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***O solo suporte da produção alimentar, do meio
ambiente e da paisagem***

Ficha técnica

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Appraisal of physical properties of Mediterranean soils in Central Spain in relation with molecular features of organic matter

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Introduction

Soil degradation processes are frequently associated to climate change and to intensive and inappropriate management of soil resources, which have often led to progressive reduction in soil productivity, erosion and desertification. Recent studies have been focused on the assessment of analytical indicators of soil quality. This comprehensive term has been defined as the continued capacity of soil to sustain biological productivity, promote quality of air and water environments and maintain biological activity within ecosystem boundaries and considering specific land use (Carter et al., 1997; Doran and Parkin, 1994).

The assessment of soil status includes independent measurement of soil quality indicators which could be divided into chemical (e.g., pH, salinity, available nutrients, pollutants), physical (e.g., water retention, hydraulic conductivity, bulk density, stable aggregates) and biological (e.g., microbial activity, mineralization rates) (Haynes, 2005). Many of these soil functions and properties are in close connection with soil organic matter (SOM), hence research on its dynamics and molecular composition would represent a key factor in the accurate assessment of soil quality (Gregorich et al., 1994). In semiarid ecosystems, physical processes are of major importance, since low SOM concentrations could result in an increase in bulk density, decrease of soil porosity, water infiltration and hydraulic conductivity as well as to a lesser preservation of soil aggregation, with derived problems of soil crusting, hardsetting and water erosion (Masri and Ryan, 2006).

Although SOM content is widely recognised as an essential component in the assessment of soil quality (Reeves, 1997), it should also be considered that SOM is a heterogeneous mixture of materials, ranging from fresh plant biomass and microbial residues to highly transformed humic substances (Baldock and Nelson, 2000; Stevenson, 1994). These SOM pools display dissimilar physical and chemical properties and have different turnover rates so are involved to a specific extent on the SOM interactions with the total soil solution and soil matrix (Baldock and Skjemstad, 1999).

Objectives

Assuming the above considerations, SOM represents a valuable source of soil quality indicators, provided that it plays a relevant role in the dynamics and function of the whole soil system. The present research approaches a detailed description of the SOM by chemical fractionation and molecular characterization techniques, aiming to shed any light on the soil functions—with special emphasis on physical properties—most closely correlated with specific SOM pools and structural features.

Materials and methods

Soil sampling

For this study samples from up to fourteen soils from continental Mediterranean ecosystems in central Spain were collected. The soils were developed on different geological substrate, climatic conditions, vegetation and use. After removing the litter layer, composite samples from the uppermost horizons were obtained by mixing the soil material from three spatial replicates in each site, to make a representative field sample. Table 1 shows the location of the sampling sites and other general characteristics of the studied soils.

Table 1. General features of the sampled sites

Soil	Location	Geographical coordinates	Altitude m a.s.l.	Parent rock	Vegetation	Soil use	Humus type (Duchaufour, 1975)	Soil classification (FAO, 2006)
A1	Parla (Madrid)	40°15'34"N 3°45'05"W	683	Limestones, marlstones and sepiolite	Brushwood+ Herbaceous	Abandoned	<i>Calcic mull</i>	Calcic Kastanozem
A2	Cantoblanco (Madrid)	40°33'8"N 3°41'22"W	731	Arkoses	Brushwood+ Herbaceous	Abandoned	<i>Calcic mull</i>	Haplic Luvisol
A3	Santa Olalla (Toledo)	40°3'18"N 4°25'57"W	463	Arkoses	Scrubland	Abandoned	<i>Calcic mull</i>	Cutanic Luvisol
C1	Villacañas (Toledo)	39°37'14"N 3°17'55"W	680	Limestones and quartzites	Vineyard	Agricultural	<i>Calcic mull</i>	Petric Calcisol
C2	Santa Olalla (Toledo)	40°4'7"N 4°25'22"W	473	Mudstones and marlstones	Cereal crop	Agricultural	<i>Calcic mull</i>	Calcic Vertisol
C3	Manzanares (Ciudad Real)	38°57'20"N 3°24'19"W	673	Limestones and quartzites	Vineyard	Agricultural	<i>Calcic mull</i>	Petric Calcisol
F1	Guadalix de la Sierra (Madrid)	40°45'35"N 3°41'9"W	940	Granites	<i>Quercus</i> + Grassland	Livestock	<i>Forest oligotrophic mull</i>	Leptic Cambisol
F2	Rascafría (Madrid)	40°54'27"N 3°53'46"W	1187	Gneisses	<i>Quercus</i>	Forest	<i>Forest eutrophic mull</i>	Haplic Cambisol
F3	Rascafría (Madrid)	40°53'35"N 3°53'33"W	1185	Dolomites	<i>Quercus</i> + Grassland	Livestock	<i>Calcic mull-moder</i>	Mollic Leptosol
R1	Bustarviejo (Madrid)	40°51'41"N 3°44'4"W	1316	Gneiss and schists	<i>Quercus</i> + <i>Pinus</i> + <i>Juniperus</i>	Forest	<i>Forest eutrophic mull</i>	Haplic Cambisol
R2	Bosque de Valdelatas (Madrid)	40°32'09"N 3°40'53"W	714	Arkoses	<i>Quercus</i> + <i>Pinus</i>	Forest	<i>Calcic mull</i>	Calcic Luvisol
P1	Rascafría-Peñalara (Madrid)	40°50'2"N 3°57'26"W	2030	Gneisses	High-mountain grassland	Livestock	<i>Oligotrophic anmoor</i>	Hemic Histosol
P2	Rascafría-Peñalara (Madrid)	40°50'17"N 3°57'13"W	1964	Gneisses	Mosses and <i>Carix</i>	Peatland	<i>Oligotrophic peat</i>	Fibric Histosol
P3	Rascafría (Madrid)	40°54'39"N 3°51'55"W	1127	Silt, sand and conglomerates	Herbaceous	Peatland	<i>Mesotrophic peat</i>	Rheic Histosol

General soil analyses

Soil analyses were performed on the fine earth soil fraction (< 2mm) of air-dried samples. Soil colour was determined in wet and dry samples by comparing with the colour sheets in the [Munsell Book of Colors \(1975\)](#). Real density, bulk density and porosity were estimated following to [Blake and Hartge \(1986\)](#). Soil texture was determined with the densimeter method ([Bouyoucos, 1927](#)). To measure soil structural stability, aggregates were subjected to wet sieving for 10 min in the apparatus described by [Kemper and Rosenau \(1986\)](#). Structural stability index (SSI) is calculated as the mass of aggregated soil (> 250 µm) remaining after wet sieving as a percent of the total mass of soil. Soil pH and electrical conductivity were measured in water employing a soil/water ratio of 1:2.5 (w:w) and 1:5 (w:w), respectively ([Chapman and Pratt, 1961](#); [Bower and Wilcox, 1965](#)). Carbonate content was estimated with the Bernard's calcimeter ([Guitian and Carballas, 1976](#)) and active carbonates following to [Drouineau \(1942\)](#). The water holding capacity (WHC) was measured in field conditions at the atmosphere pressure ([Guitian and Carballas, 1976](#)). The concentration of total organic carbon (TOC) in soil was determined by partial wet oxidation in acid medium ([Walkley and Black, 1934](#)) and the Kjeldahl's nitrogen following to [Piper \(1950\)](#). The cation exchange capacity (CEC) was determined at pH:7 by the method proposed by [Hendershot and Duquette \(1986\)](#), and the ammonia concentration was titrated with a selective ion electrode. Exchangeable bases (Ca^{2+} , Mg^{2+} , Na^{+} and K^{+}) were extracted with 1M ammonium acetate solution (pH:7) and then measured by ICP-AES. Base saturation was calculated from the total exchangeable bases and the CEC.

Field analysis

Soil water infiltration was measured in the field during the dry season in order to obtain comparable results at extreme dryness conditions. The method used was first described by Bouwer (1986) and based on the use of a double-ring infiltrometer. The initial infiltration rate or “parameter c ” represents the extent to which water can be retained into soil immediately after a rain event. On the other hand, “parameter a ” is an indirect measure of the total infiltration. Both c and a parameters were calculated from the Kostiakov (1932) equation, $K = c \cdot X^a$, where K represents the infiltration rate (Ir), X the infiltration time, and c and a the above-defined parameters. Total volume absorbed by the soil for the first hour after water input (V1h) was also calculated in order to know the response of each soil against a torrential rain event.

Study of the soil organic matter

Soil samples were previously subjected to lipid (LIP) removal by continuous Soxhlet extraction with petroleum ether (40–60°C distilled hydrocarbons mixture) for 5 hours (Almendros et al., 1996). The resulting soil residue was used for densimetric extraction of the free organic matter (FOM) or light fraction using 0.1M H_3PO_4 (density 1.2 g·cm⁻³). The organic fraction remaining as yellowish solution after removing the FOM was quantified in aliquots and referred to as free fulvic acids (FFA). Isolation and further quantification of the fulvic acids (FA), humic acids (HA) and humin (H) from the resulting soil extraction residue was carried out with 0.1 M $Na_4P_2O_7$ and 0.1 M NaOH (Duchaufour, 1975).

The HA fraction was isolated and purified for its further characterization by elemental analysis followed by visible and infrared (IR) spectroscopies. Concerning visible spectroscopy, the optical density of HA solutions was measured in a concentration of 100 mg·L⁻¹ in 0.02 M NaOH (Kononova, 1982). The E_4 was used as a surrogate of the aromaticity and diagenetic maturity of the SOM, and the E_{465} and E_{665} nm extraction ratio (E_4/E_6) was used as an indicator of the average molecular size or polydispersity of HAs (Chen et al., 1977). Concerning the IR spectroscopy the use of the 2nd derivative spectra was useful to objective measurement of peak intensity (as valleys) precluding problems of baseline tracing. The intensity of the IR peaks was standardized and expressed as total abundances [$\Sigma=100$] of aliphatic structures (2920 and 1460 cm⁻¹), oxygen-containing functional groups (1720 cm⁻¹), N-containing groups (1640 and 1540 cm⁻¹), aromatic structures (1620 and 1510 cm⁻¹), etc. The IR spectra were also useful to identify a more or less defined lignin pattern (i.e. major peaks at 1510, 1460, 1420 and 1030 cm⁻¹) with conspicuous methoxyphenol peaks at 1330 cm⁻¹ (syringyl units), 1270 cm⁻¹ (guaiacyl units). Aromaticity index (ratio between C=C aromatic band at 1510 cm⁻¹ and C–H stretching band at 2920 cm⁻¹) as well as oxidation index (ratio between C=O stretching band *circa* 1720 cm⁻¹ and 1510 cm⁻¹ band) were also calculated.

Results

Characterization of SOM

Figure 1 shows the quantitative distribution of the major soil C-fractions in the soils studied.

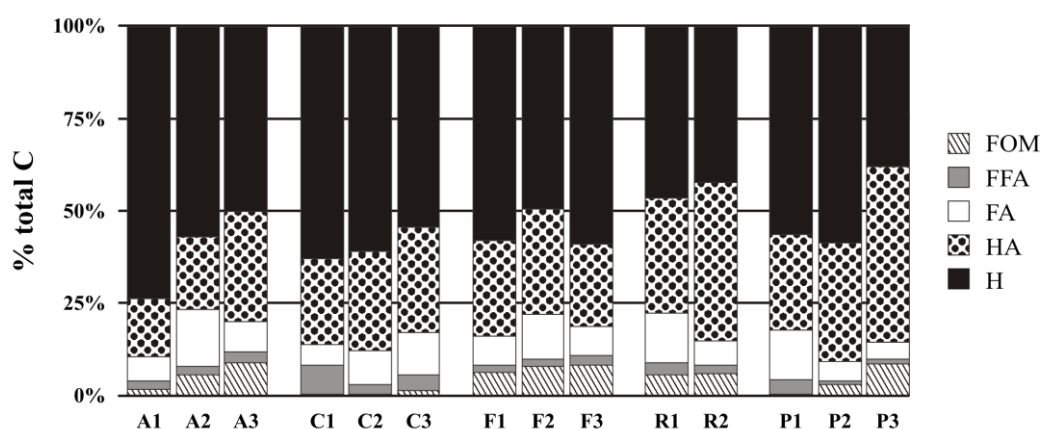


Figure 1. Distribution of total soil C into different organic fractions. FOM, free organic matter with density < 1.2 g·cm⁻³; FFA, free fulvic acid (2M H_3PO_4 -soluble); FA, fulvic acid; HA, humic acid; H, humin. A, abandoned lands (formerly cultivated soils); C, cultivated soils; F, seminatural forest under oak and brushwood vegetation; R, oak forest combined with reforested conifer forest; P, *Histosols* with peatland vegetation.

The results of the elemental analysis (% C, H, N, O) of the HAs are summarized in a classical [van Krevelen's \(1950\)](#) diagram where the atomic H/C vs. O/C ratios are represented in the plane (Figure 2). In this plot it is possible to obtain a clue on the most diagnostic structural features of the organic substances, i.e., the relative amounts of aromatic, alkyl, carboxyl, etc. units, depending on the scores of the atomic ratios of the HA samples in the plain, where maturity, in general, follows a defined trend in the main diagonal towards the origin of coordinates.

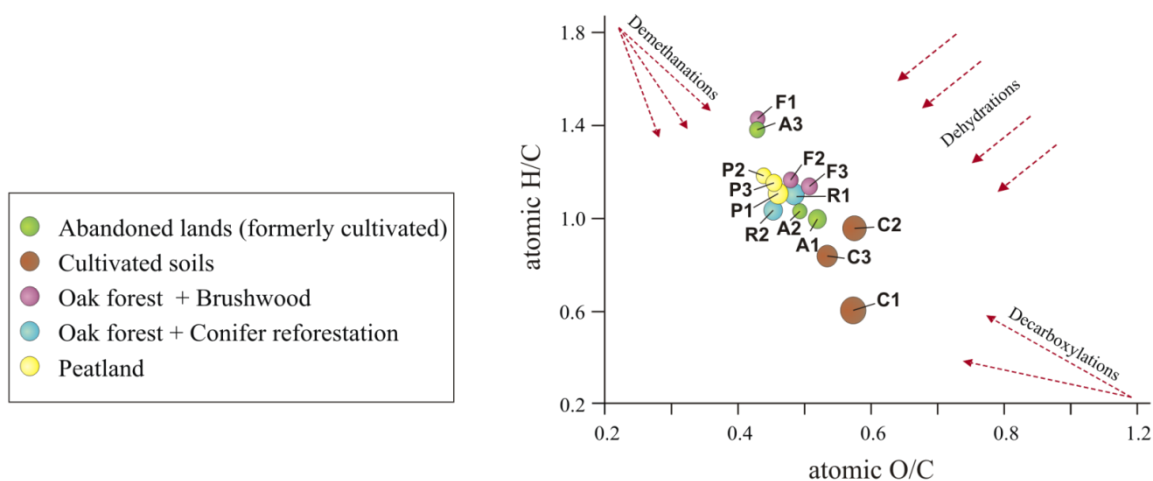


Figure 2. Van Krevelen's diagram applied to results from elementary analysis of HAs from the studied soils. Different soil types are shown with letters explained in the footnote of Figure 1, as well as with different colours. Moreover, the diameter of the circles is proportional to the E₄ optical density, which is considered as a surrogate of the aromaticity of the corresponding HAs.

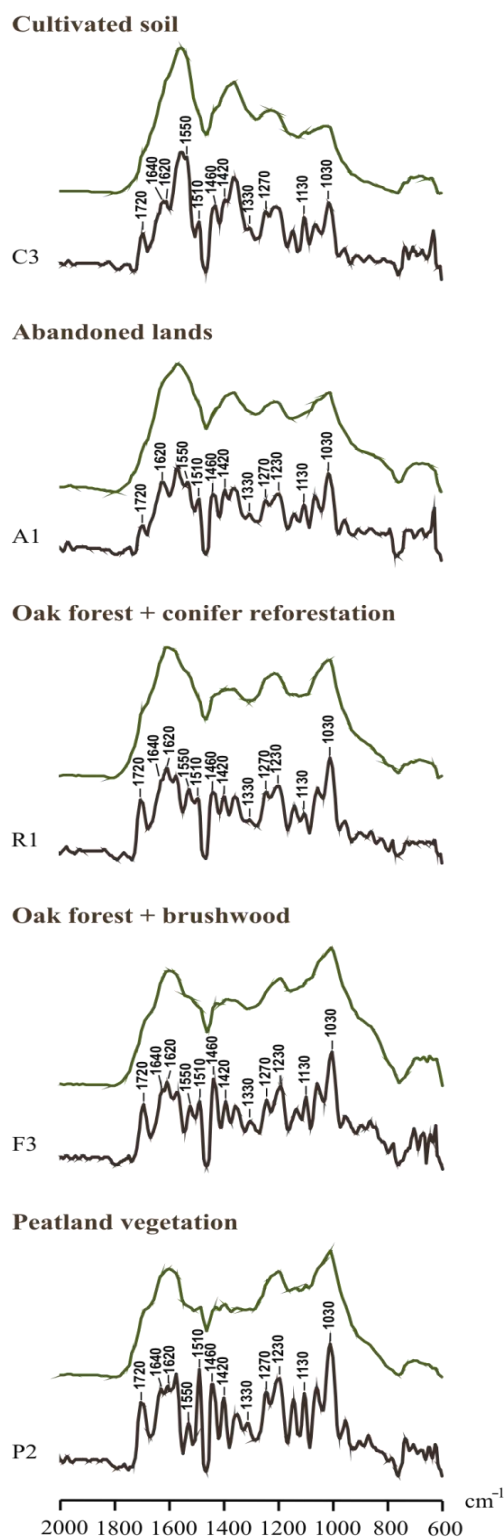


Figure 3. Infrared spectra (2000 and 600 cm^{-1} range) superimposed to its corresponding resolution-enhanced spectra.

The IR spectroscopy applied to soil HAs lead to establish useful relationships between the molecular features of the HAs and the environmental factors with a bearing on the soil C-cycle. In order to improve the pattern recognition in the IR spectra, its resolution was enhanced by a mathematical algorithm based on subtracting the raw spectrum from a positive multiple of its 2nd derivative (Almendros and Sanz, 1992). Figure 3 illustrates a series of IR spectra representative of each soil group, where the spectra are stacked (C3 to T2) in a gradient of progressive concentration of residual lignin betrayed by the above-indicated diagnostic bands.

Statistical analyses

In order to find out characteristic molecular descriptors in the SOM which could be used to forecast some typical soil physical properties which bears on soil quality, a series of linear regression models were used (Table 2). Correlation indices were calculated between soil physical variables and SOM descriptors, consisting of quantitative data for the different humic fractions as well as chemical and spectroscopic data determined in the isolated HAs.

In a second stage, and based on the Pearson's indices in the correlation matrix, a nonlinear ordination was carried out by multidimensional scaling (MDSCAL) (Kruskal, 1964). With this treatment, the different variables can be plotted as points in a plane after a dimensional reduction based on an iterative gradient which yields a final configuration where distances in the plane between pairs of points (variables) are optimized to represent the extent of the similarity between these variables defined by its correlation indices. The resulting plot is useful to illustrate clusters of variables grouped by their colinearity and including both physical characteristics and SOM descriptors showing significant correlation (and suggesting possible cause-to-effect relationships) between SOM and physical variables.

Table 2. Linear correlation indices between variables used to asses soil physical quality in addition to characteristics of the SOM.

		Bulk density	Porosity	WHC	SSI	Param. <i>c</i>	Param. <i>a</i>	Ir	V1h
Composition of SOM	Total organic C	-0.79	0.59	0.95	0.46	-0.34	-0.15	-0.40	-0.31
	Kjeldahl N	-0.79	0.58	0.94	0.46	-0.33	-0.15	-0.39	-0.28
	Soil C/N ratio	-0.58	0.54	0.53	0.31	-0.17	0.32	-0.50	-0.63
	C _{LIP}	-0.21	0.15	0.43	0.00	-0.18	0.16	0.01	0.11
	C _{FOM}	-0.10	0.20	-0.10	0.37	0.19	0.78	-0.32	-0.22
	C _{FFA}	0.47	-0.38	-0.48	-0.38	-0.20	-0.69	0.47	0.42
	C _{FA}	0.15	-0.10	-0.30	-0.10	0.11	0.07	-0.18	0.48
	C _{HA}	-0.37	0.40	0.41	-0.49	0.54	0.07	0.42	-0.38
	C _{HUMIN}	0.22	-0.34	-0.08	0.20	-0.63	-0.33	-0.27	0.14
Structural features of HAs	% C	-0.64	0.57	0.58	0.25	0.31	0.70	-0.19	-0.44
	% H	-0.46	0.40	0.39	0.52	-0.13	0.72	-0.60	-0.49
	% N	-0.11	0.09	-0.12	0.51	0.10	0.54	-0.41	0.14
	% O	0.59	-0.57	-0.46	-0.44	-0.12	-0.77	0.43	0.39
	H/C	-0.40	0.39	0.31	0.50	-0.17	0.70	-0.63	-0.48
	O/C	0.62	-0.59	-0.50	-0.40	-0.18	-0.76	0.38	0.40
	C/N	-0.06	0.06	0.27	-0.49	-0.03	-0.49	0.45	-0.17
	E ₄	0.51	-0.45	-0.36	-0.54	-0.12	-0.87	0.62	0.30
	E ₄ /E ₆	-0.54	0.40	0.66	0.42	-0.11	0.81	-0.62	-0.46
	2920 cm ⁻¹ IR (aliphatic C–H)	-0.42	0.51	0.18	0.17	0.12	0.66	-0.46	-0.46
	1720 cm ⁻¹ IR (carboxyl groups)	-0.39	0.37	0.32	0.22	0.28	0.36	0.05	-0.53
	1640 cm ⁻¹ IR (amides I)	-0.24	0.22	0.16	0.30	0.24	-0.53	0.43	0.13
	1620 cm ⁻¹ IR (aromatic C=C)	-0.35	0.34	0.21	0.39	0.25	0.59	-0.20	-0.45
	1540 cm ⁻¹ IR (amides II)	0.52	-0.44	-0.29	-0.50	-0.24	-0.50	0.36	0.06
	1510 cm ⁻¹ IR (aromatic C=C, lignin)	-0.57	0.55	0.56	0.38	0.16	0.81	-0.40	-0.01
	1460 cm ⁻¹ IR (aliphatic C–H, lignin)	-0.52	0.53	0.37	0.39	0.25	0.91	-0.41	-0.34
	1420 cm ⁻¹ IR (lignins)	-0.67	0.63	0.50	0.33	0.21	0.90	-0.49	-0.20
	1330 cm ⁻¹ IR (guaiacyl)	0.59	-0.55	-0.68	0.21	0.44	-0.33	0.61	0.72
	1270 cm ⁻¹ IR (syringyl)	-0.39	0.44	0.18	0.24	0.31	0.81	-0.40	0.17
	Aromaticity index	0.16	-0.10	-0.31	-0.30	0.02	-0.08	-0.11	-0.27
	Oxidation degree	0.08	-0.08	-0.21	-0.16	0.32	-0.16	0.36	-0.26
	Guaiacyl/syringyl units	-0.65	0.61	0.69	0.17	-0.01	0.89	-0.64	-0.22

* Significant ($P < 0.05$) indices are shown in red. WHC, water holding capacity; SSI, structural stability index; Ir, infiltration rate; V1h, volume absorbed by the soil ($\text{m}^3 \cdot \text{h}^{-1} \cdot \text{m}^2$) for the first hour after water input.

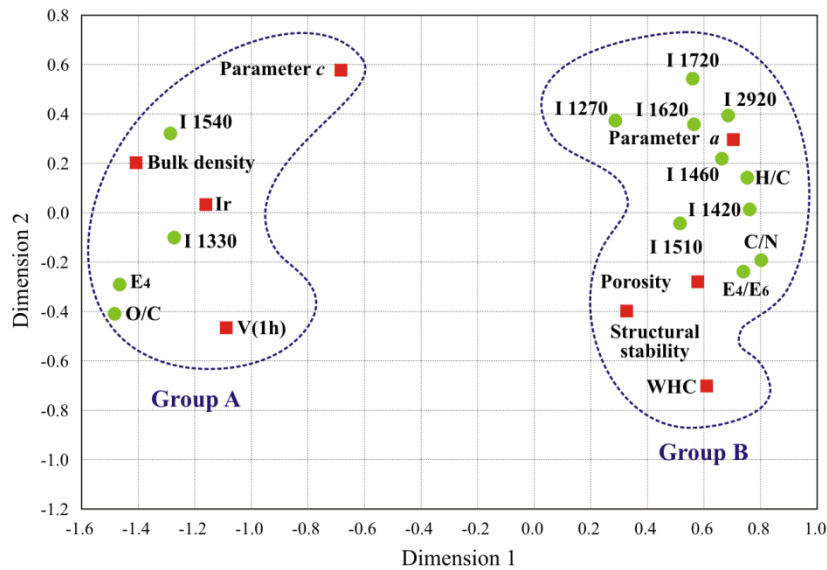


Figure 4. Multidimensional scaling used for automatic classification of the soil physical variables (red solid squares) in addition to the analytical descriptors of soil organic matter quality (green solid circles).

Discussion

The results of the statistical analyses have led to infer a series of variables (soil organic fractions and molecular characteristics of the HAs) which showed significant correlation with soil physical properties. When exclusively considering the results of the linear regression models (Table 2) some properties such as bulk density, porosity, WHC and structural stability were very significantly ($P < 0.05$) correlated with TOC. Apart from this, variability of such physical properties was also explained by the additional contribution of the SOM quality parameters, defined by the percentages of the soil humus fractions and the molecular characteristics of the HAs. In the case of bulk density and porosity, our results suggested that SOM with marked aliphatic character and relatively low degree of humification (i.e., structural resemblance with precursor plant biomacromolecules) was associated to soils with higher total porosity, which was reflected by the significant correlations found between these physical properties and diagnostic SOM characteristics such as soil C/N ratio, E_4/E_6 ratio, intensity of the 2920 cm^{-1} IR alkyl band, etc. In addition, the soil WHC showed clear correlations not only with TOC but interestingly with the relative concentration of HAs. These results supported the previous finding of the positive correlation between WHC and soil C/N ratio, which suggested that the higher evolution of the SOM was reflected in the increased water retention of the soils at field capacity. Concerning soil structural stability, there was also found a statistically significant correlation ($P < 0.05$) between this soil property and SOC. Nevertheless, the results pointed to an important additional amount of total variance which was explained by SOM qualitative descriptors, i.e., those indicating advanced diagenetic transformation of the HAs (comparatively high humification or maturity), which were associated with lower structural stability. This was the case with the concentration of HAs, soil C/N ratio and E_4 optical density of HAs.

Concerning soil hydrophysical variables, linear regression models failed in showing any statistical correlation with TOC. However, some SOM characteristics were correlated with parameter a (indicative of the rate of water saturation) which paralleled the amount of FOM. This indicated that a high level of FOM was associated to rapid water saturation of the soil. Moreover it was found that parameter a was also associated to several characteristics of the HAs in particular H/C and O/C atomic ratios, E_4 optical density, intensity of the 2920 cm^{-1} IR band, intensity of the 1510 , 1460 and 1420 cm^{-1} bands and persistence in HAs of residual lignin signature. The above HA features suggested SOM of weak humification degree and dominance of aliphatic constituents that coincided with soils of high water saturation rates (immediately after the rain events). This effect could be causally associated with moderate water repellency in soils containing HAs with substantial amounts of hydrophobic alkyl constituents.

Otherwise, multivariate statistics (MDSCAL) led to identify supplementary SOM descriptors which explained additional causes of the variability in soil properties even in cases where no simple linear correlations were found between SOM descriptors and physical characteristics. Two dimensional representation of the variables processed by MDSCAL (Figure 4) revealed additional involvement of SOM descriptors in (i) water infiltration rates (Ir), total water volume absorbed by the soil for the first hour (V1h), response of the soil for the early few minutes after the rain event (parameter c) and soil bulk density, which showed clear colinearity with the N-containing groups, the oxidation degree and the E_4 optical density of the HAs. On the other side, (ii) WHC, porosity, structural stability and the rate to which soil saturates with water (parameter a) showed a well defined colinearity with SOM characteristics such as HAs C/N and H/C atomic ratios, E_4/E_6 and the intensity of several bands in IR spectra associated to persistence in HAs of a lignin pattern. These results pointed to two well-defined groups of physical properties in our semiarid soils, either associated to the occurrence of HAs with condensed macromolecular structures and high oxidation (group A) or to a series of SOM properties interpreted as comparatively early stages of humification or maturation (group B) where aliphatic structures were comparatively more accentuated.

Conclusions

The results obtained emphasized the importance of the qualitative characterization of the SOM in order to assess its bearing on soil physical properties. The only determination of TOC ought to be complemented with additional quantitative analyses of the various SOM fractions as well as with molecular level characterization of the HAs, which help to explain additional sources of variability in soil physical properties. In the present study it has been found that the more or less advanced evolution of the SOM (defined by surrogates such as aromaticity, condensation, molecular size and spectroscopic lignin pattern reflecting the extent to which non-decomposed HA precursors remain in its structure) was also correlated in a different way with each of the soil physical variables studied. For instance, the presence of HAs with

predominantly aliphatic character and comparatively low maturity tend to be associated with the successful maintenance of the soil micropores space. These could be postulated to depend on the role of aliphatic SOM constituents in favouring waterproof aggregates through its effect in hydrophobic coatings. Therefore, assuming some cause-to-effect relationships, such correlations could be pointing out to the determining role of HAs in soil organo-mineral interactions and soil water repellence, reflected in the resulting soil physical status.

From a practical viewpoint and in the case of HAs, it was found useful to study analytical characteristics at least at the spectroscopic level, which could be used in forecasting and monitoring the soil physical status as well as for the early diagnosis of possible soil degradation processes.

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