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Original article

Characteristics of organic matter in soil surface horizons derived from calcareous and metamorphic rocks and different vegetation types from the Mediterranean high-mountains in SE Spain

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Abstract

A study was carried out on some basic characteristics of the organic matter in the surface horizons of soils from the two different geological (calcareous and acid metamorphic rocks) and ecological systems under a Mediterranean climate in Southeast Spain. The results show some noticeable differences in soil organic matter composition. This is likely due to typical Mediterranean climate and well adapted vegetation. There is a tendency towards a greater stability for the soil humus formed under slightly alkaline soil in comparison to the slightly acidic environment. The samples taken from the latter environment have a higher content in free organic matter, a lower content in total extractable humin and a greater relative proportion of aliphatic chains and lignin in the humic acids. The results also suggest some differences caused by the type of vegetation (forest and scrubland ecosystems) in the soil humus chemistry, with a more obvious negative effect under reforestations with species of *Pinus* in an acidic soil environment (a higher content in free organic matter, lesser presence of fungal-derived perylenequinonic pigments in the humic acids, and a higher content in little evolved forms of nitrogen and lignin in the humic acids). In general the organic matter under scrubland and *Quercus* vegetation is more decomposed and the humus is more evolved than under *Pinus* vegetation.

Keywords: Soil organic matter quality; Humic acids; Surface horizon; Pine trees reforestations; Mediterranean environments

1. Introduction

Mediterranean region is characterized by fragile natural ecosystems with insufficient rainfall for suitable vegetation recovery, and which suffers especially from serious processes of degradation (frequently originated by anthropic factors) that threaten it with increasing desertification [11,19], processes which are more acute in mountainous areas.

The high Mediterranean mountains, in particular those located in SE Spain, have unique environments, complex topography, and climate and are highly vulnerable to human actions.

Knowledge about soil organic matter is essential to assess the consequences of modifying some highly specific ecological and pedological conditions for the vulnerable ecosystems in the Mediterranean region. The surface organic matter is essential in the stabilization

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of soil aggregates [23,9], water infiltration and conservation of nutrients. Studies of soils in Mediterranean mountainous areas showed that the susceptibility of these soils to erosion largely depends on properties of the upper mineral soil horizon, controlled by humus form development [30].

One general characteristic of the Mediterranean environment in SE Spain is the low biomass production, and consequently there is a low organic matter and nutrient content in the surface soil horizons [8]. Small changes in the nature of the organic matter, as a result of modifications to the environmental conditions, could have a severely negative impact on the soils. Those soils which hold organic matter with greater humification will have a higher degree of stability and will be more resistant to the onset of erosive processes.

Climatic factors are generally considered to have a much greater impact on the nature of soil organic matter [20,32]. Other authors have reported that the vegetation has a decisive influence on the control of the soil organic matter composition [13,42,25]. The dominant role of the mineral substratum on organic matter quality has also been reported [40].

In this study the characteristics and evolution of the soil organic matter are studied in relation to the influence of the parent material and vegetation type in soils from the Mediterranean high-mountain area in SE Spain. Two representative mountainous areas were selected which are very different in terms of parent material and vegetation types and because they are highly susceptible to environmental degradation (mainly erosion): the Sierra Nevada National Park and the Sierra de Cazorla-Segura-Las Villas Natural Park.

The objectives of this work were to: 1) describe some characteristics of the organic matter from these soils and compared with the soil organic matter from other soils located in different parts of the Mediterranean mountainous area in SE Spain; 2) assess the effect of different vegetation types on the characteristics of the soil organic matter, and thus predict the behavior of these soils in the event of possible replacements of the natural plant cover, mainly by reforestation practices with pine trees. The results will allow to understand the influence of factors that control the humification processes, not sufficiently established in Mediterranean ecosystems [21,8].

2. Materials and methods

The soil samples were collected from the Ah horizons of uncultivated soils of the two mountainous areas: 1) Sierra Nevada National Park and 2) Cazorla-Segura-Las Villas Natural Park in SE Spain. The Sierra Nevada National Park, located in Granada and Almería provinces: Twelve soils were collected from the soils over acid metamorphic rocks (micaschists) and referred to as SN. The Cazorla-Segura-Las Villas Natural Park, located in Jaén province: Another twelve samples were collected from the soils derived from calcareous material and referred to as SC.

Sampling locations were chosen within each sampling zone were based on the vegetation types: monodominant natural forests [B: *Quercus* sp.], monodominant pine reforestations with trees about 50-year-old [R: *Pinus* sp.] and high diversity scrublands [M: different species of *Genista*, *Juniperus*, *Adenocarpus*, *Crataegus*, *Retama*, *Berberis*, *Ulex, Cistus* and *Erinacea*]. The climate in both zones is typically Mediterranean, with high seasonal contrasts, with a xeric soil moisture and a mesic soil temperature regimes [34]. Mean annual rainfall is about 866 mm for SC and 595 mm for SN. The mean annual temperature is about 11.1 °C in SC and 9.8 °C in SN. The most relevant field data are shown in Table 1.

The samples were passed through a 2 mm sieve and called the fine-earth fraction. The procedures used in analysis are outlined by the American Society of Agronomy and the Soil Science Society of America [22,17] as follows. The particle-size distribution was determined using the pipette method after the removal of the organic matter with H_2O_2 and dispersion with Na-hexametaphosphate. The organic carbon content was determined using the Tyurin method by wet combustion with a mixture of $K_2Cr_2O_7$ and H_2SO_4 and titrating the residual dichromate with ferrous sulfate. Organic nitrogen was mineralized with H_2SO_4 and selenium to NH_4SO_4, and distilled in the form of NH_4OH and titrated with diluted H_2SO_4 using the Kjeldahl method. The pH (1:1 fine-earth/water suspension) was measured by potentiometric method. The exchangeable bases were extracted with 1 N NH_4-acetate (pH 7) and determined by atomic absorption spectroscopy (AAS) and flame photometry. The cation-exchange-capacity was determined with 1 N Na-acetate at pH 8.2. The free iron oxides were extracted with citrate-dithionite using the Holmgren method and determined by AAS.

Samples also underwent various analyses to characterize the nature of the organic matter present. These analyses included organic matter sequential fractionation procedures [10]. Free organic matter (FOM) was removed by flotation in 1 M H_3PO_4 and centrifugation. The soil residue was subjected to successive extractions

Table 1
Soil type, vegetation, and parent material of the soils studied from the Mediterranean high-mountains in SE Spain

Soil	UTM	Altitude (m)	MAR (mm)	MAT (°C)	Soil type (*)	Vegetation type	Parent material
Sierra Nevada National Park (SN)							
SN-1	30SVF582992	1800	603.3	9.6	Typic Haploxeroll	Quercus forest (*Quercus pyrenaica*)	Micaschists
SN-2	30SVF585912	1850	614.9	9.3	Lithic Haploxerept	Pinus forest (*Pinus sylvestris*)	Micaschists
SN-3	30SVF728897	1500	533.5	11.5	Typic Haploxerept	Quercus forest (*Quercus pyrenaica*)	Micaschists
SN-4	30SVF729970	2700	812.8	3.8	Lithic Eutrocryept	Scrubland (*Genista versicolor*, *Juniperus hemisphaerica*)	Micaschists
SN-5	30SVF728900	1600	556.8	10.9	Typic Dystroxerept	Scrubland (*Ulex sp*., *Cistus sp*.)	Micaschists
SN-6	30SVF765934	1500	533.5	11.5	Typic Haploxerept	Quercus forest (*Quercus rotundifolia*)	Micaschists
SN-7	30SVG993974	1320	491.6	12.6	Typic Haploxerept	Pinus forest (*Pinus sylvestris*)	Micaschists
SN-8	30SVG982030	1800	603.3	9.6	Lithic Dystroxerept	Scrubland (*Adenocarpus decorticans*, *Genista* sp.)	Micaschists
SN-9	30SVG971083	2000	649.9	8.3	Typic Dystroxerept	Pinus forest (*Pinus sylvestris*)	Micaschists
SN-10	30SVG025098	1650	568.4	10.5	Typic Haploxerept	Pinus forest (*Pinus sylvestris*)	Micaschists
SN-11	30SVG769148	1820	608.0	9.5	Typic Dystroxerept	Scrubland (*Genista versicolor*, *Adenocarpus decorticans*)	Micaschists
SN-12	30SVG771168	1620	561.4	10.7	Entic Ultic Haploxeroll	Quercus forest (*Quercus rotundifolia*)	Micaschists
Sierra de Cazorla-Segura-Las Villas Natural Park (SC)							
SC-1	30SWG075973	1100	970.6	12.6	Lithic Xerorthent	Pinus forest (*Pinus pinaster*)	Limestones
SC-2	30SWG138948	1400	1128.3	10.5	Typic Haploxeroll	Quercus forest (*Quercus faginea*)	Calcareous sandstones
SC-3	30SWG128932	1250	1049.5	11.5	Lithic Ultic Haploxeroll	Quercus forest (*Quercus rotundifolia*)	Limestones
SC-4	30SWH222017	1650	1259.7	8.8	Lithic Haploxerept	Scrubland (*Erinacea anthyllis*, *Crataegus monogyna*)	Limestones
SC-5	30SWH375192	1500	1180.9	9.8	Lithic Haploxeroll	Scrubland (*Ulex sp*., *Retama sphaerocarpa*, *Thymus* sp.)	Calcareous Micaschists
SC-6	30SWH288308	1150	996.9	12.2	Typic Haploxerept	Pinus forest (*Pinus pinaster*)	Marls
SC-7	30SWH169175	700	760.5	15.4	Typic Haploxerept	Pinus forest (*Pinus pinaster*)	Clays
SC-8	30SWH437118	1590	634.0	9.9	Lithic Haploxerept	Quercus forest (*Quercus rotundifolia*)	Dolomites
SC-9	30SWH478158	1780	558.0	8.7	Lithic Haploxeroll	Scrubland (*Erinacea anthyllis*, *Berberis hispanica*)	Limestones
SC-10	30SWH445189	1550	756.0	10.1	Typic Haploxeroll	Pinus forest (*Pinus pinaster*)	Dolomites
SC-11	30SWH579223	1200	459.0	12.4	Lithic Haploxerept	Scrubland (*Juniperus thurifera*, *Ulex* sp.)	Limestones/ dolomites
SC-12	30SWH497109	1410	634.0	11.0	Lithic Haploxeroll	Quercus forest (*Quercus rotundifolia*)	Limestones

UTM: Universal Transverse Mercator Coordinates; MAR: mean annual rainfall; MAT: mean annual temperature; (*): Soil Survey Staff, USDA (1998).

with 0.1 M $Na_4P_2O_7$ and 0.1 M NaOH. The total humic extract obtained was precipitated with HCl (pH 1) to separate insoluble humic acids (HA) from the soluble fulvic acids (FA). The soil residue was then treated with 1% $Na_2S_2O_4$ at 60 °C to remove the free oxides and humin was recovered after extraction with 0.5 M NaOH. Further demineralizing treatments with 1 M HCl/HF (1:1) followed by 0.1 M NaOH extraction led to the separation of the second extractable humin fraction. The two latter organic fractions are referred to as total extractable humin (HUMIN). The organic fraction remaining in the extraction residue consists of non-extractable organic carbon (NEOC). The amounts of the above fractions in carbon were quantified by wet combustion [22].

Elementary composition (C, H, O, N) of the HA (free of ash) was determined with a Perkin-Elmer 240C microanalyzer. A Shimadzu UV-240 spectrophotometer was used for the visible spectroscopy to obtain the E_4/E_6 ratio (absorbance to 465 and 665 nm of the visible spectra) and the derivatographic spectrometry (D_{620}, D_{574} and D_{465}), both in 0.2 mg C ml^{-1} solutions of HA in 0.1 M $NaHCO_3$.

Analysis by IR spectroscopy (infrared spectra of the HA) was carried out with a Perkin-Elmer-683 spectrophotometer. Relative intensity for the band of 1620 cm^{-1} was also established. The in vitro respiratory activity of soils was determined by estimating the CO_2 released from soil samples moistened at 60% of their water holding capacity and at 24 ± 1 °C, measured for a period of 40 days with a Carmhograph-12 gas analyzer [2], and the results referred to total mineralization coefficients, defined as the percent of the total C released during the incubation period.

The results were subject to analysis by means of descriptive statistics and the method used to discriminate among the means is Fisher's least significant difference (LSD) procedure. A multifactor analysis of variance (multifactor ANOVA) was used. All the statistical analysis was performed with the Statgraphics Plus v.4.1 software program [39].

3. Results and discussion

The 12 surface soils sampled in the SN zone over an acid metamorphic substratum have neutral to acid pHs, coarse textures (mainly sandy loam) and a low levels of base cations. The 12 soils sampled in the SC are slightly alkaline, with medium textures (mainly clay loam and sandy loam), a high level of nutrients and saturated in exchangeable bases, mainly calcium. The soil C/N (carbon/nitrogen) ratio, with a mean value of 13 in both zones, suggested an optimum balance between the processes of mineralization and stabilization of organic matter and, consequently, they point out appropriate conditions for active microbial development and humus recycling. The selected analytical characteristics of soil samples (Ah horizons) are shown in Table 2.

The results from the analyses of the organic matter of the Ah horizons are expressed as mean values (Tables 3,4 and 5) considering groupings by sampling zone (SN and SC), vegetation type (B: natural forests, R: pine reforestations, and M: scrublands), and sampling zone and vegetation type considered together (SNB, SNR, SNM, SCB, SCR, and SCM).

3.1. Soil humus fractions

The fractionation of the organic matter carried out on the samples from the Ah horizons (Table 3) shows an average content in fresh and incompletely decomposed plant residues (free organic matter, FOM) of 7.55% for zone SN and 1.94% for SC. Low contents are found in SC probably as a result of an increased rate of breakdown of organic matter through an intensification of the biological activity [18], which is higher in this basic edaphic environment. The greater content in exchangeable bases in the SC (Table 2), in comparison with that found in the SN, would be responsible for the lower content of the FOM fraction in the second group. A significantly high mean value in FOM (11.7%) stands out in the reforestation areas with species of *Pinus* in an acid medium (SNR), therefore suggesting a reduction in the biological activity.

The mean values of the HA/FA ratio (humic acids/fulvic acids), a ratio that indicates a greater or lesser level of humification due to its relationship with the aromatic nature and the carbon content of the HA [36], do not show significant differences.

Significant differences are noted in the distribution of the carbon in the total extractable humin—HUMIN—fraction, that is, humic colloids insolubilized in a mineral matrix (mainly clays and oxides), forming highly stable complexes [33] and which would afford great stability for the soil and for the whole ecosystem. Point out the greater percentage of stable organic-mineral complexes in soil horizons in SC with a mean value for HUMIN of 15.2% as compared to 2% in SN, regardless of the type of vegetation.

Non-extractable organic carbon—NEOC—fraction, makes up the highest fraction of the humus in both

Table 2
Analytical data of the Ah horizons of the soils studied

Soil	Depth (cm)	SOC [a]	N [b]	C/N	pH (H_2O)	Exchangeable bases and cation exchange capacity ($cmol_c\ kg^{-1}$) Ca^{2+}	Mg^{2+}	K^+	CEC	Base saturation (%)	Free Iron (%)	Sand (%)	Silt (%)	Clay (%)	Textural classes [c]
SN-1	16	5.82	0.45	13	6.7	18.20	3.38	0.67	27.38	83.67	2.38	59.9	26.1	14.0	SL
SN-2	18	1.41	0.09	16	6.3	4.60	1.08	0.24	9.65	61.45	2.74	60.9	31.4	7.7	SL
SN-3	5	3.73	0.25	15	7.4	10.73	2.58	0.29	16.70	81.44	2.25	64.6	30.2	5.3	SL
SN-4	10	3.98	0.29	14	5.6	4.40	0.97	0.21	21.68	25.97	2.32	56.1	28.3	15.6	SL
SN-5	18	0.37	0.08	5	6.5	1.80	1.07	0.13	7.63	39.97	2.75	51.3	37.1	11.6	L
SN-6	8	1.34	0.11	12	6.5	4.30	1.27	0.51	9.39	65.70	2.36	68.7	23.7	7.6	SL
SN-7	10	1.71	0.14	12	6.5	5.50	2.23	0.21	11.64	68.64	3.75	66.3	23.6	10.1	SL
SN-8	20	2.11	0.18	12	6.2	3.80	0.65	0.41	13.08	37.84	3.48	55.9	33.9	10.2	SL
SN-9	8	2.50	0.15	17	6.7	6.60	1.37	0.26	14.17	58.08	3.57	59.2	31.3	9.6	SL
SN-10	25	1.52	0.10	15	6.8	6.00	0.95	0.39	11.76	63.18	3.64	57.3	30.6	12.0	SL
SN-11	26	3.00	0.20	15	4.9	0.75	0.25	0.16	17.15	7.05	3.84	47.5	39.8	12.7	SL
SN-12	27	4.11	0.28	15	6.1	8.25	1.50	0.29	18.79	53.70	4.04	50.6	42.1	7.2	L
Average	15	2.63	0.19	13	6.3	6.24	1.44	0.31	14.92	53.89	3.09	58.2	31.5	10.3	–
Std. deviation	7.67	1.54	0.11	3.12	0.63	4.61	0.88	0.16	5.72	22.54	0.68	6.45	5.92	3.04	–
Skewness	0.18	0.64	1.23	–1.89	–0.88	1.69	1.08	1.17	0.90	–0.74	–0.01	–0.01	0.42	0.10	–
Std. kurtosis	–1.10	0.03	1.06	3.36	1.13	2.64	0.65	0.80	0.39	0.15	–1.38	–0.48	–0.38	–0.43	–
SC-1	6	6.10	0.31	20	7.4	55.50	2.50	1.53	42.44	100	4.91	15.2	32.9	51.9	C
SC-2	8/32	3.40	0.23	15	6.9	14.25	3.37	0.26	19.90	90.75	2.37	62.6	24.9	12.5	fSL
SC-3	9/22	2.99	0.26	11	5.6	15.00	0.87	0.16	24.41	66.04	2.11	55.2	19.1	25.7	SCL
SC-4	20	1.82	0.17	11	6.5	9.00	1.12	0.44	17.19	62.24	2.42	52.4	32.8	14.8	SL
SC-5	30	3.18	0.32	10	7.8	46.50	1.62	0.46	22.31	100	0.84	52.8	27.7	19.6	vfSL
SC-6	30	0.84	0.07	12	8.1	27.75	3.50	0.51	20.01	100	2.08	33.7	39.2	27.2	CL
SC-7	13	2.09	0.17	12	7.8	14.25	5.75	1.00	23.97	88.90	1.40	19.1	51.1	29.8	ICL
SC-8	8	3.87	0.28	14	7.3	36.75	1.62	0.97	26.48	100	1.49	44.3	29.9	25.8	L
SC-9	31	4.25	0.40	11	7.7	41.25	1.37	0.34	26.45	100	1.37	51.4	25.1	23.5	SCL
SC-10	24	3.26	0.25	13	8.1	38.25	8.37	0.46	20.95	100	2.21	22.8	61.3	15.8	IL
SC-11	14/33	1.57	0.12	13	7.9	42.75	1.75	0.97	22.99	100	1.18	43.6	26.1	30.3	CL
SC-12	15/28	6.34	0.45	14	7.4	39.00	2.87	1.10	30.89	100	1.48	41.6	35.9	22.5	L
Average	20	3.31	0.25	13	7.4	31.69	2.89	0.68	24.83	92.33	1.99	41.2	33.8	24.9	–
Std. deviation	8.37	1.68	0.11	2.66	0.73	15.19	2.19	0.42	6.63	13.75	1.05	15.35	11.98	10.28	–
Skewness	–0.54	0.57	0.15	1.73	–1.50	-0.22	1.70	0.68	1.84	–1.75	2.10	–0.56	1.32	1.60	–
Std. kurtosis	–0.60	–0.08	–0.21	2.80	1.53	–0.91	1.97	–0.29	3.04	1.27	4.04	–0.63	1.09	2.84	–

[a] SOC: total organic carbon ($g\ 100\ g^{-1}$ soil).
[b] N: total nitrogen ($g\ 100\ g^{-1}$ soil).
[c] USDA system particle size classes. SL: sandy loam; L: loam; C: clay; fSL: fine sandy loam; SCL: sandy clay loam; vfSL: very fine sandy loam; CL: clay loam; ICL: silty clay loam; IL: silt loam.

Table 3
Selected characteristics of the Soil Organic Matter of the soils studied (soil humus fractions)

	Sampling zone		Sampling zone and vegetation type						Vegetation type		
	SN_{A}	SC_{B}	SNB_{a}	SNR_{b}	SNM_{c}	SCB_{d}	SCR_{e}	SCM_{f}	B_{I}	R_{II}	M_{III}
Samples	12	12	4	4	4	4	4	4	8	8	8
Total organic carbon (SOC), g 100 g^{-1} soil	2.63	3.31	3.75	1.78	2.36	4.15	3.07	2.70	3.95	2.43	2.53
Humus fractions, g C (100 g soil C)$^{-1}$											
Free organic matter (FOM)	7.55_{B}	1.94_{A}	6.48	$11.7_{c,d,e,f}$	4.45_{b}	2.20_{b}	1.21_{b}	2.40_{b}	4.34	6.46	3.42
HA/FA ratio	0.8	0.7	0.85	0.70	0.85	0.65	0.60	0.75	0.75	0.65	0.80
Total extractable humin (HUMIN)	2.02_{B}	15.24_{A}	$1.91_{d,e,f}$	$2.10_{d,e,f}$	$2.05_{d,e,f}$	$14.87_{a,b,c}$	$14.52_{a,b,c}$	$16.32_{a,b,c}$	8.39	8.31	9.18
Non-extractable organic carbon (NEOC)	54.95_{B}	44.19_{A}	$59.28_{d,f}$	$56.68_{d,f}$	48.88	$38.24_{a,b,e}$	52.68_{d}	$41.66_{a,b}$	48.76	54.68	45.27

Sampling zone ⇒ SN: Sierra Nevada National Park (acid metamorphic substratum); SC: Sierra de Cazorla-Segura-Las Villas Natural Park (calcareous substratum). Vegetation type ⇒ B: natural forests; R: pine reforestations; M: scrublands. Groupings by sampling zone and vegetation type ⇒ SNB: Sierra Nevada natural forests; SNR: Sierra Nevada pine reforestations; SNM: Sierra Nevada scrublands; SCB: Sierra de Cazorla natural forests; SCR: Sierra de Cazorla pine reforestations; SCM: Sierra de Cazorla scrublands. Mean values with a subscript letter (A,B/a,b,c,d, e,f/I,II,III) denote respect that group a statistically significant difference at $P < 0.05$ level (LSD procedure). No significant differences were found between mean values without subscript letter. Grouping criterion: Sampling zone; Sampling zone and vegetation type; Vegetation type.

Table 4
Selected characteristics of the soil organic matter of the soils studied (characterization of the HA fraction)

	Sampling zone		Sampling zone and vegetation type						Vegetation type		
	SN_{A}	SC_{B}	SNB_{a}	SNR_{b}	SNM_{c}	SCB_{d}	SCR_{e}	SCM_{f}	B_{I}	R_{II}	M_{III}
Samples	12	12	4	4	4	4	4	4	8	8	8
Elementary composition of HA											
Atomic H/C ratio	1.41	1.47	1.41	1.40	1.43	1.46	1.45	1.50	1.43	1.43	1.46
Atomic O/C ratio	0.56_{B}	0.64_{A}	0.58	0.56	0.54	0.63	0.65	0.63	0.60	0.60	0.59
C/N ratio	16.47	18.02	14.97_{e}	17.32	17.12_{e}	14.85_{e}	$21.82_{a,c,d}$	17.37	14.91_{II}	19.57_{I}	17.25
Visible spectroscopy measurements in HA											
E_4/E_6 ratio	4.57	4.51	4.60	4.87	4.24	4.47	4.83	4.25	4.53	4.85	4.24
D_{620} (visible derivatographic spectroscopy, AU)	0.016	0.018	0.014_{c}	$0.012_{c,f}$	$0.022_{a,b,e}$	0.016	0.015_{c}	0.021_{b}	0.016_{III}	0.013_{III}	$0.022_{I,II}$
D_{574} (")	0.013	0.014	0.011_{c}	$0.010_{c,f}$	$0.017_{a,b,e}$	0.013	0.012_{c}	0.016_{b}	0.012_{III}	0.011_{III}	$0.017_{I,II}$
D_{465} (")	0.017	0.021	0.014_{f}	$0.013_{c,f}$	0.022_{b}	0.019_{f}	0.016_{f}	$0.029_{a,b,d,e}$	0.017_{III}	0.014_{III}	$0.026_{I,II}$
Infrared spectroscopy of HA (relative optical density), (bands cm^{-1}/ 1620 cm^{-1})											
2920 (IR spectra)	0.80	0.73	0.83	0.81	0.76	0.76	0.70	0.74	0.80	0.76	0.75
1660 (″)	0.83	0.77	0.86_{e}	$0.91_{c,e}$	0.72_{b}	0.80	$0.70_{a,b}$	0.80	0.83	0.81	0.76
1510 (″)	0.78_{B}	0.63_{A}	0.78	$0.97_{c,d,e,f}$	0.60_{b}	0.65_{b}	0.59_{b}	0.67_{b}	0.71	0.78	0.63
1460 (″)	0.89_{B}	0.74_{A}	0.89	1.02	0.76	0.76	0.73	0.72	0.83	0.88	0.74
1420 (″)	0.64	0.63	0.64	0.71	0.59	0.65	0.62	0.63	0.64	0.66	0.61
1380 (″)	0.65	0.63	0.64	0.70	0.60	0.64	0.63	0.63	0.64	0.67	0.62
1080 (″)	0.45	0.42	0.44	0.51	0.39	0.43	0.39	0.44	0.44	0.45	0.42

Sampling zone ⇒ SN: Sierra Nevada National Park (acid metamorphic substratum); SC: Sierra de Cazorla-Segura-Las Villas Natural Park (calcareous substratum). Vegetation type ⇒ B: natural forests; R: pine reforestations; M: scrublands. Groupings by sampling zone and vegetation type ⇒ SNB: Sierra Nevada natural forests; SNR: Sierra Nevada pine reforestations; SNM: Sierra Nevada scrublands; SCB: Sierra de Cazorla natural forests; SCR: Sierra de Cazorla pine reforestations; SCM: Sierra de Cazorla scrublands. Mean values with a subscript letter (A,B/a,b,c,d, e,f/I,II,III) denote respect that group a statistically significant difference at $P < 0.05$ level (LSD procedure). No significant differences were found between mean values without subscript letter. Grouping criterion: Sampling zone; Sampling zone and vegetation type; Vegetation type.

Table 5
Soil respiratory activity of the Ah horizons of the soils studied

	Sampling zone		Sampling zone and vegetation type						Vegetation type		
	SN_A	SC_B	SNB_a	SNR_b	SNM_c	SCB_d	SCR_e	SCM_f	B_I	R_{II}	M_{III}
Samples	12	12	4	4	4	4	4	4	8	8	8
Total mineralization coefficient (TMC), mg C (100 g soil C)$^{-1}$ (40 days)$^{-1}$	1.36	1.19	1.32	1.86	0.89	1.16	1.43	0.98	1.24	1.65_{III}	0.94_{II}

Sampling zone ⇒ SN: Sierra Nevada National Park (acid metamorphic substratum); SC: Sierra de Cazorla-Segura-Las Villas Natural Park (calcareous substratum). Vegetation type ⇒ B: natural forests; R: pine reforestations; M: scrublands. Groupings by sampling zone and vegetation type ⇒ SNB: Sierra Nevada natural forests; SNR: Sierra Nevada pine reforestations; SNM: Sierra Nevada scrublands; SCB: Sierra de Cazorla natural forests; SCR: Sierra de Cazorla pine reforestations; SCM: Sierra de Cazorla scrublands. Mean values with a subscript letter (A,B/a,b,c,d, e,f/I,II,III) denote respect that group a statistically significant difference at $P < 0.05$ level (LSD procedure). No significant differences were found between mean values without subscript letter. Grouping criterion: Sampling zone; Sampling zone and vegetation type; Vegetation type.

populations with 44.2% for SC and a mean value significantly higher for SN with 54.9% of the total organic carbon. The greater presence of this fraction in SN, and since the latter is a medium with lower biological activity, this probably indicates that it is a little evolved fraction, made up by recalcitrant microbial and vegetable biopolymers, with a strong aliphatic nature [26,31,4].

One important part of the relative variability in the variables FOM and NEOC of the humus fractions, and mainly in the variable HUMIN (83%), could be explained by means of the parent material factor as it is included in the multifactor ANOVA (Table 6).

The results from the fractionation performed on the samples from SN and SC are similar to those described by other authors in forest soils from the Mediterranean mountains in SE Spain in an acid [27,31] and in a basic medium [21] environments.

3.2. Characterization of the HA fraction

Table 4 contains the essential ratios (H/C, O/C and C/N) of the elementary composition and spectroscopy measurements (visible and infrared) of the HA from the soil samples. The H/C ratio, is considered as a measure of the aliphaticity and of the degree of humification [37]. A low ratio would show that the HA have more condensed structures and thus a higher degree of condensation and a greater degree of humification. A high H/C ratio is indicative of higher aliphaticity. For the H/C ratio no significant differences were found between the groups.

The atomic ratio O/C reflects the concentration of oxygen-containing (carboxyl) functional groups in HA. Generalizing, ratios of O/C for soil HA cluster around 0.5 [35,37]. The values for the samples show a ratio of around 0.6 (Table 4). The mean values for the O/C ratio provide significant differences between SN and SC groups. The parent material factor would explain an important part of its relative variability, reaching a 35% (multifactor ANOVA, Table 6).

A higher and non significant mean value of the C/N ratio (18) was obtained for the SC compared with 16.5 for SN. This means, for the SC, a lower content in forms of little evolved nitrogen in the HA [41] and a trend towards a greater degree of maturity. Similar values for C/N were found by Schnitzer [29], Bravard and Righi [7] and Sánchez-Marañón [27]. On the contrary, it is significant the effect of the vegetation factor, with a 29% of the relative variability (multifactor ANOVA, Table 6), due to the great difference between the mean values of the C/N ratio under natural forests vegetation and under reforestations (Table 4).

The fundamental spectrophotometric characteristic of the soil HA, the E_4/E_6 ratio, would decrease when the condensation and the aromaticity of the humic substances rise, typical of organic materials with a greater degree of maturity and evolution [37,20]. The results of the visible spectroscopic analyses provide very similar E_4/E_6 ratio values and without any significant differences for the two zones sampled (SN and SC) and for any of the groupings established according to the type of vegetation. These values indicate a relatively high degree of aromaticity of the humic substances when compared with the value ranges from other authors in studies from SE Spain [31] (6.1–8.9, mean 7.5); [27] (4.5–6.5, mean 5.5); [21] (3.6–5.7, mean 4.6).

Despite the great level of homogeneity observed in the E_4/E_6 ratio, the highest values are reached by the samples from under reforestation with pine trees in both sampling zones (SNR and SCR), while under scrubland, regardless of the zonal origin, the samples show lower ratios.

The visible derivatographic spectroscopy of the HA revealed intense valleys near 620, 574 and 465 nm (D_{620}, D_{574} and D_{465}). These diagnostic spectral bands suggest the presence of perylenequinonic pigments

Table 6
Influence of the parent material and vegetation factors on the analyzed variables. Results of the multifactor ANOVA

	Parent material factor		Vegetation factor		Interactions		Residual [c]
	rvar [a]	*F* [b]	rvar	*F*	rvar	*F*	rvar
Total organic carbon (SOC), g 100 g^{-1} soil	4.6	1.1	19.2	2.3	1.9	0.2	74.3
Humus fractions, g C (100 g soil $C)^{-1}$							
Free organic matter (FOM)	35.1	14.6**	7.2	1.5	14.3	3.0	43.3
HA/FA ratio	4.2	0.8	3.6	0.4	0.5	0.1	91.6
Total extractable humin (HUMIN)	82.7	89.2***	0.3	0.2	0.3	0.2	16.7
Non-extractable organic carbon (NEOC)	28.2	11.6**	14.7	3.0	13.3	2.7	43.7
Elementary composition of HA							
Atomic H/C ratio	6.8	1.3	2.1	0.2	0.1	0.0	91.0
Atomic O/C ratio	34.9	10.1**	1.4	0.2	1.6	0.2	62.0
C/N ratio	4.7	1.5	28.6	4.4*	8.7	0.28	58.0
Visible spectroscopy measurements in HA							
E_4/E_6 ratio	0.1	0.0	10.8	1.1	0.1	0.0	88.9
D_{620} (visible derivatographic spectroscopy, AU)	1.4	0.4	40.7	6.6**	2.2	0.4	55.7
D_{574} (″)	1.2	0.4	39.5	6.3**	2.7	0.4	56.5
D_{465} (″)	9.4	3.5	40.7	7.5**	0.9	0.2	49.0
Infrared spectroscopy of HA (relative optical density), (Bands cm^{-1}/1620 cm^{-1})							
2920 (IR spectra)	7.9	1.6	2.8	0.3	2.4	0.3	86.9
1660 (″)	8.4	2.7	6.0	1.0	29.2	4.7*	56.3
1510 (″)	16.5	6.1*	10.1	1.9	24.9	4.6*	48.5
1460 (″)	17.9	5.0*	10.2	1.4	8.0	1.1	63.9
1420 (″)	0.7	0.2	11.6	1.5	18.8	2.5	68.9
1380 (″)	1.5	0.3	10.5	1.2	10.0	1.2	78.0
1080 (″)	4.6	1.2	3.9	0.5	23.5	3.1	67.9
Soil respiratory activity							
Total mineralization coefficient (TMC), mg C (100 g soil $C)^{-1}$ (40 $days)^{-1}$	2.3	0.6	28.9	4.0*	3.8	0.5	65.0

[a] rvar: relative variability (variability explained for each factor or its interactions and which corresponds with the percentage of the sum of squares of each factor with regards to the total sum of squares of the analysis).
[b] F statistic; significant at the 95% (*), 99% (**) and 99.9% (***) confidence level.
[c] Residual: variation component associated to other variation sources.

formed by a variety of soil microfungi [6]. Table 4 shows the mean values of the intensities for these bands in which appear differences, although they are not significant, when grouping the samples together by their sampling zone, with a higher value in the basic medium for SC. If the grouping is performed according to the vegetation, the differences become significant with higher values in the samples taken under scrubland in both mediums (SCM and SNM) and where the metabolism of the fungi would appear to be more active. The significant effect of vegetation on variables D_{620}, D_{574} and D_{465} would be reflected by a 40% of relative variability for this factor (multifactor ANOVA, Table 6).

The reforestations in the acid medium in SN (SNR) favor, to a lesser extent, the development of microbial populations in the soil that are responsible for the concentration of perylenequinonic pigments. The amount of fungal-derived pigments in the soil could as a valid indicator of the impact of the reforestations practices in the structure of the soil microbial system and the mechanisms responsible for the accumulation of the HA [43]. Also, the ongoing presence of these compounds might be considered a characteristic feature of the humification processes in the Mediterranean mountains in SE Spain [21,28].

The infrared spectra of the HA are clearly defined by bands that are differentiated according to the proportions in which the functional groups appear. The data for the intensities of the main bands are summarized in Table 4.

The band at 2920 cm^{-1} corresponds to the aliphatic C-H vibrations [15]. Despite the great homogeneity observed, without significant differences, in terms of the aliphatic content in the different groupings of HA, a higher mean intensity is noted in the samples from the acid medium in SN, which would denote their less evolved nature.

At around 1660 cm^{-1}, vibrations of peptide bonds appear to be generally aliphatic and N-containing groups [38]. High intensities in this area of the spectra indicate a high content in little evolved forms of nitrogen. For this band, the differences per groups (sampling zone and vegetation type) are statistically significant, with the greater content in the samples from SN standing out, especially in the samples under species of *Pinus* (SNR).

A similar sense of lower evolution, and which may imply the presence of a less stabilized HA fraction, is to be found in the band at 1510 cm^{-1}. This band can be assigned both to amide II vibrations [15] and to aromatic C=C vibrations [5]. A significantly higher mean value for this intensity is noted in SN, which is remarkable in SNR.

The main bands related to lignin are at 1460, 1420, and 1380 cm^{-1} [3,28], with the values from the 1460 cm^{-1} band standing out, produced by aliphatic C-H groups, and related to the 2920 cm^{-1} band. The clearest difference found, with statistical significance, is recognized in the chemical nature of the HA in an acid environment (SN), with a structure closer to that of lignin, and therefore less evolved. Highlight the highest mean value, although it is not significant, in the samples under reforestation with *Pinus* (SNR). The intensities of these bands related to lignin show a clear reduction under the basic soil environment and under scrubland vegetation.

The band at 1080 cm^{-1}, typical of C-O and C-H deformations, indicates the presence of polysaccharides or carbohydrate-like substances [16,38]. In the samples from SN, a tendency is noted for preserving these types of less transformed substances somewhat better, mainly in the SNR samples.

In the variables of the IR spectra 1660 and 1510 cm^{-1} it is significant the interaction between the parent material factor and the vegetation factor (multifactor ANOVA, Table 6), which is responsible of the relative variability in a percentage of between 25% and 30%. In variable 1510 cm^{-1} the parent material factor also has an independent and significant effect (17% of the relative variability), whereas in variable 1460 cm^{-1}, for the same factor, the relative variability represents the 18%.

3.3. Soil respiratory activity

Table 5 shows the total mineralization coefficients (TMC) of the samples from the Ah horizons, obtained on the basis of the measures of the daily release of CO_2 over the 40 days that the incubation lasted. The in vitro respiratory activity provides an estimate of the biodegradability of the organic matter in the soil [12] and its degree of maturity. From the point of view of the capacity for preserving the ecosystem, low values for the mineralization coefficients are interesting, since they provide information about the stability of the organic matter and, therefore, about the soils in which the latter is to be found. A high level of biodegradability of the soil organic matter as a result of an alteration in the natural decomposition patterns, with the negative consequences that it would imply for the physical and chemical properties of the soil, may be deemed to be one of the main factors in the degradation of the soil [1].

The results presented show some differences between the groups, although they are not significant, with a mean value for SN and for SC of 1.36 and 1.19 mg C (100 g soil C)$^{-1}$ (40 days)$^{-1}$, respectively. The samples from SNR provide a higher mean TMC (1.86 mg C (100 g soil C)$^{-1}$ (40 days)$^{-1}$) than the rest of the groups, and the samples from under *Pinus* (R) are those which provide a significantly higher value with regards to scrublands (Table 5). Multifactor ANOVA results (Table 6) confirm the significant effect that the type of vegetation has on the TMC parameter, with 29% of the relative variability. The results obtained in this study provide general readings lower than those found in nearby Mediterranean ecosystems in a basic medium [21].

As is deduced from the preceding sections (Sections 3.1., 3.2. and 3.3.), the different analyses of the organic matter from the surface horizons of the soil profiles studied indicate that the samples belonging to SN show a lower degree of humification. The reason for this lower humification may lie in the acid edaphic conditions of the soils [24]. In the SC environment, the presence of carbonates might enhance a better humification process and might result in the formation of HA having a better degree of maturity [18].

Taking in consideration together the SC and SN environments (24 samples) very few correlations can be established between the climatic parameters (mean annual rainfall and mean annual temperature) and those established for the characterization of the soil organic matter. Emphasize the correlation between mean annual rainfall and HUMIN fraction ($r = 0.5752$; P-value < 0.01), and the correlation between mean annual rainfall and NEOC fraction ($r = -0.5680$; P-value $<$ 0.01). These results make clear the favorable effect of an increase on the rainfall amount over the formation of stable organic-mineral complexes and a decrease in the little evolved fraction NEOC. It would be established thus the importance of the geochemical environment against climatic conditionings in the humification processes in the surface horizons of the soils studied.

Comparison between the three types of vegetations allows us to recognize a certain diversification in the processes for the formation of the humic substances depending on the nature of the organic residues. It has been found that the HA of the soils under scrubland have a greater degree of transformation, greater evolution and a predominance of more stable compounds. It is reasonable to expect that the high plant diversity provided by the scrubland affects below-ground diversity, expressed in a greater microhabitat heterogeneity [12], and determines an increase in the degree of humification [44]. This implies that the scrubland might provide greater stability for the surface horizons of the soil, and so would have a positive influence on the conservation of the edaphic medium and the related ecosystems, in comparison with other plant formations.

Apart from the samples under scrubland, the samples under *Quercus* and under *Pinus*, in an edaphic basic medium (SC), are those which would generate a humus with a greater degree of transformation. Furthermore, the results would seem to indicate that the reforestations with species of *Pinus* have a greater negative impact on the acid medium than on the basic medium, whereas in the latter they are much better assimilated by the edaphic conditions with a more efficient evolution of the plant residues.

It might be thought that the reforested pine forests in SC, appear to have undergone a more efficient naturalization than in SN, thereby reaching a certain equilibrium with the environmental conditions and biological activity, typical of a basic soil reaction. Another reason why great analytical differences are not noted between the samples under natural forests (SCB) and the samples under reforested forests (SCR) lies in the fact that *Pinus pinaster* in the SC area has invaded, over the last century, deforested areas of *Quercus*. Hence, a biogenic background representative of the original *Quercus* vegetation would still remain in place, overlapping the organic compounds derived from the pine trees [13].

It was observed that several of the characteristics analyzed indicate that the organic residues of the soils developed under *Quercus* vegetation are generally more humificated than those provided by *Pinus*, i.e. in the samples taken from soils subjected to intensive reforestation. These results concur with those from different authors since they point out that the degree of humification in soils under coniferous forests is generally lower than that found in soils under evergreen oak or deciduous forests [14,42,25]. Coniferous forests would enrich the humus in organic components (NEOC fraction, lignins and amides in the HA, etc.) so giving rise to limited humification processes.

On the basis of the results obtained, everything seems to indicate the existence of other factors, apart from parent material and vegetation ones, which exert a remarkable influence on the characteristics of the soil organic matter and on the control of the humification/degradation processes. One of these factors could undoubtedly be the kind of land management; extremely complex aspect to be established in the Mediterranean basin, which has a thousand-year-old history of anthropic influence.

The information obtained with the study will be useful in further studies on optimizing land management, from an environmental perspective, in the Mediterranean mountain ecosystems. The effort must head for the ecological sustainability of the land uses. In the ecosystems studied, the final aim would be to protect natural forests and strengthen, wherever necessary, the presence of well-constituted scrublands. Vegetation destruction or inadequate substitution (as sometimes reforestations with pine trees) can change the fragile soil balance and create its irreversible degradation. In this equilibrium, soil organic matter has a huge importance by its profound influence on soil properties (biological, physical and chemical) and ecosystem functioning.

4. Conclusions

The samples selected, grouped by sampling zone and vegetation type, presented an unexpectedly high level of homogeneity in their humus composition despite the different types of vegetation and parent material. The results show that the humification processes in the surface horizons of the soils studied which were derived from basic rocks, nonetheless, were more favorable than those from acid rocks.

Some changes in soil organic matter induced by the vegetation type have also been noticed. In particular, the samples from scrubland, with a greater aboveground diversity, were more humificated than those with homogeneous natural or reforested tree coverage. The humification processes seem to be less favorable for the stabilization of organic substances under pine reforestations, especially in soils derived from acid rocks, which would have an unfavorable effect on the evolution of the biogeochemical cycles that would reduce the soil quality.

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