



Carbon accumulation in *Umbrisols* under *Quercus pyrenaica* forests: Effects of bedrock and annual precipitation

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ARTICLE INFO

Article history:

Received 29 June 2008

Received in revised form 21 April 2009

Accepted 25 April 2009

Keywords:

Soil organic matter
Soil carbon sequestration
Metal complexation
Soil acidification

ABSTRACT

The objective of this study was to determine the effect of bedrock, mean annual precipitation and slope orientation on soil organic carbon (SOC) accumulation of *Quercus pyrenaica* Willd forests. Twelve different oak stands, along a rainfall gradient over two bedrock types (granites and schists), were selected for this study. Properties of the diagnostic soil horizons were determined. Bedrock type was the principal factor affecting soil development and fertility. Accumulated SOC varied between 33 and 185 Mg C ha⁻¹, the amounts of C accumulated over schists being significantly higher than over granites because of higher soil acidity, 'silt + clay' content and metal complexation. The SOC content in the entire profile was over 125 times higher than the C accumulated in the stand forest litter at the schist sites and 50 times higher at the granite sites. Soil acidity and metal complexation hampered microbial decomposition of soil organic matter, producing SOC accumulation and forming thick *umbric* Ah/AB-horizons, being thicker at sites with high values of mean annual precipitation than at sites with low ones. Mineral N release was low in these soils.

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1. Introduction

As is well known, there is worldwide concern about global warming of the Earth as a consequence of the increase of greenhouse-type gases (GHG) in the atmosphere, as a result of human activity. The most important of these GHG is CO₂, whose atmospheric concentration has increased from 280 ppm during the pre-industrial period to nearly 360 ppm today (Acosta et al., 2002). The different compartments of forest ecosystems play a dominant role in the global C cycle as they are capable of sequestering C.

Many of the biogeochemical processes that regulate C exchange with the atmosphere take place in temperate forest-ecosystems (Schlesinger, 2005). In addition to aboveground vegetation, upper soil horizons (epipedons) also accumulate soil organic matter (SOM); therefore, soils must be considered as a C pool. Almost 75% of the C in ecosystems is found in the soil (Acosta et al., 2002) and there is still a great potential for C sequestration by soils if mechanisms of C capture and storage are clarified. A net increase in global SOC content could decrease the concentration of atmospheric CO₂ and also improve soil productivity, due to SOM gains (García-Oliva et al., 2006).

The SOC dynamic is known to differ in boreal forests, high elevation forests, tropical forests and semi-arid forest ecosystems (Kimble et al., 2003). In addition, little is known about C fluxes and compartments in

forest ecosystems, and this lack of basic data limits the implementation of appropriate forest managements, seeking C sequestration.

In the Mediterranean environment, climatic conditions and, principally, water deficit usually limit plant production. This is especially true in deciduous forests, whose growth period coincides, to a great extent, with summer drought (Moreno et al., 1996; Gallardo and González, 2004). However, previous studies of nutrient cycling in four deciduous oak (*Quercus pyrenaica* Willd) forests located in western Spain (Sierra de Gata Mountains) under different precipitation regimes revealed that their productivity was generally low (Martín et al., 1995; Gallardo et al., 1999; Turrión et al., 2002), comparing these values with those of other forests at similar latitudes (Cole and Rapp, 1981). Deciduous oak forest productivity decreases when precipitation increases (Gallardo, 2000) because of bio-element leaching and the consequent soil acidification. This limited soil fertility and productivity in these western-Spain forests result in their abandonment and, sometimes, later degradation. To increase the environmental value of these forests, it is of interest to know their capacity of sequestering soil organic C (SOC). Unfortunately, the geological substrate for soil formation at these sites varies widely; it is sometimes not possible to distinguish exactly whether differences in soil fertility, soil carbon accumulation and oak growth are due to variations in climatic conditions or in geological parent material.

Accordingly, the objective of this study was to determine the effect of bedrock, mean annual precipitation (MAP) and slope orientation (SLO) on soil C accumulation under deciduous forests on the Sierra de Gata Mountains (western Spain). An evaluation of the influence of diagnostic horizon soil properties on that C-sequestration process was also performed.

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2. Materials and methods

2.1. Site description

The study was carried out in the Sierra de Gata Mountains, located in the Central Iberian Massif (central western Spain), within an area ranging from 40° 10' to 40° 23' N and 6° 37' to 6° 51' W (Fig. 1). The study district included the villages of Fuenteguinaldo, Casillas de Flores, Robleda, El Payo and Navasfrías in the province of Salamanca, and Villamiel, Hoyos and San Martín de Trevejo in the province of Cáceres (western Spain).

Bedrocks at the sites are granites and schists (Paleozoic) and the dominant soils are cambic Umbrisols (WRB, 2006). These soil profiles are characterized by a dark, thick umbric-Ah horizon, rich in humified SOM, having therefore a very low bulk-density (usually lower than 1.0 Mg m⁻³ in Ah horizons) and a consequently high porosity. The dominant soil textures are sandy loam over granites and silty loam over schists; mean values of 'fine silt + clay' are 33 and 60% for soils over granites and over schists, respectively (Gallardo et al., 1980a). Clay minerals belong to the illite-vermiculite series, chlorite being the most frequent clay fraction; kaolinite frequently appears in soils over granites, but gibbsite is also present at times in these acid and humic soils (Gallardo et al., 1980b).

Concerning the water balance of these systems, Moreno et al. (1996) pointed out in previous studies that precipitation of 1200 mm yr⁻¹ is the limit for a percolating, open water regime. Excess water flux appears as superficial streams, while precipitation below this figure does not result in an excess of water outside the soil body.

Additional information about the study area can be found in Gallardo et al. (1980a,b, 1981), Gallardo (2000) and Turrión et al. (2008), among others.

The forest stands were selected along a net topographic and precipitation gradient, differentiating two transects (North and South) across the Sierra de Gata Mountains (Fig. 2). All these stands are coppices with *Q. pyrenaica* (deciduous oaks) as the dominant species, tree density being about 800 trees ha⁻¹. All the plots studied had, and currently have, similar management.

Before 1960 (gas distribution expanded after this year), the main economic activity in the district studied was charcoal production for sale to urban areas. However, livestock grazing is currently the common land use practice, because of the low value of timber and charcoal.

Table 1 shows the location of the sites and their main characteristics: altitude, bedrock, SLO, MAP, mean annual temperature (MAT), etc.

2.2. Climatic data

Climatic data were compiled from a database of the villages closest to the plots studied (Spanish Agencia Estatal de Meteorología).

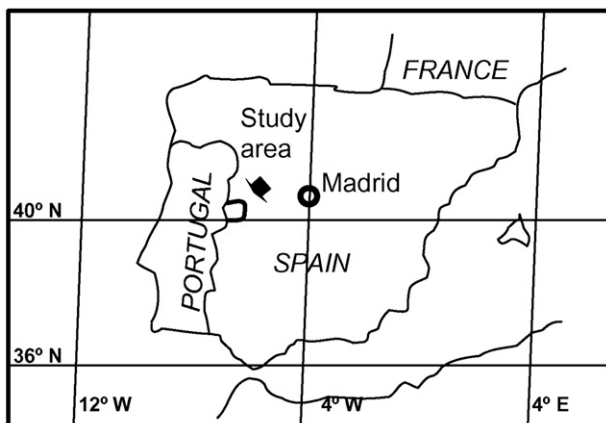


Fig. 1. Study area location (Sierra de Gata Mountains, Western Spain).

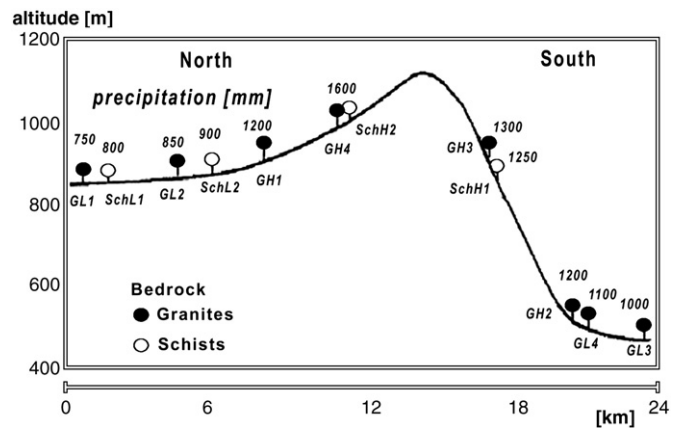


Fig. 2. Distribution of the different sites along the precipitation gradient in the Sierra de Gata Mountains. Italic letters indicate the respective mean annual precipitation (mm yr⁻¹) at each site.

Thermometers and lysimeters were installed in the Fuenteguinaldo (driest, north slope orientation), Navasfrías (wettest, north slope orientation) and San Martín de Trevejo (south slope orientation) sites (above and below forest canopy), and values were registered in data-loggers. In addition, rainfall samples were recovered every time it rained (Moreno et al., 1996).

2.3. Soil and plant sampling

A soil profile was opened in each site and it was described following soil description guidelines (FAO, 1990). Ten soil samples were collected from each horizon, later forming a composite sample. These samples were air-dried, crushed and sieved (<2 mm). Fresh soil was used for mineralization studies. For each forest site, eight samples of stand forest litter were collected with a 0.5 × 0.5 m² steel frame laid out on the soil surface in November 1995, when practically all the leaves had fallen.

2.4. Soil analyses

Soil pH was measured in water (soil:solution ratio of 1:2.5) using a glass electrode. The effective cation exchange capacity (CEC) was determined using an unbuffered 0.1 M BaCl₂ solution (Hendershot and Duquette, 1986). Cations K⁺ and Na⁺ were measured by flame emission, and Ca⁺² and Mg⁺² were determined by atomic absorption on a Varian AA-1475. Exchangeable Al⁺³ was determined photometrically by the pyrocatechol violet method (Kerven et al., 1989).

Table 1

General characteristics of the forest sites selected: location, altitude, bedrock type, mean annual precipitation (MAP), mean annual temperature (MAT), slope orientation (SLO) and litter production (LTP).

Plot	Location (S. de Gata)	Altitude [m a.s.l.]	Bedrock	MAP [mm yr ⁻¹]	MAT [°C]	SLO	LTP [Mg DM ha ⁻¹ y ⁻¹]
GL1	Fuenteguinaldo	850	Granites	750	13.3	North	186
GL2	Casilla de Flores	880	"	850	Nd	North	157
GL3	Hoyos	450	"	1000	Nd	South	318
GL4	San Martín B	480	"	1100	15.1	South	275
GH1	Navasfrías A	900	"	1200	11.8	North	200
GH2	San Martín A	500	"	1200	15.1	South	179
GH3	Villamiel A	880	"	1300	14.2	South	269
GH4	Navasfrías B	980	"	1600	11.3	North	179
SchL1	Robleda	850	Schists	800	Nd	North	200
SchL2	Villasrubias	880	"	900	Nd	North	179
SchH1	Villamiel B	850	"	1250	14.2	South	186
SchH2	Navasfrías C	980	"	1600	11.3	North	200

Nd: no data available. L: low rainfall; H: high rainfall; G: granites; Sch: schists and greywackes; DM: dry matter.

SOC content was first determined by dry combustion and then by conductivimetric detection, using a Carmhograph 12 Wösthoff Analyzer.

Accumulated SOC in the total profile was calculated taking into account SOC content and bulk density per horizon, their thickness, and the percentage of gravels.

Total soil N (N_t) was measured by micro-Kjeldahl digestion followed by steam distillation and final ammonium titration. Mineral N was extracted with 0.0125 M CaCl_2 and determined by photometrical batch methods on a Varian DMS 90 photometer. $\text{NO}_3\text{-N}$ was determined directly by UV absorption according to Scharpf and Wehrmann (1976), and $\text{NH}_4\text{-N}$ by the sodium salicylate/hypochlorite method of Kandeler and Gerber (1988). Inorganic N (N-in) was calculated by adding $\text{NO}_3\text{-N}$ plus $\text{NH}_4\text{-N}$.

Organically bound Al and Fe (Al_{pyr} and Fe_{pyr}) were extracted with 0.1 M pyrophosphate solution (Wada and Higashi, 1976) and then determined by atomic absorption. The simultaneously extracted organic C (C_{pyr}) was measured on a Beckman 915A Total Carbon Analyzer.

All the laboratory analyses were performed in triplicate.

2.5. Mineralization studies

Mineralization studies were performed on fresh soil samples taken from epipedons, according to Isermeyer (1952), in closed chambers and under laboratory-controlled conditions. Samples were first wet to 60% of the water holding capacity and incubated in 1 L jars at 25 °C for 16 days; the moisture content was kept constant by weighing the samples. The evolved $\text{CO}_2\text{-C}$ was trapped in 0.02 M NaOH and titrated with 0.02 M HCl against a phenolphthalein indicator after precipitation with 1 M BaCl_2 . C mineralization data shown are the means of five parallel incubations. Soil respiration was then measured in optimal conditions for soil microbial development, giving a maximum potential SOM mineralization.

Kinetic C mineralization parameters (mineralizable C quantity and kinetic coefficients) were determined. Three different models have been used to describe the C mineralization dynamics in the samples studied.

The first model is referred herein (Murwira et al., 1990) as the first-order exponential equation:

$$C_t = C_L(1 - e^{-kt})$$

Where C_L represents the amount of total potentially mineralizable C (g C kg^{-1}) and k is the mineralization rate constant (d^{-1}). The half-life time of C pool was determined as:

$$t_{1/2} = 0.693 / k$$

The second model considers an exponential equation with two components or pools of mineralizable C, one that decomposes faster during the first weeks of incubation (active pool) and another that decomposes slowly (recalcitrant pool):

$$C_t = C_1(1 - e^{-k_1t}) + C_2(1 - e^{-k_2t})$$

Where C_1 and C_2 represent the active and recalcitrant pools decomposing at specific rates of k_1 and k_2 . The sum $C_1 + C_2$ has the same physical meaning as C_L in the first-order exponential model.

Finally, the third (special) model is an approximation of the double exponential model, but applied when the incubation experiments are short in comparison with the half-life of the large recalcitrant pool:

$$C_t = C_1(1 - e^{-k_1t}) + k_2t$$

Where C_1 and k_1 have the same meaning as C_L and k in the first order model, and k_2t represents the large recalcitrant C pool that mineralizes at a low, constant rate (Fernández et al., 2007).

Mineralized N was simultaneously determined in the same laboratory experiment, measuring the content of N-in at the beginning and end of the incubation period (16 days). The resulting value is called N mineralization (N_{min16}).

2.6. Plant analyses

Plant material was dried at 65 °C for 48 h, weighted and milled. C was determined by dry combustion and conductivimetric detection with a Carmhograph 12 Wösthoff Analyzer, and total N with a Heraeus Macro-N Analyzer.

2.7. Statistical analysis

The data set was statistically analysed using the Statgraphic-Plus 5.0 software package. For determining the significant differences between parameters, a general linear model (GLM) was applied, using the following as predictive factors: Bedrock type (two levels: granite and schist); mean annual precipitation (two levels: high, percolating system when $\text{MAP} > 1200 \text{ mm yr}^{-1}$; and non-percolating system when $\text{MAP} < 1200 \text{ mm yr}^{-1}$, according to Moreno et al. (1996)); slope orientation (two levels: northern and southern slope orientations); and interactions between factors.

The SLO factor and the interactions between factors were not significant for any of the parameters studied, except for accumulated C in the stand litter. These factors were therefore deleted from the model. When an effect studied turned out to be significant, differences among levels were evaluated using the Bonferroni test.

Correlations between variables were established applying regression analysis. To study the carbon mineralization kinetic models, non-linear regression curves were fitted applying the SPSS 14.0 software package; coefficients of determinations (r^2) were used for comparison between models.

A factor analysis (FA) statistical approach was applied to analyze interrelationships among the large number of variables analyzed in this study and to explain these variables in terms of their common underlying dimensions (principal factors). This statistical approach is a way of condensing the information contained in a large number of variables into a smaller set of dimensions, with minimum loss of information (Hair et al., 1992). The four basic analysis steps followed in this study were: 1) data collection and generation of the correlation matrix, 2) extraction of initial component solution, 3) rotation and 4) interpretation and construction of scales or component scores to use in further analyses. The variances extracted by this component analysis are called the 'eigenvalues'. For determining the number of factors, the criteria 'eigenvalue > 1' was adopted (Kaiser Criterion).

The GLM was applied for analyzing both soil properties and the rotated principal component scores obtained from the FA.

3. Results

3.1. General soil parameters

Some physical–chemical and chemical features of the soils studied are shown in Tables 2 and 3. All the soils studied were acid, but a lower pH value in epipedons is associated to sites with higher MAP; a significant relationship between pH and MAP was consequently found (Table 4). In addition to this, significantly lower pH values were found in soils developed over schists than in those over granites (Table 4).

Effective CEC of the soil horizons had low to very low values, in spite of the relatively high SOC contents. The dominant cation in the exchange complex was Ca^{2+} , especially in the sites with low MAP. Exchangeable Ca^{2+} values decreased with increasing MAP as, in

concordance, the exchangeable Al^{3+} (Al_{ex} ; Tables 2 and 3) did. This Al_{ex} had significant relationships with MAP ($p < 0.01$) and bedrock ($p < 0.001$), having significantly higher values in soils on schists (in accordance with the lower soil pH values) than on granites. Al_{ex} also had higher values in sites with high MAP than in sites with low MAP.

MAP had no significant effect on the SOC content in the epipedons (Table 4), but low-MAP sites showed either lower thickness of this *Ah* horizon and/or low SOC accumulation in the profile [$Mg\ C\ ha^{-1}$]. Nevertheless, bedrock type had a significant effect ($p < 0.05$) on SOC concentration.

Soil N contents had a parallel distribution with SOC values; both C and N contents reached significantly higher values at the sites over schists than over granites (Table 4).

Na pyrophosphate dissolved considerable amounts of organically bound Al (Al_{pyr}) and Fe (Fe_{pyr}), but also humic substances (C_{pyr}) linked to these metals, particularly in soils over schists with higher MAP. In sites with higher MAP, in contrast to the sites with lower MAP, maximum Al_{pyr} content appeared in the *AB* horizons, indicating Al leaching (Tables 2 and 3). Therefore, as can be seen in Table 4, MAP had a significant effect on Al_{pyr} ($p < 0.05$) there. However, both Al_{pyr} and Fe_{pyr} showed significant differences with bedrock ($p < 0.01$ and $p < 0.001$, respectively), having higher values in soils over schists than those over granites as well.

$N-NO_3^-$ concentrations in *Ah* horizons showed significantly higher values in soils over granites than those over schists, but no MAP effect was observed. In contrast, $N-NH_4^+$ concentrations were significantly

affected only by MAP, with significantly higher $N-NH_4^+$ values in plots with higher MAP (Table 4), indicating restricted nitrification.

3.2. Carbon accumulation

The SOC content in the entire profile ranged from 33 to 185 $Mg\ C\ ha^{-1}$ (Table 5). The soils on schists showed significantly higher amounts of SOC in the entire profile than the soils on granites ($p < 0.01$). However, the effects of MAP and SLO were not significant on the SOC content of the entire profile.

The amount of stand litter ranged from 0.73 to 1.42 $Mg\ C\ ha^{-1}$ (Table 5). Although the C accumulated in this litter did not show significant differences in relation to bedrock and MAP (Table 5), this organic layer showed significant differences according to SLO ($p < 0.001$) and to the interaction MAP*SLO ($p < 0.01$), south SLO favouring C accumulation as litter.

SOM accumulation is the characteristic process in the genesis of these soils (specially in soils over schists), a thick and dark-coloured *umbric-Ah* horizon appearing, with friable consistence, low bulk density (around $0.8\ Mg\ m^{-3}$) and high P retention (Turrión et al., 2008). Some diagnostic properties of the soils studied here, principally in GH4 and SchH2 soils (such as high water-holding capacity, acid pH, scarce available P and SOC and N_t accumulation) were similar to those of *Andosols*. In contrast, other properties differed quite a bit from those typical of *Andosols* (WRB, 2006).

Table 2
General soil properties of soil profiles over granites.

	Depth [cm]	pH (H_2O)	CEC [$cmol_c\ kg^{-1}$]	Ca_{ex}	Al_{ex} [$g\ kg^{-1}$]	BS [%]	SOC [$g\ kg^{-1}$]	C_{pyr}	N_t	C/N	Al_{pyr} [$g\ kg^{-1}$]	Fe_{pyr}
GL1												
<i>Ah</i>	0–20	5.9	7.9	5.3	0.01	98	28	4.7	2.2	12.7	0.50	0.51
<i>Bw1</i>	20–40	5.5	2.4	0.6	0.11	63	6.0	1.6	1.4	4.3	0.35	0.34
<i>Bw2</i>	40–70	5.3	2.2	0.2	0.16	44	3.0	0.6	0.4	7.5	0.23	0.20
<i>BC</i>	70–100	5.0	2.6	0.2	0.23	30	1.8	0.3	0.4	4.5	0.17	0.09
<i>C</i>	>100	5.0	3.2	0.6	0.26	37	1.4	0	0.4	3.5	0.20	0.05
GL2												
<i>Ah</i>	0–10	6.3	9.0	6.4	0.01	100	22	6.9	2.4	9.3	0.09	0.25
<i>Bw1</i>	10–20	5.5	4.1	2.0	0.03	82	7.2	6.0	0.8	9.0	0.07	0.16
<i>Bw2</i>	20–90	5.8	5.8	3.6	0.05	94	3.3	3.0	0.5	6.6	0.05	0.06
<i>BC</i>	>90	5.7	6.5	3.2	0.11	83	1.5	1.0	0.5	3.0	0.07	0.09
GL3												
<i>Ah</i>	0–8	5.8	10.4	6.5	0.01	98	26.3	6.1	3.5	17.8	0.09	0.36
<i>Bw</i>	8–30	5.3	2.9	1.4	0.03	87	7.5	1.7	0.7	10.7	0.14	0.30
<i>BC</i>	>30	5.1	2.9	0.6	0.13	56	2.2	1.2	0.4	5.5	0.06	0.16
GL4												
<i>Ah</i>	0–30	5.7	5.0	2.1	0.03	85	13.1	4.4	1.6	8.1	0.54	0.47
<i>Bw</i>	30–70	5.6	3.0	0.9	0.07	70	7.5	2.8	0.7	10.7	0.66	0.47
<i>BC</i>	>70	5.6	2.6	0.8	0.08	72	3.5	1.3	0.5	7.0	0.18	0.16
GH1												
<i>Ah</i>	0–25	5.6	5.3	2.8	0.09	81	19.9	3.3	0.8	24.9	0.56	0.32
<i>Bw1</i>	25–40	5.7	4.2	1.0	0.21	61	7.2	2.0	0.8	9.0	0.71	0.39
<i>Bw2</i>	40–65	5.5	4.4	0.8	0.33	45	4.2	1.3	0.4	10.5	0.29	0.17
<i>BC</i>	65–90	5.4	5.0	1.1	0.42	42	0.2	0.2	0.4	0.6	0.29	0.08
<i>C</i>	>90	5.2	5.3	0.2	0.56	16	0.2	0.1	0.4	0.4	0.34	0.05
GH2												
<i>Ah</i>	0–15	5.2	6.8	2.9	0.06	83	44	6.5	3.1	14.3	0.35	0.29
<i>Bw1</i>	15–35	4.9	4.9	0.7	0.31	39	8.3	3.6	0.7	11.9	0.41	0.08
<i>Bw2</i>	35–65	5.0	4.1	0.7	0.25	46	2.9	1.0	0.6	4.8	0.31	0.01
<i>BC</i>	>65	5.1	5.1	0.4	0.32	26	0.7	0.5	0.5	1.4	0.26	0.01
GH3												
<i>Ah</i>	0–20	5.3	6.1	2.6	0.06	84	25	8.3	1.8	13.8	0.47	0.63
<i>AB</i>	20–40	5.3	3.3	0.6	0.15	59	15	7.3	1.1	13.8	0.92	0.72
<i>Bw</i>	>40	5.2	3.3	0.3	0.20	38	3.4	3.4	0.5	6.8	0.31	0.13
GH4												
<i>Ah</i>	0–20	4.9	5.4	0.4	0.37	20	71	22	4.0	17.8	3.9	1.3
<i>AB</i>	20–50	5.1	3.4	0.2	0.22	23	50	21	2.8	17.9	5.2	1.43
<i>C</i>	>50	5.7	0.8	0.01	0.02	56	1.0	0.4	0.8	1.3	1.3	0.28

SOC: organic C; C_{pyr} : C extractable by pyrophosphate; N_t : total N; CEC: cation exchangeable capacity; BS: base saturation; Ca_{ex} : exchangeable Ca^{2+} ; Al_{ex} : exchangeable Al^{3+} ; Al_{pyr} : Al extractable by pyrophosphate; Fe_{pyr} : Fe extractable by pyrophosphate. GL: soils over granites and low rainfall; GH: soils over granites and high rainfall.

Table 3

General soil properties of soil profiles over schists.

	Depth [cm]	pH (H ₂ O)	CEC [cmol _c kg ⁻¹]	Ca _{ex}	Al _{ex} [g kg ⁻¹]	BS [%]	SOC [g kg ⁻¹]	C _{pyr}	N _t	C/N	Al _{pyr} [g kg ⁻¹]	Fe _{pyr}
SchL1												
Ah	0–10	5.0	5.5	2.2	0.13	71	45	6.9	3.0	15.0	0.60	1.7
AB	10–20	4.8	3.5	0.4	0.25	35	23	5.9	2.2	10.5	0.51	0.88
Bw	20–30	4.9	2.9	0.2	0.23	30	18	4.3	1.9	9.5	0.49	0.76
BC	>30	5.1	2.6	0.1	0.25	30	7.2	1.3	1.2	6.0	0.28	0.26
SchL2												
Ah	0–20	5.4	5.4	1.2	0.20	57	69	15	4.3	15.9	1.8	0.86
Bw	20–40	5.6	2.4	0.4	0.14	44	29	10	2.2	13.3	2.0	0.73
BC	>40	5.5	2.7	0.4	0.18	46	16	7.2	1.4	11.2	0.89	0.45
SchH1												
Ah	0–15	5.1	4.3	0.5	0.31	26	70	17	4.0	17.5	3.8	1.6
AB	15–30	5.1	3.4	0.4	0.24	26	62	16	3.2	19.3	4.1	1.5
Bw	30–40	5.2	1.6	0.4	0.16	49	16	5.5	1.4	11.7	1.8	0.81
BC	>40	5.3	1.3	0.2	0.14	40	4.9	1.0	0.9	5.4	0.3	0.16
SchH2												
Ah	0–25	4.7	6.6	0.6	0.42	20	74	19	4.4	16.8	3.1	1.8
AB	25–40	4.8	4.5	0.4	0.33	21	53	17	2.4	22.2	3.2	1.5
Bw	40–60	4.9	2.8	0.3	0.23	29	25	8.1	1.9	12.9	2.5	1.4
BC	>60	5.0	2.9	0.6	0.20	39	16	5.1	1.4	11.4	2.1	1.2

SOC: organic C; C_{pyr}: C extractable by pyrophosphate; N_t: total N; CEC: cation exchangeable capacity; BS: base saturation; Ca_{ex}: exchangeable Ca²⁺; Al_{ex}: exchangeable Al³⁺; Al_{pyr}: Al extractable by pyrophosphate; Fe_{pyr}: Fe extractable by pyrophosphate; SchL: soils over schists and low rainfall; SchH: soils over schists and high rainfall.

Table 4

Means and standard deviations of soil epipedon properties.

	pH (H ₂ O)	CEC [cmol _c kg ⁻¹]	Ca _{ex}	Al _{ex} [g kg ⁻¹]	BS [%]	SOC [g kg ⁻¹]	C _{pyr}	N _t	NO ₃ ⁻ -N [mg kg ⁻¹]	NH ₄ ⁺ -N [mg kg ⁻¹]	Al _{pyr} [g kg ⁻¹]	Fe _{pyr}
GL	5.9±0.3	8.1±2.3	5.1±2.0	0.02±0.01	95±7	32±21	5.5±1.2	2.4±0.8	27±16	0.15±0.10	0.31±0.25	0.40±0.11
GH	5.4±0.2	6.1±0.8	2.8±0.2	0.07±0.02	82±1	30±13	6.0±2.5	1.9±1.1	38±16	4.4±1.2	0.46±0.10	0.41±0.19
SchL	5.2±0.3	5.4±0.1	1.7±0.7	0.17±0.05	64±10	57±17	10.9±5.7	3.7±0.9	3.2±1.9	0.30±0.10	1.19±0.83	1.31±0.64
SchH	4.9±0.3	5.4±1.6	0.54±0.04	0.37±0.08	23±4	72±3	18.5±1.4	4.2±0.3	18±9	1.4±0.7	3.45±0.43	1.69±0.11
Factors												
Bedrock	**	ns	*	***	***	*	**	*	*	ns	**	***
MAP	*	ns	*	**	**	ns	ns	ns	ns	**	*	ns

Significance levels: *, ($p < 0.05$), **, ($p < 0.01$), ***, ($p < 0.001$), ns: not significant. GL: soils over granites and low rainfall; GH: soils over granites and high rainfall; SchL: soils over schists and low rainfall; SchH: soils over schists and high rainfall; SOC: organic C; N_t: total N; CEC: cation exchangeable capacity; BS: base saturation; Al_{ex}: exchangeable Al³⁺; Al_{pyr}: Al extractable by pyrophosphate; Fe_{pyr}: Fe extractable by pyrophosphate.

Significance levels of the effects of bedrock type (granite or schist) and mean annual precipitation (MAP), obtained applying a general linear model analysis (GLM).

Table 5

Carbon accumulation in the soil profile and in the stand litter.

Plots	SOC accumulation in the profile	C accumulation in the litter	Total accumulated C (soil + leaf litter)
	[Mg C ha ⁻¹]	[Mg C ha ⁻¹]	[Mg C ha ⁻¹]
GL1	50.6	0.86	51.5
GL2	32.7	0.73	33.4
GL3	41.4	1.42	42.8
GL4	45.0	1.32	46.3
GH1	42.3	1.07	43.4
GH2	54.2	0.92	55.1
GH3	48.8	1.18	50.0
GH4	171	0.85	172
SchL1	47.7	0.95	48.6
SchL2	116	0.89	117
SchH1	114	0.96	115
SchH2	185	0.95	186
Factors			
Bedrock	**	ns	*
MAP	ns	ns	ns
SLO	ns	***	ns
MAP*SLO	ns	**	ns

Significance levels: *, ($p < 0.05$), **, ($p < 0.01$), ***, ($p < 0.001$), ns: not significant. GL: soils over granites and low rainfall; GH: soils over granites and high rainfall; SchL: soils over schists and low rainfall; SchH: soils over schists and high rainfall; MAP: mean annual precipitation; SLO: Slope orientation.

3.3. C and N mineralization

Table 6 shows the parameters derived from models applied to C–CO₂ emissions, such as calculated soil labile C (C_L), half-life time ($t_{1/2}$), initial potential rate of C mineralization ($C_L * k$) and total mineralized C and N in 16 days (C_{min16} and N_{min16}). The C mineralized during the total incubation period fits very well to a single exponential model, giving the highest regression coefficient ($r^2 > 0.974$), higher than those obtained with models considering two C pools (double exponential or exponential plus lineal). Values of C_{min16} and N_{min16} were lower in soils with high MAP than in soils with low MAP, indicating that labile organic substances are more abundant in the latter group. C_{min16} and N_{min16} values were independent of the geological substrate considered.

4. Discussion

4.1. Soil pH

The sites with higher MAP showed significantly lower pH and base-saturation values than the drier sites (Table 4), due to more intense base leaching. The soil acidification produced in the wetter sites is more intense if the original bedrock has poor basic cation content (e. g., schists), as evidenced by the significant relationship between soil pH and the bedrock factor (Table 4).

Table 6
Mineralization rate constant (k), concentrations of the soil labile C pool (C_L), initial potential rate (C_L*k), half-life time of the labile pool ($t_{1/2}$), C and N mineralized over 16 days ($C_{\min 16}$ and $N_{\min 16}$) and their standard deviations.

	C_L [g C kg ⁻¹ soil]	k [10 ⁻² d ⁻¹]	C_L*k [g C kg ⁻¹ soil d ⁻¹]	$t_{1/2}$ [d]	$C_{\min 16}$ [g kg ⁻¹ soil]	$N_{\min 16}$
GL	9.4 ± 1.01	8.2 ± 1.1	0.75 ± 0.02	8.8 ± 1.2	6.6 ± 0.5	14 ± 5
GH	3.7 ± 0.78	10.3 ± 1.2	0.38 ± 0.05	6.7 ± 1.1	2.9 ± 0.7	5.7 ± 3.8
SchL	8.0 ± 0.96	8.3 ± 2.1	0.65 ± 0.09	8.7 ± 2.2	5.7 ± 0.1	18 ± 11
SchH	3.0 ± 0.35	6.7 ± 0.2	0.20 ± 0.03	10.4 ± 0.3	1.9 ± 0.2	7.5 ± 4.5
Factors						
Bedrock	ns	ns	*	ns	ns	ns
MAP	**	ns	***	ns	**	ns

Significance levels: * ($p < 0.05$), ** ($p < 0.01$), *** ($p < 0.001$), ns: not significant. GL: soils over granites and low rainfall; GH: soils over granites and high rainfall; SchL: soils over schists and low rainfall; SchH: soils over schists and high rainfall; MAP: mean annual precipitation.

4.2. Carbon accumulation in soil

The soils studied have a high capacity to accumulate SOC (between 33 and 185 Mg C ha⁻¹; Table 5). Gallardo and González (2004) found that the total C accumulation in close forest soils ranged from 57 to 126 Mg C ha⁻¹, while the C sequestered by the above-ground biomass ranged from only 32 to 49 Mg C ha⁻¹.

The SOC content in the entire soil profile was over 125 times higher than the C accumulated in stand litter at the sites on schists and only 50 times higher at the sites on granites, indicating higher *in-situ* SOM mineralization on the latter soils. Dupouey et al. (1999) performed a complete C balance for French forests (which covered 540 plots from the European forest monitoring network). Their data showed the total mean ecosystem C was 137 Mg C ha⁻¹; of this total, soil represented 51% (71 Mg C ha⁻¹), litter 6% and roots 6% as well. The IPCC (2000) showed mean values of 447 Mg C ha⁻¹ for tropical rain forests in the total system and 162 Mg C ha⁻¹ (36% of the total) in SOC pool.

SOC content accumulated in the entire profile was not affected by MAP (Table 5). However, the initial potential rate of C mineralization (C_L*k) and the total C mineralized (C_L) were significantly lower at the wetter sites than at the drier sites (Table 6), as indicated before. That means that the soluble, labile SOM fractions are leached throughout the soils suffering higher rainfall, because summer dryness affects all soils similarly in the area studied (Moreno et al., 1996).

Bedrock had a significant effect on SOC accumulation in the complete soil profile and also in the total C accumulated in soil plus stand litter (Tables 5 and 7). Soil texture, derived from parent material, was the key factor in that SOM accumulation (Gallardo et al., 1980a).

The accumulated C in stand litter was affected only by SLO and MAP*SLO interaction. The significant effect of the MAP*SLO interaction

Table 7
Correlation matrix, after Varimax rotation, of components obtained by factor analysis (GLM).

Parameters	Components		
	1	2	3
Al _{ex}	0.764	-0.622	
Al _{pyr}	0.751	-0.599	
BS	-0.741	0.666	
Ca _{ex}		0.885	
CEC		0.935	
C_L			-0.733
C_{pyr}	0.866	-0.430	
k			0.946
N_t	0.967		
pH (H ₂ O)	-0.553	0.706	
SOC	0.963		
Factors			
Bedrock	*	**	ns
MAP	*	**	ns

Significance levels, * ($p < 0.05$), ** ($p < 0.01$), ns: not significant. Significance levels obtained by GLM for the effects of bedrock type (granite or schist) and mean annual precipitation (MAP), applied to the components.

on stand litter amount means that only in plots with low MAP values were there significant differences between north and south SLO (plots with southern exposition had significantly higher accumulation of stand litter than plots with north SLO). In contrast, the SLO effect was not significant in plots with high MAP. SLO directly influenced MAT (Table 1) and, therefore, in plots with low MAP values, plots with north SLO showed amounts of C litter accumulation significant lower than plots with south SLO, promoting faster SOM decomposition. Martín et al. (1995), carrying out *in-situ* decomposition experiments on leaf decomposition (using litter-bags) at the sites GL1, SchH2 and SchL2 (all sites having north SLO), observed that leaf litter decomposed rapidly in all plots. This suggests that soil and litter humidity (rather than temperature) is the factor limiting SOM mineralization in the Sierra de Gata Mountains with a northern orientation; our results agree with this affirmation. It is important to indicate that no permanent organic layer (O horizon) was observed in the soils studied here.

The SOM accumulation over schists was higher because of higher acidity and SOM stabilization by Fe and Al sesquioxides. There were also higher amounts of fine-silt and clay fractions (60% of 'fine silt + clay') in comparison with granite soils (Gallardo et al., 1980a), which have sandy or loam-sandy textures (33% of fine silt + clay).

SOC contents in Ah and AB horizons were positively correlated with exchangeable Al³⁺ ($r^2 = 0.73^{***}$) and with the sum of pyrophosphate-extractable Al and Fe (Al_{pyr} + Fe_{pyr}; $r^2 = 0.66^{***}$), indicating that these metals exert a protective effect on SOM. Amounts of amorphous Al and Fe liberated from primary rock minerals depended, in turn, mainly on the bedrock material.

Parent material could thus control SOM stabilization in Sierra de Gata Mountain soils, since neither MAP nor SLO had significant effects on SOM accumulation, and biomass production had no significant correlation with SOM accumulation ($r^2 = 0.10$), either.

It is important to note that GH4 showed values for all the soil parameters studied more similar to values in soils over schists than those over granites, it accumulated high amounts of SOC (Table 5) and its soil profile was characterised by thick umbric Ah + AB horizons (Tables 2 and 3). Concentrations of pyrophosphate extractable Al and Fe were also higher in the AB than in the Ah horizons in this soil, indicating an illuvial sesquioxide process, fluxing downwards from the Ah to the AB horizon. A similar process had also been found in Andosols developed from non-volcanic materials in Galicia (NW Spain) by García-Rodeja et al. (1987). Therefore, SOC accumulation in the plots studied could be attributed to SOM stabilisation by formation of stable Al³⁺- and Fe³⁺-humus complexes.

4.3. Carbon and nitrogen mineralization

Soils incubated *in vitro*, at identical assay conditions, respond to intrinsic soil properties, because differences in C mineralization rates cannot be attributed to a variation in climatic site conditions. In agreement with this, SOC mineralization correlated significantly with Fe_{pyr} and Al_{pyr} ($r^2 = -0.92^{***}$) and exchangeable Al³⁺ ($r^2 = -0.91^{***}$)

in the soils studied, indicating complexation of humus by Al^{3+} as a fundamental mechanism of SOC stabilization (Turrión et al., 2002). Complexation of humus by Al and Fe thus appears to control humus mineralization in soils in the Sierra de Gata Mountains. Other studies have also provided strong evidence that C mineralization is negatively related to contents of amorphous Al and Fe, and to allophane content (Brunner and Blaser, 1989), and that SOM can be protected against microbial degradation by complexation with Al and Fe.

SOM stabilization by complexation with Al had consequences not only for SOC mineralization, but also for the release of the nutrients by humic substances. C and N mineralizations were closely correlated ($r^2 = 0.84^{**}$) here, as postulated by McGill and Cole (1981) in a conceptual model on the soil cycling of C, N, P and S. Therefore, available N was also the lowest at the sites with high amounts of Al_{pyr} and Fe_{pyr} and high MAP (GN4, SchH1, and SchH2).

An inverse significant relationship between C and N mineralization rates and contents of amorphous and allophanic constituents was also reported by Boudot et al. (1988) in Highland soils. Furthermore, in soils with high contents of SOC and $Al_{pyr} + Fe_{pyr}$ (higher MAP), ammonification dominated over nitrification (Fig. 1), consistent with results obtained by González-Prieto et al. (1992) in humic soils from northwestern Spain. These authors found a low density of nitrifiers in these soils; generally, soil conditions in sites with high MAP are not favourable to nitrifiers, which are sensitive to soil acidity and high exchangeable- Al^{3+} concentrations.

According to a mechanistic approach, SOM is composed of a continuum of materials whose cycling rates vary from days or weeks to millennia (Olk and Gregorich, 2006). These diverse organic materials can be conceptually divided into discrete kinetic pools with distinct levels of resistance to mineralization, but time of incubation affects the fitting of two-pools models (Alvarez and Alvarez, 2000): the longer the experiment, the better the description of the mineralization pattern, because the contribution of the most resistant C pool to mineralization increases. This could be the reason why the double pool models tested in the short-time incubation assay had a worse coefficient of determination in our *in vitro* experiment.

4.4. Forms of mineral nitrogen

NO_3^- -N was the dominant N-in form in soils over granites, probably due to their higher soil pH and a higher macroporosity from their sandy or loam-sandy soil textures on granite saprolites.

NH_4^+ -N reached a significant percentage of N-in only at the sites with relatively high MAP (especially in soil on schists). At these sites, due to the heavy winter rainfall, soil conditions may be less favourable for nitrification because of temporal water-logging periods, in addition to the previously-mentioned effect of lower soil pH (González-Prieto et al., 1992).

4.5. Factor analysis

Factor analysis (FA) was applied for examining the relationships among measured soil properties and some independent linear combinations (principal factors) of a set of variables. According to the Kaiser Criterion (Kaiser, 1958), the first three components were retained. They explained almost 92% of the total variance of the original data set. The correlation matrix obtained after a Varimax rotation of the three FA-obtained components is shown in Table 7 (correlation coefficients lower than 0.4 are not shown).

- *Component 1* is mainly an organic factor because it represents an estimation of SOM quantity, where SOC, total N and C_{pyr} show the highest weights; parameters that showed higher values in soils over schists than over granites had positive correlations with this factor.
- *Component 2* is mainly a physicochemical factor (possibly influenced by pH) and is related to CEC and exchangeable Ca^{2+} ;

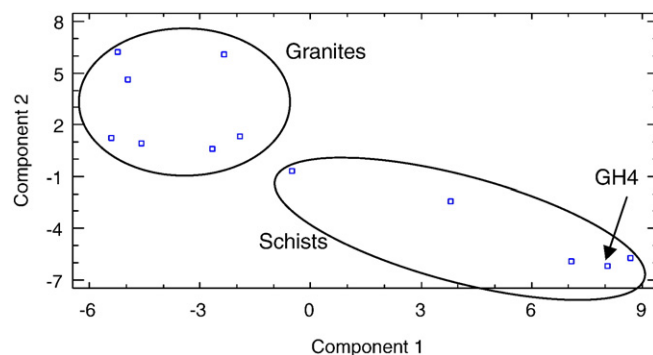


Fig. 3. Component scores (Components 1 and 2) of each plot studied.

these parameters showed higher values in soils over granites than over schists.

- *Component 3* is a dynamic factor related to the mineralization parameters (k constant) and C_L , with positive and negative correlation, respectively.

Fig. 3 shows the graph of scores from the first two components (Components 1 and 2) of each plot studied. Two zones can be differentiated based on parent material; the GH4 site showed an anomalous behaviour, in that its soil properties are closer to soils over schists than over granites.

5. Conclusions

Rainfall amount and bedrock type determined the soil content of basic exchangeable cations; however, parent material mainly influences the relative accumulation of free sesquioxides in soils, giving higher values for Al_{ex} and $Al_{pyr} + Fe_{pyr}$ content on the sites over schists than over granites. This high release of Al and Fe in the soils studied facilitates (in addition to soil acidity) the formation of metal-organic complexes that protects SOM from mineralization. This in turn leads, to SOC accumulation and immobilization of the organically-bound nutrients at the sites with high rainfall ($>1200 \text{ mm yr}^{-1}$) and over schists. Consequently, soils over schists showed significantly higher capacity to accumulate SOC than soils over granites, due to the finer texture (more fine silt + clay content) and a higher acidity that hampers SOM mineralization.

A high capacity of SOC sequestration (up to 185 Mg C ha^{-1}) is observed in the forest soils studied here, contrasting with the limited amount of C sequestered in the forest stand litter. Soils in these forest sites are, therefore, characterized by thick *umbric Ah/AB* horizons.

Acknowledgements

The authors thank the Junta de Castilla y León for allowing the use of forest plots, and the European Union (MEDCOP/AIR and PROTOS/TERI Projects) and the Spanish Fund C.I.C.Y.T. for their economic supports. We are indebted to C. Nolan for revising the English version.

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