# Multivariate statistical assessment of functional relationships between soil physical descriptors and structural features of soil organic matter in Mediterranean ecosystems

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## ABSTRACT

Current environmental research is paying increasing attention to reliable analytical surrogates of soil quality. In this work a series of molecular features of soil organic matter were studied in different soil types from Central Spain with the purpose of identifying the soil functions most closely correlated with specific pools of soil organic matter and their structural characteristics. Soil physical variables—including bulk density, total porosity, aggregate stability, available water capacity and water infiltration parameters (Kostiakov's equation coefficients)—were determined. The major soil organic fractions (lipids, particulate free organic matter, fulvic acids, humic acids and humin) were quantified using standard procedures and the soil organic matter was characterised by spectroscopic techniques. Statistical data treatments including simple regression, canonical correlation models and multidimensional scaling suggested two well-defined groups of physical properties in the studied soils: (i) those associated with organic matter of predominantly aromatic character (e.g., water infiltration descriptors), and (ii) soil physical variables related to organic matter with marked aliphatic character and comparatively low degree of humification (e.g., porosity, aggregate stability, available water capacity and field air capacity). From the practical viewpoint, the results support the idea that the detailed structural study of the soil organic matter is useful for accurately monitoring soil physical status. The only determination of total soil organic carbon ought to be complemented with qualitative analyses of the organic matter fractions, at least at the spectroscopic level, which to large extent help to explain the origin of the variability in soil physical properties and can be used for the early diagnosis of possible degradation processes.

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## 1. Introduction

Monitoring soil quality is an essential step for preventing degradation processes frequently associated to intensive or inappropriate management of the soil resource. The concept of soil quality has been revised in recent years from a functional perception, being defined as the continued capacity of the soil to sustain biological productivity, preserve the quality of air and water and maintain biological activity within ecosystem boundaries (Doran et al., 1996; Larson and Pierce, 1991). This definition emphasises the value of the soil to perform specific functions. As a result, increasing attention has been paid on the exploration of soil variables which could be readily used as soil indicators (Arshad and Coen, 1992; Doran and Parkin, 1994; Powers et al., 1998; Reynolds et al., 2002). These indicators could be divided into chemical (e.g., pH, salinity, concentration of available nutrients, pollutants), physical (e.g., water retention, hydraulic conductivity, bulk density, stability of aggregates) and biological properties (e.g., microbial populations, mineralisation rates) (Haynes, 2005). Most of these parameters are in close connection with soil organic matter (SOM), which represents a key factor in the maintenance of the soil quality (Gregorich et al., 1994).

Furthermore, in the Mediterranean region, the loss of soil quality is of special concern due to the particular fragility of these ecosystems. Soils developed in Central Spain are characterised by a large range of parent materials, landforms, plant communities and seasonal water regimes but, at the same time, show a series of common features such as shallow horizons, unfavourable physical conditions (limited water availability, hardened horizons, poor soil structure, etc.) and vulnerability to soil erosion due to irregular and frequently intensive precipitation (Rodeghiero et al., 2011), making water availability one of the most important limiting factors.

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The climate largely influences the biological activity, leading to relatively low total organic C (TOC) concentrations in the Mediterranean regions (Rodríguez-Murillo, 2001) and consequently poor soil quality. In this line, the present study tackles the assessment of the quality of different Mediterranean soils—with special attention paid to physical status—by monitoring a set of quality indicators (bulk density, porosity, aggregate stability, available water capacity, etc.). Furthermore, the study of the distribution of organic C among different pools allows recognising soil features particularly affected by definite SOM fractions (i.e., particulate, extractable humic substances, humin…). On further examination, solid-state $^{13}$C nuclear magnetic resonance (NMR), visible and infrared (IR) spectroscopies were applied to demineralised soil samples and to laboratory-isolated humic acids (HAs), allowing qualitative identification of its structural components, and results described comparatively.

Bearing in mind the importance of SOM on soil quality and the peculiarities of the Mediterranean scenario, this research focuses on establishing correlations between soil physical attributes and the SOM in order to assess the extent to which SOM characteristics work as valid predictors in forecasting the physical response in the soils. This exploratory research would lead to establish the basis for the proper selection of organic amendments whose addition to the soil could represent an effective management strategy against degradation processes in Mediterranean areas.

## 2. Materials and methods

### 2.1. Soil sampling sites

Soil samples from fourteen Mediterranean ecosystems with marked continental features in Central Spain were collected. The study area comprises different locations of Madrid and Castilla–La Mancha and lies in the Inner Plateau (*Meseta Central*) of the Iberian Peninsula. Soils are developed on different geological substrates with altitudinal ranges between 470 and 2030 m a.s.l. (Table 1). The mountain landscapes are dominated by acid parental material (granites, gneisses and schists). The foothill areas exhibit detrital sedimentary rocks (arkoses), and the valley regions are defined by characteristic landforms of sedimentary basins (fluvial terraces, alluvial plains, moorlands, etc.) mainly composed of limestone, dolomite, gypsum, etc. The climate is Mediterranean-type with large winter-to-summer temperature contrast and pronounced summer droughts, when the water balance is strongly deficient (80 to 400 mm). Moreover, unreliable and torrential precipitations are frequent (AEMET, 2013). The soils also differed in terms of vegetation (reforested pine tree forest, seminatural evergreen oak forest, Mediterranean brushwood, herbaceous vegetation, etc.) and land use (forestry, agricultural, livestock, abandoned lands, etc.). Table 1 summarises the location and main soil-forming factors in the studied areas as well as the different soil types: Kastanozems, Luvisols, Calcisols, Vertisols, Cambisols, Leptosols and Histosols (IUSS-WRB, 2007) (Table 1 and Fig. 1).

### 2.2. Sample collection and analytical procedures

After removing the litter, and for representative field sampling, soil material was collected from the uppermost organo-mineral horizon (i.e., in which the SOM was physico-chemically interacting with the soil mineral matrix). Composite soil samples were prepared by mixing the soil material (ca. 500 g) from three spatial replicates separated about 10 m in each site. Samples were air-dried at room temperature and sieved to 2 mm to obtain the fine earth fraction.

Soil colour was determined in moist and dry samples by comparing with the Munsell (1975) colour sheets. Soil pH and electrical conductivity were measured in soil/water suspensions (1:2.5, w:w and 1:5 w:w, respectively) (Bower and Wilcox, 1965; Chapman and Pratt, 1961). Considering the large carbonate content in several of the soils under

study, the Walkley and Black (1934) method based on wet oxidation in acid medium, was used to determine the concentration of TOC in soil, whereas the Kjeldahl's method was applied for nitrogen analysis according to Piper (1950). Carbonate content was measured as calcium carbonate with the Bernard's calcimeter (Guitián and Carballas, 1976). Soil active carbonate was also determined with the Bernard's calcimeter, after pre-treatment of 2.5 g soil samples with 0.2 M ammonium oxalate for 2 h in a rotary agitator (Drouineau, 1942). The cation exchange capacity was determined with ammonium acetate solution at pH 7 (Hendershot and Duquette, 1986), and the ammonium concentration was titrated with a selective ion electrode. Exchangeable bases ($Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$) were extracted with 1 M ammonium acetate (pH 7) and measured by inductively coupled plasma atomic emission spectroscopy. Base saturation was calculated from the total exchangeable bases and the cation exchange capacity. Soil bulk density was determined using a cylindrical core of known volume (Blake and Hartge, 1986) and soil particle density was measured with a pycnometer. Soil porosity was calculated from the values of bulk density and soil particle density. Soil texture was determined with the densimeter method (Bouyoucos, 1927) after removing the SOM with 0.5 M hydrogen peroxide and soil dispersion for 16 h in a solution of 0.5 M sodium hexametaphosphate and sodium carbonate. The water retention values of the soils were measured at the field capacity (FC, −0.03 MPa) and at the permanent wilting point (PWP, −1.5 MPa) using a pressure plate apparatus. Available water capacity (AWC) was calculated as the difference between FC and PWP (Guitián and Carballas, 1976). From these measurements, it was also possible to estimate the volume of air stored in the soil at some standardised value of soil water content or matric potential. In this case, this was done at the FC water content by the equation: $100 - (FC / P)$, where the water content at FC was expressed in volumetric units, and P represented the total porosity of the soil. The resulting air-filled porosity was referred to as field air capacity, FAC (Topp et al., 1997). To measure soil structural stability, aggregates <2 mm were subjected to wet sieving for 3 min in the apparatus described by Kemper and Rosenau (1986). Soil particles passing through a 0.25 mm sieve were dried at 60 °C, weighed and referred to as unstable aggregates. The material remaining on the 0.25 mm sieve (stable aggregates + coarse grains) was dispersed with 5% sodium hexametaphosphate. The coarse material was washed with deionised water, dried at 60 °C and weighed. The initial and final weights of aggregates were corrected for the weight of these coarse particles. The water structural stability index (SSI) was calculated as the weight of aggregated soil (>250 μm) remaining stable after wet sieving and referred to as a percentage of the total aggregate weight.

### 2.3. Field analyses

Soil water infiltration was measured in the field during the dry season in order to work under comparable extreme dryness conditions with the different soils. The method used was first described by Bouwer (1986) and based on the double-ring infiltrometer. The infiltration rate was monitored by the decrease of the water level within the inner ring. Water in the outer ring was kept at the same level as in the inner one to prevent lateral flow and promote vertical water movement in the soil. The data (3 field replicates) was used to plot the infiltration curves (infiltration rate vs. time). Using exponential regression functions, the data were adjusted to the Kostiakov's (1932) equation, $K = c \cdot X^{-a}$, where K represents the infiltration rate, X the infiltration time, c the *initial* infiltration rate and a the rate of decline of infiltration. The parameter c informs on the extent to which water can be retained into the soil immediately after the rain event, whereas parameter a informs on the soil hydric saturation (Hemmat et al., 2007). In addition, the average infiltration rate (Ir) after 60 min was calculated as an index of the infiltration capacity of the soil, not only during the first few minutes but also after an extended rain event.