: respiration rate; GI: germination index; DHase: dehydrogenase activity; ASI: aggregate stability index; Ks: saturated hydraulic conductivity; BD: bulk density; PD: particle density; WR: water retention; AWC: available water content. Statistical significance: *$P < 0.05$; **$P < 0.01$; ***$P < 0.001$; n.s.: not significant differences; Student's *t*-test for two groups.

components, γ^{LW}, γ^{+} and γ^{-} (calculated using Eq. (1)) and the potential wettability of SOM. The variables were grouped according to SCG dose and soil type, the two factors that showed the most significant differences in the statistical analysis (Table 2).

According to WDPT, the original soils were fairly wettable, having penetration times < 1 s, and SCG was severely water repellent (817 s). This value is lower than those found by Comino et al. (2017) for SCG (3180 s), but they are both considered as severely water repellent (600–3600 s). These differences could be attributed to the conditions used for instant coffee preparation (pressure and temperature). The addition of SCG appear only to affect the penetration time of soil when the highest dose of SCG was used (not significantly in SV, Table 3), increasing the soil hydrophobicity (slightly water repellent: 5–60 s). However, when the data is normalized by applying logarithms (logWDPT + 1), the addition of SCG significantly affected this variable.

In SCG, the highest value of CA was observed for water, followed by formamide and diiodomethane (Table 3), because of the hydrophobic character of SCG. However, when SCG was added to both soils, the higher CA were found for diiodomethane due to the apolar character of the liquid, which generated higher CA with the solid. This fact is due to solid soil particles at neutral and basic pH usually have negative charges (Ndlovu et al., 2014). When SCG was added, an increasing trend of all CA was observed, except for formamide with 2.5% SCG in SR. This fact was probably due to the absence of symmetry of the polarity of this liquid being preferable of electron acceptor character ($\gamma^{+} = 39.6$ and $\gamma^{-} = 2.28$; van Oss, 1994). It has also been demonstrated in previous studies that the addition of other organic amendments, such as olive mill pomace co-compost, cattle manure, goat manure or leaves, increased also the CA (Aranda et al., 2016; Liyanage and Leelamanie, 2016). Nevertheless, according to contact angle soil water repellency classification, SCG was classified as low water repellent (81–86°), lower than the subcritical repellency angle of 90° (Tillman et al., 1989), which indicate low soil hydrophilicity. Therefore, all the soil-SCG mixtures with CA lower than 40 were considered as “not significantly water repellent” according to King (1981). The lack of coincidence regarding the hydrophobicity classification among the WDPT and CA are in accordance with Aranda et al. (2016), who attributed the complexity of the relationship between both parameters classes to the measurement method.

The γ^{LW} values of soil samples are in the range of 38 and 47 mJ m^{-2} (Table 3), which are slightly lower than those obtained for other Mediterranean soils (Plaza et al., 2015). Note that this component decreases its value as the percentage of SCG increases, this behavior is probably because the SCG generates a more ordered structure of water molecules at the solid-liquid interface (Ontiveros-Ortega et al., 2014). From the analysis of the base-acid (γ^{+} and γ^{-}) components of the surface free energy of soils and their treatment with SCG, the studied soils can be considered monopolar in nature [van Oss model]. Soils in general, are considered as a Lewis base ($\gamma^{+} \approx 0$ and $\gamma^{-} \neq 0$). If we analyze the behavior of the electron donor component, we observe that in all cases the addition of SCG supposes a decrease in the electron donor character of the soil. On the other hand, it is observed that this decrease of the basic character (in the Lewis sense) of the soil is not significant between 0 and 2.5, but it is between 2.5 and 10% SCG (Table 3). If we consider that according to van Oss model, a monopolar material present hydrophilic character when $\gamma^{+} \approx 0$ and $\gamma^{-} \leq$

Table 3

Water repellency parameters for soil microcosm samples and SCG. Mean values ± SD (n = 5). Significant differences are indicated by different letters ($P < 0.05$, ANOVA, Tukey post-hoc). F ratio of the two ways ANOVA is also shown ($P < 0.001$***; $P < 0.01$**; $P < 0.05$*).

Soil	SCG %	WDPT (s)	logWDPT + 1	CA (°)			Surface free energy components (mJ m^{-2})				PWSOM
				H_2O	Formamide	Diiodomethane	γ^{LW}	γ^-	γ^+	Total	
SR	0	0.3 ± 0.2 a	< 1 a	17.8 ± 7 a	11.2 ± 5 a	19.8 ± 7 a	47.03 ± 1.02c	51.70 ± 1.44b	0.45 ± 0.14 a	56.41 ± 0.85b	1.28 ± 0.05 a
SR	2.5	1 ± 0.6 a	1b	21.4 ± 9 ab	15.8 ± 11 a	23.4 ± 10 ab	44.94 ± 2.28 bc	47.15 ± 5.46b	0.67 ± 0.34 a	56.09 ± 1.55b	1.24 ± 0.06 a
SR	10	14.9 ± 22.9b	2c	28 ± 6c	15.2 ± 3 a	35.4 ± 10 ab	41.45 ± 3.92 ab	38.90 ± 3.15 a	1.28 ± 0.52 a	55.87 ± 1.43b	1.51 ± 0.08 a
SV	0	0.3 ± 0.3 a	< 1 a	18 ± 4 a	13.2 ± 7 a	27.8 ± 12 ab	43.81 ± 4.10 bc	50.73 ± 1.83b	0.80 ± 0.48 a	56.41 ± 0.41b	2.57 ± 0.30b
SV	2.5	1.4 ± 0.4 a	1b	18 ± 4 a	15.6 ± 7 a	28 ± 15 ab	43.44 ± 5.07 bc	50.60 ± 1.42b	0.79 ± 0.68 a	56.09 ± 2.08b	2.59 ± 0.14b
SV	10	7.3 ± 8.6 ab	2c	27.4 ± 10 ab	27 ± 11b	39.2 ± 10b	38.38 ± 2.96 a	38.92 ± 8.76 a	1.15 ± 0.95 a	55.87 ± 4.38 a	3.10 ± 0.35c
SCG	–	816.6 ± 19.97	3.9 ± 0.01	83 ± 6.08	38 ± 5.29	28 ± 2.65	40.60 ± 1.64	0.044 ± 0.01	5.78 ± 0.70	41.61 ± 1.45	1.95 ± 0.10
		F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio
Soil type		239.8***	0.01	0.63	1.65	3.02	8.65*	0.10	3.11	2.26	226.8***
SCG dose		1648.6***	54.3***	9.08**	2.34	4.07	8.57**	12.4**	5.11*	2.32	8.04**
Soil type × SCG dose		269.1***	1.16	0.38	0.65	0.15	0.11	0.40	0.20	0.86	1.42

Parameter abbreviations from Table 2.

28.2 mJ m^{-2} (van Oss, 1994), SCG addition reduce soil hidrophylicity (Table 3) and in parallel it acidifies it, as it will be discussed later.

Likewise, the potential wettability of SOM (PWSOM; i.e., hydrophobic aliphatic/hydrophilic aromatic functional groups from ATR-FTIR of bulk soil samples), traditionally used to evaluate soil hydrophobicity (Matějková and Šimon, 2012), show a similar trend to that found in other works (Ellerbrock et al., 2005; Comino et al., 2017). This trend indicated that higher aliphatic compound concentration in the organic amendment generates a higher hydrophobic character, and therefore higher water repellence, as also shown by Aranda et al. (2016) on the effects of olive mill pomace co-compost on wettability and soil quality in olive groves in with long-term field experiments. In this case, the addition of SCG generated an increase in aliphatic compounds concentration, which leads to an increase in water repellence, but not significantly.

Moreover, it would be interesting to discuss the hydrophobic behaviour of the samples, from the point of view of soil type. Assayed soils (SR and SV) present different geochemical conditions. SV has a less sandy texture, more carbonated and a higher pH (Table 1), which did not influence the parameters related to hydrophobicity decisively, as evidenced by the lack of relationship between the type of soil and the WDPT and CA test and the SFE components (Table 2). For WDPT and CA-H_2O parameters, the increase in hydrophobicity is somewhat higher in SR. Therefore, the presence of a sandier texture in SR (Table 1) could influence in a certain way the slight increase of its water repellency, as has been reported by different authors (Dekker et al., 2005; Woche et al., 2005; González-Peñaloza et al., 2013). The higher content of smectites and carbonates in SV may also influence this fact, as we will further discuss. Similar behavior is found in the electron-donor parameter γ^-, decreasing with increasing SCG%, significantly with 10% (Table 3), and not significantly in SR with respect to SV. Remember that for a monopolar material of electron-donor nature ($\gamma^+ = 0, \gamma^- \neq 0$), a decrease of γ^- indicates a decrease in its hydrophylicity, being the limit that differentiates a hydrophobic and hydrophilic material ($\gamma^+ = 0, \gamma^- \leq 28.2$, van Oss, 1994). Even when no correlation is found between γ^- and CO_3^{2-} for all samples (n = 30), a positive correlation was found for SV samples (n = 15) (r = 0.516; $P < 0.05$); indicating that a lower content in carbonates, and a higher content in SCG (Table 3) give rise to higher hydrophobicity. This inverse relationship between water repellence and carbonates in soils has been described by several authors (Cerdá and Doerr, 2005; Aranda et al., 2016), but scarcely described for organic amendments in soils. These authors explained the differences in soils in terms of soil acidity, and suggested that the alkalinity of calcareous soils is responsible for the decreasing in hydrophobicity.

There are interesting correlations between the variables related to hydrophobicity (Table 4). Highlight the good correlation that exists between the components of SFE (γ^{LW}, γ^+, γ^-) and the WDPT parameter. In this sense we observe that high values of γ^{LW}, that give information on the structuring capacity of the water molecules around the surface of the soil particles, correspond to lower water drop penetration time values as expected. The correlation between γ^- that indicates the degree of hydrophilicity (lower hydrophilicity lower γ^-) is also reasonable, as is the WDPT indicating that a lower value of γ^- implies less hydrophilicity and therefore greater water drop penetration time.

3.4. Relationship between soil hydrophobicity and other properties related to soil quality

These relationships have been established based on the values found for SCG dose and soil type (Table 5), the two factors that showed the most significant differences in the statistical analysis, since the incubation time is not significant for most variables (Table 2).

3.4.1. Relationship with soil chemical properties and soil organic matter quality

The addition of SCG significantly modified some properties such as

Table 4
Pearson's correlation coefficients matrix between the hidrophobicity properties and chemical, physical and biological properties.

	WDPT	log WDPT + 1	CA H_2O	CA formamide	CA diiodomethane	γ^{LW} SFE	γ^{+} SFE	γ^{-} SFE	Total SFE
WDPT									
log WDPT + 1	0.678***								
CA H_2O	–	0.437*							
CA formamide	–	–	0.393*						
CA diiodomethane	–	0.514**	–	–					
γ^{LW} SFE	–	−0.573***	–	−0.379*	−0.859***				
γ^{+} SFE	–	0.511**	–	–	0.605***	−0.746***			
γ^{-} SFE	–	−0.583***	−0.761***	−0.369*	–	–	–		
Total SFE	–	–	–	−0.648***	−0.431*	0.464**	–	–	
PWSOM	–	–	–	–	0.373*	−0.437*	–	–	−0.423*
OC	0.536**	0.868***	0.492**	0.453*	0.513**	−0.599***	0.424*	−0.714***	−0.459*
CEC	–	–	–	–	0.438*	−0.481**	–	−0.365*	−0.446*
HQI	−0.406*	−0.826***	−0.411*	−0.447*	−0.387*	0.506**	−0.370*	0.621***	0.366*
CO_3^{2-}	–	–	–	–	–	–	–	–	–
TEC	0.488**	0.842***	0.582***	0.440*	0.457*	−0.544**	0.415*	−0.709***	−0.403*
HA/FA	–	–	–	–	–	–	–	–	–
HWSC	0.652***	0.836***	0.381*	0.411*	0.473**	−0.535**	–	−0.661***	−0.437*
A4/A6	–	–	–	–	–	–	–	–	–
RR	0.498**	0.866***	0.514**	0.372*	0.563***	−0.662***	0.610***	−0.638***	–
GI	–	–	−0.446*	–	–	–	–	–	–
DHase	–	–	–	–	–	–	–	–	–
ASI	–	0.676***	0.373*	–	0.383*	−0.417*	–	−0.580***	–
Ks	0.536**	0.868***	0.492**	0.453*	0.514**	−0.600***	0.424*	−0.714***	−0.459*
BD	–		–	–	–	–	–	–	–
PD	−0.380*	−0.713***	–	−0.503**	−0.514**	0.651***	−0.415*	0.498**	0.515**
Total porosity	−0.482**		–	–	–	0.361*	−0.458*	–	–
Macroporosity	−0.448*	−0.649***	–	−0.455*	−0.580***	0.718***	−0.534**	0.399*	0.442*
WR −33 kPa	–	0.496**	–	0.494**	0.464**	−0.557***	–	−0.456*	−0.575***
WR −1500 kPa	–	0.636***	0.574***	0.523**	0.429*	−0.482**	–	−0.730***	−0.579***
AWC	–	–	−0.558***	–	–	–	–	0.623***	–

Parameter abbreviations from Tables 1 and 2. Statistical significance: $^{*}P < 0.05$; $^{**}P < 0.01$; $^{***}P < 0.001$; n = 30.

OC, TEC and HWSC, increasing its values (Tables 2 and 5). The addition of 2.5 and 10% SCG increased the amount of OC in both soils, with values reaching 5% in SR and 5.6% in SV (Table 5), which indicated a favorable aspect of the use of SCG as soil organic amendment, due to the little amount of OC (< 1%) in the Mediterranean agricultural soils (Rodríguez Martín et al., 2016). This fact has been reported in previous studies (Cervera-Mata et al., 2018, 2019a, Comino et al., 2017, 2020). The results obtained also showed an increase in SOM fractions (TEC and HWSC) with the addition of SCG, which indicates an increase in the more labile pool, and a decrease in the quality of SOM, expressed as HQI (13 units in both soils with 10% SCG; Table 5). Furthermore, the SCG addition increased the A4/A6 ratio and therefore, the molecular complexity of OC decreased, since this property is inversely related to the degree of humification of SOM (Stevenson, 1994). This ratio indicates differences between soil typologies (Tables 2 and 5), with lower values in SV, showing a better distribution in partial and total humified humic acids, and higher evolution of HA in this soil. Other properties affected significantly by soil type were carbonates and CEC, being higher in SV than in SR (Table 1). These results suggest that OM levels increase with SCG addition, the quality of this organic matter is reduced, especially in SR samples.

The variables related to hydrophobicity, γ^{-} and logWDPT + 1, are those that present the highest number of correlations and most significant with the parameters of the soil quality (Table 4). The OC, TEC and HWSC indicators correlate with γ^{-} (r = −0.714, −0.709 and −0.661, respectively), so that the greater OM content, the greater the hydrophobicity in the soil samples, in agreement with Aranda et al. (2016). In the correlations between γ^{-} (and all those parameters related to hydrophobicity) with those parameters of OM quality (HQI, HA/FA and A4/A6), we only found a significant correlation with HQI, which supports the idea that there is an inverse relationship between OM quality and hydrophobicity. This relation between the quantity and the quality of OM in relation to hydrophobicity may be due to the strong stability and low humification degree of the organic material added to the soil, with little evolution for the incubation days established in the trial (Table 2). These results showed, in agreement with Leue et al. (2015), that water drop infiltration time is related to OM composition and quality and could have implications, yet little known, for preferential movement of water and reactive solutes in soil.

3.4.2. *Relationship with soil physical properties*

The addition of SCG showed significant influences on all physical soil properties except for total porosity (Tables 2 and 5). Physical properties were in general more favourable in amendment soils with higher aggregate stability index (ASI), hydraulic conductivity (Ks), macroporosity, water retention and lower bulk and particle density, which were also shown by Cervera-Mata et al., 2019a. Hence, this raw material had a positive influence on water retention, increasing its value at both potentials (−33 and −1500 kPa). Therefore, water retention increased with increasing water repellency, which is according to Liyanage and Leelamanie (2016), who found that samples with hydrophobic manure showed increased water retention. However, the relative increase of WR-1500 kPa was greater than for WR-33 kPa, and, therefore, the AWC decreased with the addition of SCG. This same trend was found by other authors who used SCG (Cervera-Mata et al., 2019a), or other organic amendments (Aranda et al., 2016; Forge et al., 2016; Killi et al., 2014; Lozano-García et al., 2011). Aranda et al. (2016) attributed this phenomenon to the hidrofobicity of the organic amendment added to the soil. The macroporosity and bulk density, significantly higher in SR samples (Tables 2 and 5), decreased with the incorporation of SCG, which can be observed in SEM images (Fig. 1). The results also showed an increase in ASI with the addition of SCG, with values reaching 0.93 (average of both soils), and an increase in Ks, 245% and 230%, in the case of SR and SV, respectively, with the addition of 10% SCG. Coinciding with Lützow et al. (2006), an increase of hydrophobicity has a positive impact on soil structural stability. Leelamanie et al. (2013), found that higher amounts of green manure (very hydrophobic material) increased stable aggregates. Regarding

Table 5

Soil quality parameters of soil microcosm. Mean values ± SD (n = 5). Significant differences are indicated by different letters ($P < 0.05$, ANOVA, Tukey post-hoc). F ratio of the two ways ANOVA is also shown ($P < 0.001$***; $P < 0.01$**; $P < 0.05$*)

Chemical, physicochemical and biological properties												
Soil	SCG %	pH (H_2O)	OC (%)	CEC ($cmol_+ kg^{-1}$)	HQI	CO_3^{2-} (%)	TEC (mg C kg^{-1})	HA/FA ratio	HWSC (mg C kg^{-1})	A4/A6 ratio	GI (%)	DHase (µgTPF g^{-1} h^{-1})
SR	0	7.5 ± 0.2 b	1.23 ± 0.17 a	21.07 ± 1.74 a	17.40 ± 3.01 c	1.0 ± 0.4 a	5198 ± 1154 a	11.6 ± 3.1 a	228 ± 132 ab	4.5 ± 0.2 b	104 ± 27 a	34.68 ± 8.04 c
SR	2.5	7.4 ± 0.1 b	2.28 ± 0.17 b	21.75 ± 0.63 a	9.59 ± 0.80 b	1.2 ± 1.1 a	8571 ± 1492 b	11.7 ± 1.9 a	702 ± 124 c	5.2 ± 0.2 c	99 ± 18 a	58.64 ± 13.65 d
SR	10	6.7 ± 0.2 a	5.09 ± 0.98 d	24.81 ± 0.75 b	4.97 ± 0.74 a	1.0 ± 0.2 a	18382 ± 2831 c	11.5 ± 3.3 a	1574 ± 499 d	5.1 ± 0.3 c	81 ± 12 a	38.26 ± 14.03 c
SV	0	8.3 ± 0.1 d	1.47 ± 0.16 a	26.95 ± 1.89 c	18.54 ± 2.52 c	40.2 ± 1.2 d	5342 ± 510 a	11.8 ± 2.8 a	173 ± 88 a	4 ± 0.2 a	101 ± 33 a	17.04 ± 9.90 a
SV	2.5	8.3 ± 0.2 d	2.66 ± 0.30 c	26.52 ± 0.67 c	10.05 ± 0.93 b	39.3 ± 1.6 c	8224 ± 1093 b	12.1 ± 2.4 a	511 ± 68 bc	4.1 ± 0.1 a	98 ± 14 a	32.28 ± 3.49 bc
SV	10	8.0 ± 0.1 c	5.62 ± 1.74 e	29.28 ± 1.96 d	5.33 ± 0.36 a	36.8 ± 1.3 b	16964 ± 1756 c	13.5 ± 3.1 a	1394 ± 249 d	4.4 ± 0.2 b	98 ± 16 a	21.10 ± 4.93 a
		F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio
Soil type		508.2***	6.51*	104.1***	0.47	8990.2***	3.53	0.01	16.5*	67.7***	0.55	41.9***
SCG dose		64.9***	279.3***	17.3***	107.0***	7.26**	281.4***	0.55	263.5***	13.2*	0.35	14.3**
Soil type × SCG dose		8.35**	0.26	0.09	0.04	6.17*	1.02	0.45	4.01*	4.92*	0.40	0.81

Physical properties										
Soil	SCG %	ASI	Ks (cm h^{-1})	BD (g cm^{-3})	PD (g cm^{-3})	Total porosity (cm^3 cm^{-3})	Macroporosity (cm^3 cm^{-3})	WR -33kPa (%)	WR -1500kPa (%)	AWC (mm cm^{-1})
SR	0	0.72 ± 0.02 a	6.56 ± 0.64 a	1.03 ± 0.09 b	2.53 ± 0.09 c	59.20 ± 2.48 a	37.61 ± 2.72 d	21.59 ± 1.08 a	12.15 ± 0.37 a	0.97 ± 0.13 bc
SR	2.5	0.85 ± 0.06 b	10.94 ± 0.63 b	1.01 ± 0.1 ab	2.46 ± 0.05 bc	59.00 ± 4.04 a	36.45 ± 3.88 cd	22.56 ± 1.40 a	15.38 ± 3.63 b	0.73 ± 0.29 ab
SR	10	0.93 ± 0.05 c	22.68 ± 3.33 c	0.96 ± 0.08 ab	2.31 ± 0.03 a	58.39 ± 3.55 a	30.00 ± 3.04 b	28.39 ± 0.69 b	22.95 ± 3.50 c	0.54 ± 0.35 a
SV	0	0.79 ± 0.03 b	7.54 ± 0.52 a	0.97 ± 0.08 ab	2.48 ± 0.05 bc	60.88 ± 3.84 a	32.18 ± 3.49 bc	28.70 ± 0.82 bc	15.70 ± 0.32 b	1.26 ± 0.09 c
SV	2.5	0.86 ± 0.06 b	12.52 ± 1.06 b	0.93 ± 0.08 ab	2.42 ± 0.05 b	61.45 ± 3.81 a	31.64 ± 4.10 bc	29.81 ± 0.44 c	18.07 ± 0.79 b	1.10 ± 0.21 c
SV	10	0.95 ± 0.06 c	24.91 ± 1.43 d	0.90 ± 0.07 a	2.25 ± 0.08 a	59.79 ± 3.70 a	21.10 ± 3.63 a	35.68 ± 1.31 d	28.00 ± 2.84 d	0.71 ± 0.27 ab
		F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio	F ratio
Soil type		4.43	6.48*	15.1**	5.83*	3.99	23.7***	336.2***	43.1***	25.0***
SCG dose		24.0***	278.1***	4.82*	35.7***	0.75	20.6***	116.5***	115.8***	20.6***
Soil type × SCG dose		0.79	0.26	0.12	0.29	0.19	0.09	0.04	1.33	1.53

Parameter abbreviations from Tables 1 and 2.

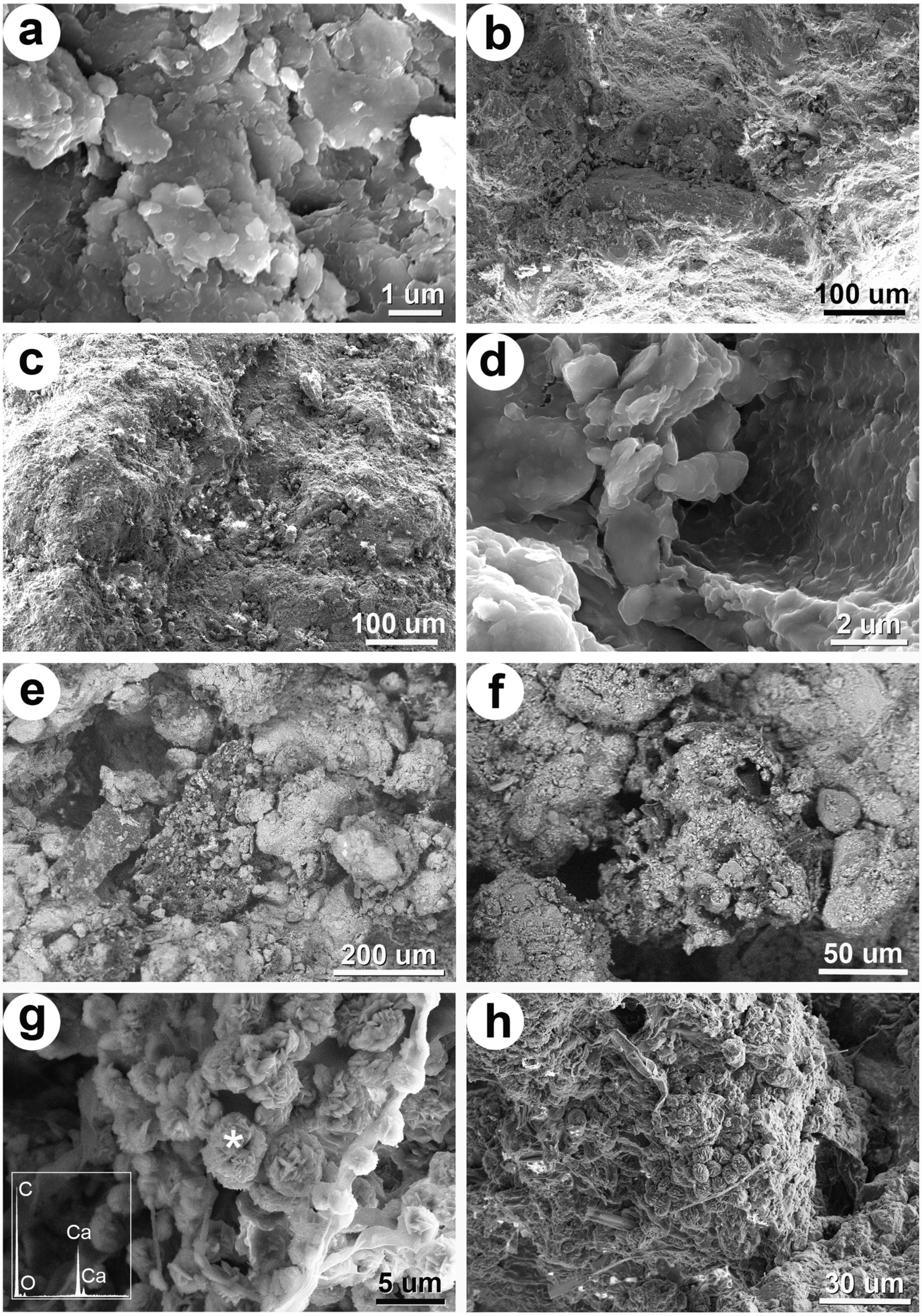

Fig. 1. SEM images from selected samples of Red soil (SR) and Vega soil (SV); a: SR 0% SCG, 0 days incubation; b: SR 0% SCG, 0 days incubation; c: SV 0% SCG, 0 days incubation; d: SV 10% SCG, 60 days incubation; e: SR 10% SCG, 60 days incubation; f: SV 10% SCG, 60 days incubation; g: SR 10% SCG, 60 days incubation; h: SV 10% SCG, 60 days incubation. Images a, b, c, d, g and h were made with secondary electrons; images e and f were made with retrodispersed electrons (backscattered conditions). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cultivation time, the BD decreased significantly and total porosity increased significantly during the incubation (Table 2), which can be attributed to the moisture change cycle during the pot assay (Cervera-Mata et al., 2019a). The effect on soil porosity could make easier the incorporation of soil organic matter intrapeds (Bronick and Lal, 2005). The higher porosity and the inclusion of SCG within aggregates can be observed in Fig. 1e, f (SEM images).

Correlations between these parameters and the water storage and γ^- component are of especial interest (Table 4). Electron-donor γ^- showed negative correlations with WR at −33 kPa and −1500 kPa, and positive correlation with AWC, showing the sensibility of SFE components to evaluate these soil properties. Therefore, although samples with water repellency seem to retain more water, it appears to be less available for plant growth. Hence, SFE components, especially γ^-, play an interesting role in the soil water balance, in agreement with Aranda et al. (2016). Other physical parameters correlated with γ^- are

Ks and porosity (total and macroporosity); and in a not significant way, BD, that show a trend between high hydrophobicity and low density (Table 2). The negative correlation between γ^- and ASI is remarkable, implying an important role of hydrophobicity in the structural development of the soil and in the stabilization of soil aggregates, already demonstrated by other authors in field experiments with plants natural covers, olive mill pomace compost and olive mill wastewater (Plaza et al., 2015; Aranda et al., 2016; Mahmoud et al., 2012) in agricultural Mediterranean soils. Also, as stated by Lützow et al. (2006) and Bachmann et al. (2008), the increase in the stability of the soil aggregates with the increase in hydrophobicity would also contribute to the occlusion of OM incorporated as a stabilization mechanism. Therefore, an increase in soil water repellency could imply an increase in soil quality by improving one of its essential indicators, such as structural stability (Bünemann et al., 2018).

3.4.3. Relationship with soil morphology (SEM)

The microstructure of initial soil samples (SR and SV) is laminar (in the sense of Osipov and Sokolov, 1978), in which the finest soil particles (clay and silt) are oriented parallel to the surface of the aggregates (ped) in face-to-face interactions (Fig. 1a). According to Ndlovu et al. (2014), these face-face interactions of illites and smectites (the main phyllosilicates in these soils) are favoured in basic pH (7.2–8.2; Table 1). At a higher organizational level, the soil mass is differentiated into equidimensional and coalescent microaggregates of about 200 µm in diameter, separated by fissures (Fig. 1b, c).

In the case of samples added with SCG, the microstructure is more open at a lower level, resembling a honeycomb (Osipov and Sokolov, 1978). In this microstructure, some interactions of face-to-edge clay particles are perceived (Fig. 1d; central part of the photograph). According to Ndlovu et al. (2014), the particles of the phyllosilicates illite and smectite have negative surface charges on the faces and pH-dependent on the edge: mainly negative when the pH is basic and positive when it is acidic. The presence of positive charges on the edges of the clay particles facilitate face-to-edge joints; this fact could partly explain the microstructural change that occurs when SCG is added, since this residue decreased the soil pH (they are acidic: 5.8; Table 1), thus facilitating the presence of face-edge joints. At a higher structural level, microaggregates (sizes between 150 and 200 µm) are more separated, with sharper surfaces and a greater number and volume of pores

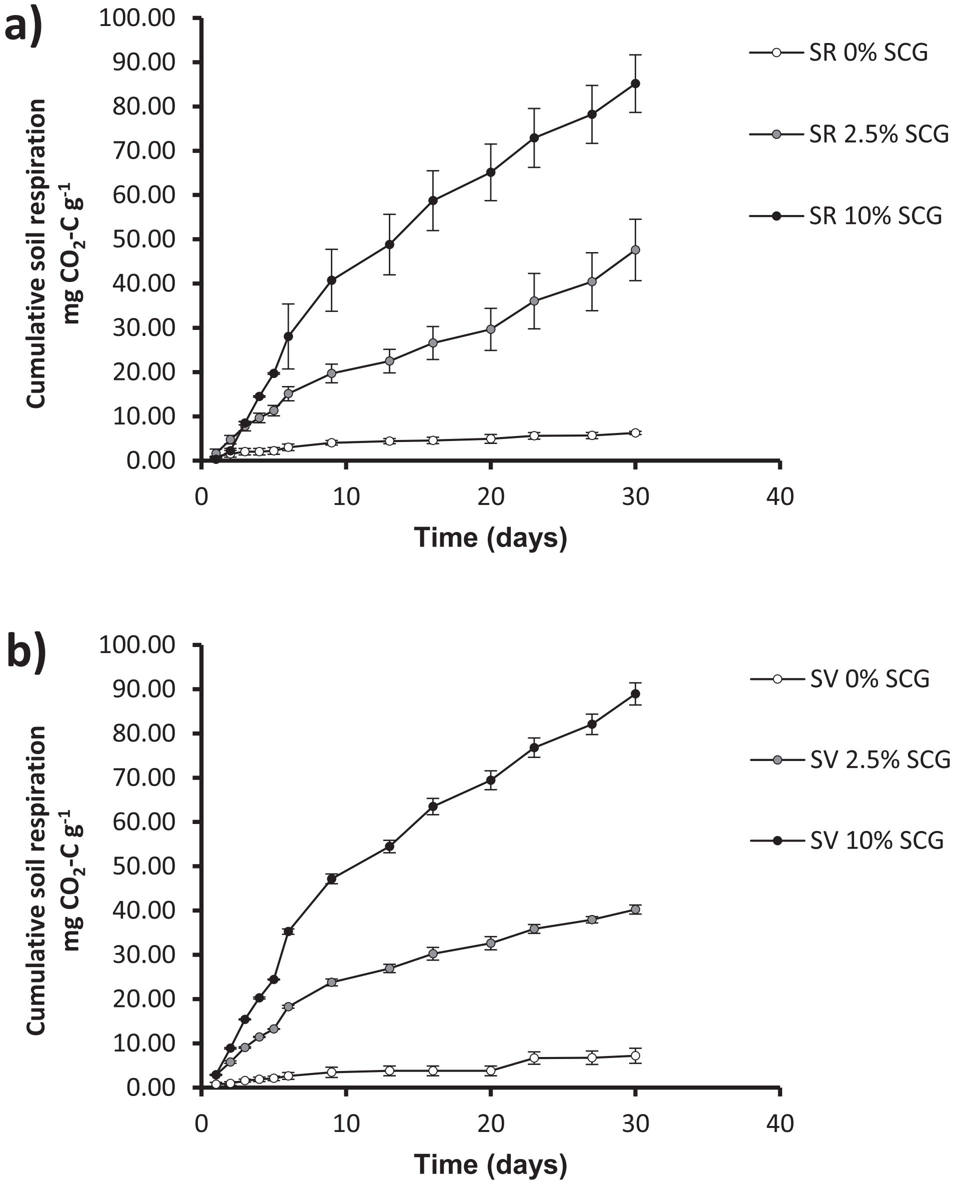

Fig. 2. Cumulative respiration rate (mg CO_2-C g^{-1}) during the 30 days of incubation. (a) Red soil (SR); (b) Vega soil (SV). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

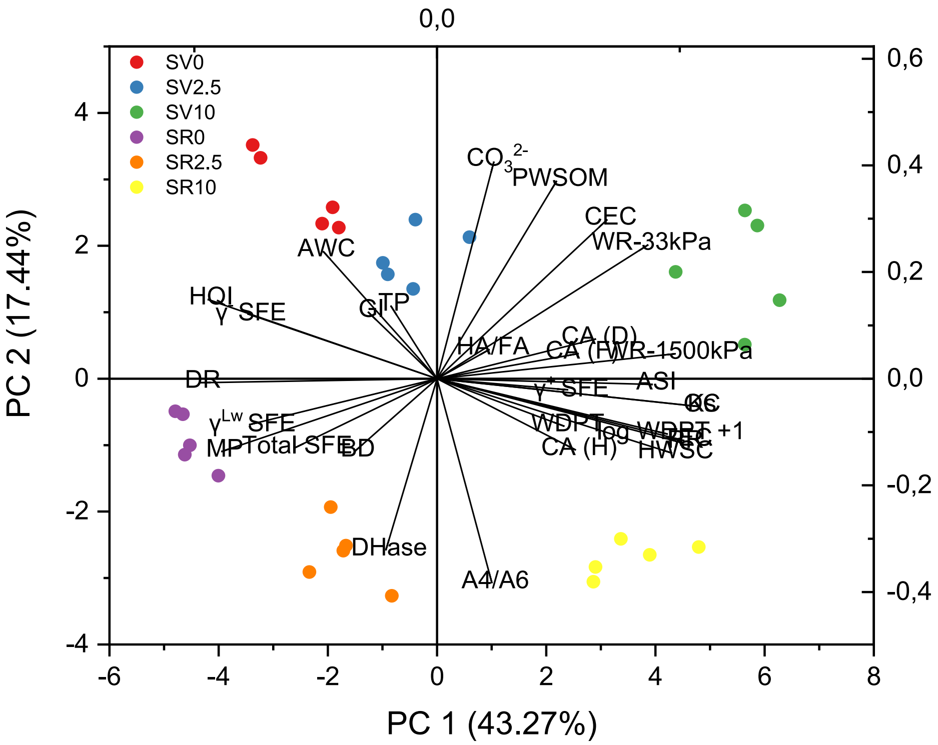

Fig. 3. Superimposed graph of principal component analysis (PCA) scores obtained for samples and loadings of each parameter analyzed. Abbreviations from Table 2.

(Fig. 1e, f) than native soils (Fig. 1b, c). In these images and those reported by Cervera-Mata et al., 2019a, it has been observed that in SV samples, SCG particles interacted more intensely with mineral particles than in SR, where they tend to be more on the surface, and less covered with mineral particles than in the case of SV. This particularity could be attributed to the fact that in SV there is a higher content of smectite and carbonates, which interact better with organic matter (Six et al., 2002). On another note, we must take into account the role that microorganisms (bacteria and fungi) play in the formation of the soil structure through the production and the use of labile organic compounds and the physical union of soil particles (Bronick and Lal, 2005). Thus, the samples added with SCG showed conspicuous biological activity, mainly fungal hyphae (Fig. 1g, h) and the massive organic cementation bonding mineral grains (Fig. 1e, f). These features are supported by the aggregate stability index and other physical parameters (Table 5). Thus, the physical entanglement of soil particles by fungal hyphae observed may be an important way of increasing aggregate stability in non-carbonated and sandy soils, in agreement with Delgado et al. (2007). The hydrophobic compounds released by fungal hyphae and other microorganisms are one of the responsible of the increase of the hydrophobicity in the soil (Schaumann et al., 2007). The Fig. 1g, corresponding to SR, shows an interesting issue. The spherulitic forms associated to fungal hyphae are not conidiophores, but they are druses of carbonates (detected by EDX). This fact is not observed in SV (Fig. 1h), only in SR. The technique used does not allow us to determine whether it is calcite or aragonite ($CaCO_3$ polymorphs). It is a process of biomineralization, that is, the formation of minerals with the help of living beings; the biomineralization of calcium carbonate by fungi is described in the literature (Bindschedlet et al., 2016). The precipitation of calcium carbonate linked to fungal activity in SR and not in SV could be explained because DHase is higher in SR (Table 5) and as indicated by Zhang et al. (2010), the biomineralization of carbonates is proportional to this activity. The biomineralization of carbonates by means of some fungi colonies could be considered as an inorganic process of C fixation in the soil; another positive aspect of quality improvement generated by SCG addition.

Calcareous soils (SV) would seem to be less prone to developing water repellency than acidic (SR), which could be explained by the lower fungal activity registered at pH more than 7 (Mataix-Solera and Doerr, 2004). The pH values showed in Table 5, make possible this fact, due to the higher fungal activity observed with SEM in the amended SR decarbonated soil samples, which are more hydrophobic samples. SEM images allow us to make another interpretation of the differences between SV and SR. Gao et al. (2018) stated that clays could decrease soil hydrophobicity by coating hydrophobic surfaces. As stated above, SCG particles appear more covered by mineral soil particles (carbonates and/or smectites) and more incorporated into the soil mass in SV than in SR. Both the incorporation into the soil mass and the coating would cause the masking of the SCG hydrophobicity (surface property), to be much greater than the hydrophobicity of mineralogical soil particles (see WDPT values, Table 3).

3.4.4. Relationship with soil biological properties

Respiration rate (RR) significantly increased with the addition of SCG and with similar values for both soils (Tables 2 and 5). As shown in Fig. 2a, b, 85.2 and 89 mg CO_2-C g^{-1} in SR and SV respectively were emitted after 30 days with 10% SCG addition. These data are very high compared to those obtained by other authors after incubation of raw materials like olive tree pruning, with values around 0.6–0.9 mg CO_2-C g^{-1} (Gómez-Muñoz et al., 2016). The data reflected in Fig. 2, indicated that the CO_2 emitted in samples added with 2.5 and 10% SCG, is not proportional to the amounts of SCG added. That is, soils with 2.5% SCG emitted relatively more CO_2 than those added with 10%, a result that is corroborated with DHase data, as discussed below.

DHase (intracellular enzyme indicative of soil biological activity; Defrieri et al., 2011) in SR is significantly higher in samples with 2.5% of SCG, being affected negatively with 10% of SCG (Tables 2 and 5), with values similar to no amended samples. SV has less biological activity than SR, even with the same addition of SCG, probably due to the more stabilized SOM in SV (Comino et al., 2020), or because this SOM is occluded in aggregates (Cervera-Mata et al., 2019a) and/or cover by mineral particles (Fig. 1f).

It is difficult to explain the lack of coincidence in the results of RR and DHase, since both parameters represent the overall activity of soil microorganisms. In both soils, the addition of SCG increased significantly the RR, in proportion to the amount added. However, the DHase decreased significantly when the amount of SCG raised from 2.5% to 10%. According to Vela-Cano et al. (2019), the addition of SCG changed the soil bacterial community structure and therefore, we could hypothesize that the biological activity could be interrupted due to the toxicity of SCG. These changes in the soil bacterial community structure could have consequences in the correlation between DHase and RR. The germination index (GI) was used to value the possible phytotoxicity of a material; GI over 100% means the absence of toxicity and also that it is a good substrate for plant growth (Comino et al., 2017). GI (Table 5) decreasing with SCG incorporation, but not significantly, giving values over the toxicity range 60% (Zucconi et al., 1981) or 50% (Eshetu, 2013), and far away from those obtained for the SCG sample (35%), and therefore clearly phytotoxic, showing its capacity to affect plant growth. The phytotoxicity of SCG has been also demonstrated both in field assays (Yamane et al., 2014), greenhouse assays (Vardon et al., 2013) and in vitro assays (Cervera-Mata et al., 2018; Hardgrove and Livesley, 2016). This fact has been attributed to some toxic compounds of SCG such as caffeine, tannins and polyphenols (Leifa et al., 2000).

All the parameters related to hydrophobicity are significantly related to the respiration rate (Table 4), indicating that a higher hydrophobicity is associated with higher soil respiration, this being really dependent on the SCG amount, with no influence of soil type (Tables 2 and 5). This is the opposite that established by Leelamanie (2016), who found a moderate negative lineal correlation between soil respiration and soil-water contact angle. On the other hand, the negative correlation entre CA-H_2O and GI seems to indicate a negative effect of hydrophobicity over plant growth, but again this is associated also to the SCG content (Table 4).

3.5. Multifactor ANOVA and principal component analysis

A multifactor ANOVA was performed to determine the control that the SCG dose and soil type (being these variables those that showed major significant differences, Table 2) exert on water repellency parameters (Table 3) and soil quality parameters (Table 5). The most significant interactions among SCG dose and soil type were observed in the case of chemical properties (pH, CO_3^{2-}, HWSC and A4/A6, Table 5) which was also reported by Comino et al. (2020). The interaction of these two factors does not influence the physical and biological parameters (Table 5) and in the case of hydrophobic related parameters is only seen in WDPT, however the effect is less than what SCG dose would have alone.

A principal component analysis was performed to reduce and explain the variability of the system. A matrix containing all results obtained along the experiment was selected. In Fig. 3 the score values of the samples in the spaced defined by PC1 and PC2 are shown, which captured 60.71% of variance. The first component, explaining the 42.56% of variance, group samples according to SCG dose, being the samples with 10% SCG the ones with the higher values in this PC. The most important parameter in this PC, is the OC, which presents a loading of 0.27, followed by HWSC, TEC, WDPT, WR and CA. The second component, explaining the 17.44% of variance, group the samples according to soil type, presenting the SV samples positive values in this component y while SR samples present negative values. The dominant parameter in this component is the carbonate content, with a loading of 0.41, followed by PWSOM, CEC and AWC for positive values, while negative values are mainly due to the influence of DHase and A4/A6. Likewise, this analysis corroborates the high correlation between the properties related to hydrophobicity (WDPT and CA) with ASI, OC and high water retention. All these parameters close to the samples with 10% SCG. On the other hand, the greater DHase activity of the Red soil is also corroborated and as it dominates in the samples with 2.5% SCG. In the negative scores of PC1 there is also the parameter A4/A6 ratio indicating a lower evolution of HA in this soil.

4. Conclusions

The addition of spent coffee grounds as raw material on two Mediterranean agricultural soils modified many of their physical and chemical, related to soil quality, highlighting the properties related to soil hydrophobicity. Specifically, the SCG influenced soil hydrophobicity, increasing the WDPT and the CA.

In addition, this residue modified the preexisting equilibria in the soil between the donor and acceptor character according to the van Oss model, decreasing the electrodonor character which is characteristic of the mineral fraction. This influence on hydrophobicity had a differential and determining effect, depending on the soil type, increasing to a greater extent in SR, more sandy, decarbonated and poor in smectite. Hydrophobicity and water retention at different potentials were positively related. However, a negative and significant relation between hydrophobicity and available water content was detected. Given the importance of water availability for the plant in agricultural soils, further research is needed when organic raw materials with a strong hydrophobic character are used. The positive relationship between SCG and hydrophobicity and the changes observed in soil structure, with a greater degree of aggregation, porosity and structural stability, allow us to establish a positive relationship between hydrophobicity, fungal hyphae development and structure. The addition of SCG stimulated biological activity, although high doses seem to limit some parameters, such as DHase. The positive relationship between hydrophobicity and biological activity seems consistent with the literature, which could be justified by the stimulation of fungal activity that in turn generates hydrophobicity.

Overall, the addition of SCG could be considered positive from the perspective of soil quality, although some parameters denoted an opposite trend, such as humus quality index and available water content. Hence, soil management protocols must be carefully adapted to the quality of the organic amendment used and the type of soil of a given agro-environmental system.

The data of this research clearly refers to the evaluation of the direct effect and under laboratory conditions. Therefore, future research at the field level in greenhouse agriculture, urban agriculture or intensive agriculture in general would be necessary.

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.

Acknowledgments

This work was supported by project AGL2014-53895-R from the Spanish Ministry of Economy and Competitiveness and by the European Regional Development Fund (FEDER). Authors are also grateful to PAIDI funding for research groups RNM-127 and FQM-363. We also thank technical support provided by the Universidad de Jaén and Scientific-Technical Instrumentation Center (Funding by Universidad de Jaén, MINECO, Junta de Andalucía and FEDER). This paper will form part of Ana Cervera-Mata's doctoral thesis, which is being developed within the context of the 'Nutrition and Food Sciences Programme' at the University of Granada. We also acknowledge Melanie Davies for English proofreading.

References

Alburquerque, J.A., Gonzálvez, J., García, D., Cegarra, J., 2006. Measuring detoxification and maturity in compost made from "alperujo", the solid by-product of extracting olive oil by the two-phase centrifugation system. Chemosphere 64, 470–477.

Al-Hamamre, Z., Foerster, S., Hartmann, F., Kröger, M., Kaltschmitt, M., 2012. Oil extracted from spent coffee grounds as a renewablr dource for fatty acid methyl ester manufacturing. Fuel 96, 70–76.

Anderson, J.P.E., 1982. Soil respiration. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), Methods of Soil Analysis. Part 2, second ed., Agron. Monogr. 9. ASA and SSSA, Madison, pp. 831–871.

Aranda, V., Calero, J., Plaza, I., Ontiveros-Ortega, A., 2016. Long-term effects of olive mill pomace co-compost on wettability and soil quality in olive groves. Geoderma 267, 185–195.

Arshad, M.A., Coen, G.M., 1992. Characterization of soil quality: physical and chemical criteria. Am. J. Altern. Agric. 7, 25–31.

Bachmann, J., Guggenberger, G., Baumgartl, T., Ellerbrock, R.H., Urbanek, E., Goebel, M.O., Kaiser, K., Horn, R., Fischer, W.R., 2008. Physical carbon-sequestration mechanisms under special consideration of soil wettability. J. Plant Nutr. Soil Sci. 171, 14–26.

Ballesteros, L.F., Teixeira, J.A., Mussatto, S.I., 2014. Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin. Food Bioprocess Technol. 7, 3493–3503.

Bindschedlet, S., Cailleau, G., Verrecchia, E., 2016. Role of fungi in the biomineralization of calcite. Minerals 6, 41.

Bisdom, E.B.A., Dekker, L.W., Schoute, J.F.T., 1993. Water repellency of sieve fractions from sandy soils and relationships with organic material and soil structure. Geoderma 56, 105–118.

Bronick, C.J., Lal, R., 2005. Soil structure and management: a review. Geoderma 124, 3–22.

Bünemann, E.K., Bongiorno, G., Bai, Z., Creamer, R.E., De Deyn, G., de Goede, R., Fleskens, L., Geissen, V., Kuyper, T.W., Mäder, P., Pulleman, M.M., Sukkel, W., van Groenigen, J.W., Brussaard, L., 2018. Soil quality – a critical review. Soil Biol. Biochem. 120, 105–125.

Casida, L.E., Klein, D., Santoro, T., 1964. Soil dehydrogenase activity. Soil Science 98, 371–376.

Cerdá, A., Doerr, S.H., 2005. Influence of vegetation recovery on soil hydrology and erodibility following fire: an 11-year investigation. Int. J. Wildland Fire 14, 423–437.

Cervera-Mata, A., Martín-García, J., Delgado, R., Sánchez-Marañón, M., Delgado, G., 2019a. Short-term effects of spent coffee grounds on the physical properties of two Mediterranean agricultural soils. Int. Agrophysics 33, 205–216.

Cervera-Mata, A., Navarro-Alarcón, M., Delgado, G., Pastoriza, S., Montilla-Gómez, J., Llopis, J., Sánchez-González, C., Rufián-Henares, J.Á., 2019b. Spent coffee grounds improve the nutritional value in elements of lettuce (Lactuca sativa L.) and are an ecological alternative to inorganic fertilizers. Food Chem. 282, 1–8.

Cervera-Mata, A., Pastoriza, S., Rufián-Henares, J.Á., Martín-García, J.M., Delgado, G., 2018. Impact of spent coffee grounds as organic amendment on soil fertility and lettuce growth in two Mediterranean agricultural soils. Arch. Agron. Soil Sci. 64–6, 790–804.

Chau, H.W., Biswas, A., Vujanovic, V., Si, B.C., 2014. Relationship between the severity, persistence of soil water repellency and the critical soil water content in water repelente soils. Geoderma 221–222, 113–120.

Comino, F., Aranda, V., Domínguez-Vidal, A., Ayora-Cañada, M.J., 2017. Thermal destruction of organic waste hydrophobicity for agricultural soils application. J. Environ. Manage. 202, 94–105.

Comino, F., Cervera-Mata, A., Aranda, V., Martín-García, J.M., Delgado, G., 2020. Short-term impact of spent coffee grounds over soil organic matter composition and stability in two contrasted Mediterranean agricultural soils. J. Soils Sediments 20, 1182–1198.

Cruz, R., Baptista, P., Cunha, S., Pereira, J.A., Casal, S., 2012. Carotenoids of lettuce (Lactuca sativa L.) grown on soil enriched with spent coffee grounds. Molecules 17, 1535–1547.

de Blas, E., Rodríguez-Alleres, M., Almendros, G., 2010. Speciation of lipid and humic fractions in soils under pine and eucalyptus forest in northwest Spain and its effect on water repellency. Geoderma 155, 242–248.

Defrieri, R.L., Sarti, G., Tortarolo, M.F., Escobar-Ortega, J., García de Salamone, I., ĎAuria, F., Effron, D., 2011. Biochemical and microbiological properties of Argentinean Patagonia soil with implanted forest species. J. Soil Sci. Plant Nutr. 11 (3), 111–124.

Dekker, L.W., Oostindie, K., Ritsema, C.J., 2005. Exponential increase of publications related to soil water repellency. Soil Res. 43 (3), 403–441.

Delgado, R., Sánchez-Marañón, M., Martín-García, J.M., Aranda, V., Serrano-Bernardo, F., Rosúa, J.L., 2007. Impact ofski pistes on soil properties: a case study fromamountainous area in the Mediterranean region. Soil Use Manag. 23, 269–277.

Diehl, D., Schaumann, G.E., 2007. The nature ofwetting on urban soil samples: wetting kinetics and evaporation assessed from sessile drop shape. Hydrol. Process. 21, 2255–2265.

Doerr, S.H., Thomas, A.D., 2000. The role of soil moisture in controlling water repellency: new evidence from forest soils in Portugal. J. Hydrol. 231–232, 134–147.

Dumroese, R.K., Monteville, M.E., Pinto, J.R., 2015. Using container weights to determine irrigation needs, a simple method. Native Plants J. 16, 67–71.

Ellerbrock, R.H., Gerke, H.H., Bachmann, J., Goebel, M.O., 2005. Composition of organic matter fractions for explaining wettability of three forest soils. Soil Sci. Soc. Am. J. 69, 57–66.

Eshetu, B., 2013. Compost of different stability affects the molecular composition and mineralization of soil organic matter. Open J. Soil Sci. 3, 58–69.

Forge, T., Kenney, E., Hashimoto, N., Neilsen, D., Zebarth, B., 2016. Compost and poultry manure as preplant soil amendments for red raspberry: comparative effects on root lesion nematodes, soil quality and risk of nitrate leaching. Agr. Ecosyst. Environ. 223, 48–58.

Gao, Y., Lin, Q., Liu, H., Wu, H., Alamus, 2018. Water repellency as conditioned by physical and chemical parameters in grassland soil. Catena 160, 310–320.

García-Ruiz, R., Ochoa, V., Hinojosa, M.B., Carreira, J.A., 2008. Suitability of enzyme activities for the monitoring of soil quality improvement in organic agricultural systems. Soil Biol. Biochem. 40, 2137–2145.

Ghani, A., Dexter, M., Perrott, K.W., 2003. Hot-water extractable carbon in soils : a sensitive measurement for determining impacts of fertilization, grazing and cultivation. Soil Biol. Biochem. 35, 1231–1243.

Goebel, M., Bachmann, J., Woche, S.K., Fischer, W.R., 2005. Soil wettability, aggregate stability, and the decomposition of soil organic matter. Geoderma 128, 80–93.

Goebel, M.O., Bachmann, J., Reichstein, M., Janssens, I.A., Guggenberger, G., 2011. Soil water repellency and its implications for organic matter decomposition – is there a link to extreme climatic events? Glob. Change Biol. 17, 2640–2656.

Gómez-Muñoz, B., Valero-Valenzuela, J.D., Hinojosa, M.B., García-Ruiz, R., 2016. Management of tree pruning residues to improve soil organic carbon in olive groves. Eur. J. Soil Biol. 74, 104–113.

González-Peñaloza, F.A., Zavala, L.M., Jordán, A., Bellinfante, N., Bárcenas-Moreno, G., Mataix-Solera, J., Granged, A.J.P., Granja-Martins, F.M., Neto-Paixão, H.M., 2013. Water repellency as conditioned by particle size and drying in hydrophobized sand. Geoderma 209–210, 31–40.

Gross, G., Jaccaud, E., Hugget, A.C., 1997. Analysis of the content of the diterpenes cafestol and kahweol in coffee brews. Food Chem. Toxicol. 35 (6), 547–554.

Hardgrove, S.J., Livesley, S.J., 2016. Applying spent coffee grounds directly to urban agriculture soils greatly reduces plant growth. Urban Forest. Urban Green. 18, 1–8.

IUSS Working Group WRB, 2015. World Reference Base for Soil Resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.

Jiménez-De-Santiago, D.E., Yagüe, M.R., Antúnez, M., Bosch-Serra, A.D., 2019. Diagnosis of soil hydrophobicity linked to pig slurry use in a calcareous soil. Spanish J. Soil Sci. 9, 169–179.

Jordán, A., Zavala, L.M., Mataix-Solera, J., Doerr, S.H., 2013. Soil water repellency: Origin, assessment and geomorphological consequences. Catena 108, 1–5.

Kamil, M., Ramadan, K.M., Awad, O.I., Ibrahim, T.K., Inayat, A., Ma, X., 2019. Environmental impacts of biodiesel production from waste spent coffee grounds and its implementation in a compression ignition engine. Sci. Total Environ. 675, 13–30.

Kemper, W.D., Rosenau, R.C., 1986. Aggregate stability and size distribution. In: A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. ASA and SSSA, Madison, WI. p. 425–442.

Killi, D., Anlauf, R., Kavdir, Y., Haworth, M., 2014. Assesing the impact of agro-industrial olive-wastes in soil water retention: implications for remediation of degraded soils and water availability for plant growth. Int. Biodeterior. Biodegrad. 94, 48–56.

King, P.M., 1981. Comparison of methods for measuring severity of water repellence of sandy soils and assessment of some factors that affect its measurement. Soil Res. 19 (3), 275–285.

Leelamanie, D.A.L., 2016. Occurrence and distribution of water repellency in size fractionated coastal dune sand in Sri Lanka under Casuarina shelterbelt. Catena 142, 206–212.

Leelamanie, D.A.L., Karube, J., Samarawickrama, U.I., 2013. Stability analysis of aggregates in relation to the hydrophobicity of organic manure for Sri Lankan Red Yellow Podzolic soils. Soil Sci. Plant Nutr. 59, 683–691.

Leifa, F., Pandey, A., Soccol, C.R., 2000. Solid state cultivation–an efficient method to use toxic agro-industrial residues. J. Basic Microbiol. 40, 187–197.

Leue, M., Gerke, H.H., Godow, S.C., 2015. Droplet infiltration and organic matter composition of intact crack and biopore surfaces from clay-illuvial horizons. J. Plant Nutr. Soil Sci. 178, 250–260.

Liu, K., Price, G.W., 2011. Evaluation of three composting systems for the management of spent coffee grounds. Bioresour. Technol. 102, 7966–7974.

Liyanage, T.D.P., Leelamanie, D.A.L., 2016. Influence of organic manure amendments on water repellency, water entry value, and water retention of soil samples from a tropical Ultisol. J. Hydrol. Hydromechanics 64, 160–166.

Lozano-García, B., Parras-Alcántara, L., del Toro Carrillo de Albornoz, M., 2011. Effects of oil mill wastes on surface soil properties, runoff and soil losses in traditional olive groves in southern Spain. Catena 85, 187–193.

Lützow, M.V., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., Flessa, H., 2006. Stabilization of organic matter in temperate soils: Mechanisms and their relevance under different soil conditions – a review. Eur. J. Soil Sci. 57, 426–445.

Mahmoud, M., Janssen, M., Peth, S., Horn, R., Lennartz, B., 2012. Long-term impact of irri- gation with olive mill wastewater on aggregate properties in the top soil. Soil Tillage Res. 124, 24–31.

Spanish MAPA, 1994. Métodos Oficiales de Análisis. Tomo III; Ministerio de agricultura, pesca y alimentación; Secretaría General Técnica Ministerio de Agricultura, Pesca y Alimentacion: Madrid; p. 662.

Mataix-Solera, J., Cerdà, A., Arcenegui, V., Jordán, A., Zavala, L.M., 2011. Fire effects on soil aggregation: a review. Earth-Sci. Rev. 109, 44–60.

Mataix-Solera, J., Doerr, S.H., 2004. Hydrophobicity and aggregate stability in calcareous topsoils from fire-affected pine forests in southeastern Spain. Geoderma 118, 77–88.

Matějková, Š., Šimon, T., 2012. Application of FTIR spectroscopy for evaluation of hydrophobic/hydrophilic organic components in arable soil. Plant Soil Environ. 58, 192–195.

Mingorance, M.D., Barahona, E., Fernández-Gálvez, J., 2007. Guidelines for improving organic carbon recovery by the wet oxidation method. Chemosphere 68, 409–413.

Mohawesh, O., Mahmoud, M., Janssen, M., Lennartz, B., 2014. Effect of irrigation with olive mill wastewater on soil hydraulic and solute transport properties. Int. J. Environ. Sci. Technol. 11, 927–934.

Ndlovu, B., Forbes, E., Farrokhpay, S., Becker, M., Bradshaw, D., Deglon, D., 2014. A preliminary rheological classification of phyllosilicate group minerals. Miner. Eng. 55, 383–389.

Ontiveros-Ortega, A., Vidal, F., Gimenez, E., Ibáñez, J.M., 2014. Effect of heavy metals on the surface free energy and zeta potential of volcanic glass: Implications on the adhesion and growth of microorganisms. J. Mater. Sci. 49, 3550–3559.

Osipov, V.I., Sokolov, V.N., 1978. Relation between the microfabric of clay soils and their origin and degree of compaction. Bull. Int. Assoc. Eng. Geol. – Bull. l'Association Int Géologie l'Ingénieur 18, 73–81.

Petrik, S., Obruca, S., Benesová, P., Márová, I., 2014. Bioconversion of spent cofee grounds into carotenoids and other valuable metabolites by selected red yeast strains. Biochem. Eng. J. 90, 307–315.

Plaza, I., Ontiveros-Ortega, A., Calero, J., Aranda, V., 2015. Implication of zeta potential and surface free energy in the description of agricultural soil quality: effect of different cations and humic acids on degraded soils. Soil Tillage Res. 146, 148–158.

Rodríguez-Entrena, M., Espinosa-Goded, M., Barreiro-Hurlé, J., 2014. The role of ancillary benefits on the value of agricultural soils carbon sequestration programmes: evidence from a latent class approach to Andalusian olive groves. Ecol. Econ. 99, 63–73.

Rodríguez Martín, J.A., Álvaro-Fuentes, J., Gonzalo, J., Gil, C., Ramos-Miras, J.J., Grau Corbí, J.M., Boluda, R., 2016. Assessment of the soil organic carbon stock in Spain. Geoderma 264, 117–125.

Sánchez-Marañón, M., Soriano, M., Delgado, G., Delgado, R., 2002. Soil quality in mediterranean mountain environments. Soil Sci. Soc. Am. J. 66, 948.

Schaumann, G.E., Braun, B., Kirchner, D., Rotard, W., Szewzyk, U., Grohmann, E., 2007. Influence of biofilms on the water repellency of urban soil samples. Hydrol. Process. 21, 2276–2284.

Senesi, N., D'Orazio, V., Ricca, G., 2003. Humic acids in the first generation of EUROSOILS. Geoderma 116, 325–344.

Six, J., Conant, R.T., Paul, E.a., Paustian, K., 2002. Stabilization mechanisms of soil organic matter: Implications for C-saturatin of soils. Plant Soil 241, 155–176.

Soil Survey Staff, 2014. Soil Survey Field and Laboratory Methods Manual, Soil Survey Investigations. Report No. 51, Version 2.0. In: R. Burt and Soil Survey Staff (eds.). U. S. Department of Agriculture, Natural Resources Conservation Service.

Stevenson, F.J., 1982. Humus Chemistry: Genesis, Composition, Reactions. Wiley, New York.

Swift, R.S., 1996. Organic matter characterization (chap. 35). In: Sparks, D.L., et al. (Eds.), Methods of Soil Analysis, Part 3, Chemical Methods. ASA/SSSA, Inc., Madison, WI, USA. Soil Sci. Soc. Am. Book Series, n° 5, p. 1018e1021.

Stevenson, F.J., 1994. Humus chemistry: genesis, composition, reactions, 2nd. John Wiley and Sons, New York.

Tillman, R.W., Scotter, D.R., Wallis, M.G., Clothier, B.E., 1989. Water repellency and its measurements by using intrinsic sorptivity. Aust. J. Soil Res. 27, 637–644.

Tinoco, P., Piedra Buena, A., Zancada, M.C., Sanz, J., Almendros, G., 2010. Biogeochemical proxies of anthropic impact in mediterranean forest soils. Soil Use Manage. 26, 320–331.

Van Oss, C.J., 1994. Interfacial Forces in Aqueous Media. Dekker, New York.

Van Oss, C.J., Chaudhury, M.K., Good, R.J., 1988. Interfacial Lifshitz-van der Waals andpolar interactions in macroscopic systems. Chem. Rev. 88, 927–941.

Vardon, D.R., Moser, B.R., Zheng, W., Witkin, K., Evangelista, R.L., Strathmann, T.J., Rajagopalan, K., Sharma, B.K., 2013. Complete utilization of spent coffee grounds to produce biodiesel, bio-oil, and biochar. ACS Sustain. Chem. Eng. 1, 1286–1294.

Vela-Cano, M., Cervera-Mata, A., Purswani, J., Pozo, C., Delgado, G., González-López, J., 2019. Bacterial community structure of two Mediterranean agricultural soils amended with spent coffee grounds. Appl. Soil Ecol. 137, 12–20.

Woche, S.K., Goebel, M.O., Kirkham, M.B., Horton, R., van der Ploeg, R.R., Bachmann, J., 2005. Contact angle of soils as affected by depth, texture, and land management. Eur. J. Soil Sci. 56, 239–251.

Yamane, K., Kono, M., Fukunaga, T., Iwai, K., Sekine, R., 2014. Field evaluation of coffee grounds application for crop growth enhancement, weed control, and soil improvement. Plant Prod. Sci. 17, 93–102.

Zhang, N., He, X.D., Gao, Y.B., Li, Y.H., Wang, H.T., Ma, D., Zhang, R., Yang, S., 2010. Pedogenic carbonate and soil dehydrogenase activity in response to soil organic matter in artemisia ordosica community. Pedosphere 20, 229–235.

Zucconi, F., Pera, A., Forte, M., De Bertoldi, M., 1981. Evaluating toxicity in immature compost. Biocycle 22, 54–57.