Storage of organic carbon and Black carbon in density fractions of calcareous soils under different land uses

Mireia Llorente [a,*], Bruno Glaser [b], M. Belén Turrión [a]

[a] *Sustainable Forest Management Institute, University of Valladolid-INIA. Avda. Madrid 44, 34071 Palencia, Spain*
[b] *Institute of Soil Science and Soil Geography, University of Bayreuth, Universitätsstr. 30, D-95440 Bayreuth, Germany*

ARTICLE INFO

ABSTRACT

The association between soil particles and their spatial arrangement plays a key role in soil organic matter (OM) dynamics. Density fractionation combined with ultrasonic dispersion enables separation and study of soil OM fractions, considered on the basis of the mechanisms of physical protection: non-physically protected OM (FF), OM occluded into aggregates (OF), and OM stabilized in organo-mineral complexes (DF). In the present study, whole soils and density fractions of calcareous soils under three different management systems — native *Quercus ilex* forest, a *Pinus halepensis* plantation and cropped land — were analyzed for organic C (OC), total N, and Black carbon (BC) content. Black carbon is often considered as a very recalcitrant pool in the soil. However, as well as BC content of soils has seldom been quantified, long-term studies on BC stability are scarce and conclusions about BC stability are not widespread.

About 67% of the total C in the topsoil was lost as a result of converting the natural *Q. ilex* forest to cropped land, 100 years ago. After crop abandon, the stock of OC in the topsoil greatly increased upon reforestation of the studied plot with *P. halepensis*. An average recovery of 71% of the previously lost OC had been recovered, after 40 years of pine plantation. The changes in OC stocks affected mainly the free fraction (FF). Black carbon represented between 1.2 and 2.3% of the TOC of soil with the highest concentrations in OF. The maintenance of BC proportion through land uses suggests an equilibrium between inputs and outputs, and leads to the suspicion that BC could be less stable and less resistant to biodegradation than is often taken for granted.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The reservoir of soil organic matter (SOM) has been proposed as both a significant source and sink of atmospheric CO_2. Because of this, the capacity of soils to accumulate and stabilize organic carbon has received great attention in recent years. In particular, SOM is recognized as an important compartment in C-driven climate change (Sanderman et al., 2003). The long-term storage of C in soil ecosystems is determined by the balance between the rate of incorporation of new organic matter (OM) in soil and the decomposition of SOM (Johnson, 1995). The properties of the soil matrix play an important role in the protection of SOM against biodegradation. It is generally accepted that Black carbon (BC) represents a long-term carbon sink in soil (Kuhlbusch, 1998; Schmidt and Noack, 2000) and that, therefore, BC plays an important role in the global carbon cycle. The amount of available data about BC content of soils is already considerable, but for Mediterranean ecosystems it is still scarce, particularly in calcareous soils.

Calcareous soils, which represent approximately 12% of the world soil resources (FAO, 1996), are of particular interest because of the high stability of their OM. Some studies of the decomposition dynamics of SOM in calcareous soils (García et al., 1997; Llorente et al., 2008; Llorente and Turrión, 2010) have shown that the decomposition rates in such soils are lower than those in other soils with similar organic carbon content.

SOM is heterogeneous and it is possible to distinguish OM fractions that vary in their stability and therefore in their intrinsic decay rates, ranging from a few days to hundreds of years (Schimel et al., 1985). The location of SOM within the soil matrix is considered a major factor determining its turnover (Tamon et al., 2006). There are two main mechanisms of SOM physical stabilization based on the location of the SOM within the soil matrix: (1) physical protection by aggregates; and 2) OM stabilization by organo-mineral complex formation. Physical fractionation methods, such as density fractionation (after ultrasonic dispersion or not), enable separation and study of SOM fractions differing in dynamics, structure and function (Golchin et al., 1994a; Six et al., 2001). Several studies have addressed the effect of land use on the size and composition of different SOM fractions (e.g., Preston et al., 1994; Golchin et al., 1995; Guggenberger et al., 1995; Gregorich et al., 1996; Helfrich et al., 2006). Subdividing SOM according to physical properties highlights the observation that

* Corresponding author. Tel.: +34 639 053 753.
  E-mail address: mireia.llorente@pvs.uva.es (M. Llorente).

physical location within the soil matrix is a key factor determining turnover (Balesdent, 1996).

SOM fractionation by density following ultrasonic dispersion enables separation and study of three different fractions according to the different mechanisms of physical protection (Sohi et al., 2001). Based on these stabilization mechanisms, it is possible to distinguish three SOM fractions: (1) "free" OM (free fraction, FF), isolated before ultrasonic break-down of stable aggregates; (2) OM occluded within aggregates (occluded fraction, OF), isolated after ultrasonic dispersion to break the aggregates; and 3) organo-mineral fraction (dense fraction, DF) recovered as the residual (heavy) material. Many studies (e.g. Golchin et al., 1994b; Six et al., 2002b; John et al., 2005) have shown that the unprotected FF represents a labile SOM pool with a rapid turnover rate. In contrast, OF and DF are more stable pools, with turnover times ranging from decades to centuries. Therefore, density fractions may be affected differently by changes in land use.

In Mediterranean forests, very prone to wildfires, Black carbon is expected to be found in relevant amounts. Thus it is worth to quantify its presence in the overall soil, and also its distribution among the density fractions.

In this study, carried out with soils from a calcareous moor in the region of *Castilla y León* (northwestern Spain), we studied 36 soils, taken from plots under contrasting land uses: native *Quercus ilex* stands, cereal crops, and *Pinus halepensis* plantations. Density separation was carried out in combination (or not) with ultrasonic dispersion in order to obtain SOM fractions according to different mechanisms of physical stabilization. The objectives of the present study were a) to compare the effect of land use on SOM content, b) to study the effect of land use/land cover on the distribution and characteristics of density fractions, and c) to quantify and to compare the effect of land use on BC content and distribution on whole soil and density fractions.

2. Materials and methods

2.1. Site description

The study was carried out in a calcareous moor in the region of Castilla y León (northwestern Spain), UTM: 30T 384465 E 4639001N. The mean annual rainfall in the region is below 400 mm, under a xeric moisture regime, and the mean annual temperature is approximately 12.3 °C. The altitude of the moor is between 800 and 900 m, with low slopes (<7%). The soils (Xerepts, according to USDA, 2006) are quite homogeneous in spite of differences in their land use history. The native vegetation in the studied calcareous soils is Holm-oak wood (*Q. ilex* subsp *ballota*). In the 19th century, most of the natural forest was converted into agricultural land (cereal crops), but since the 1950s, reforestation with *P. halepensis* has been carried out on abandoned agricultural land.

2.2. Sampling procedures

A land use map of the calcareous moor of Castilla y León was elaborated with a GIS (ArcGis 9.0 for Windows) (Fig. 1). The map was used to select the sampling plots on the basis of the following criteria: a) *Q. ilex* forest, cropped land, and *P. halepensis* plantations in adjacent areas; b) minimum area of each land use, 1 ha; and c) establishment of each land use for at least 40 years. For this study, plots of the above-mentioned land uses were selected in three different regions of the calcareous moor, and four representative plots were sampled (0–10 cm depth). A total of 36 topsoils (0–10 cm depth) (3 regions×3 land uses×4 plots) were thus sampled. A composite sample, by joining 3 soil subsamples, was obtained for each plot.. Visible plant residues and roots were removed; soil was air-dried, sieved (<2 mm) and stored in plastic bags until analysis.

For soil characterization, % of carbonates, texture, pH, total N, total C, organic C, and C/N were determined. Total concentrations of soil C and N were determined with an automated C/N analyzer (CHN-2000, Leco). Organic carbon was calculated as the difference between total and carbonate carbon. Soil total calcium carbonates were determined by use of 1 M HCl titrated with 0.5 M NaOH (FAO, 2007).

2.3. Ultrasonic equipment

We used a Branson 450 W Sonicator, equipped with a titanium probe. The probe depth was fixed in 15 mm. The sonicator was calibrated by determining the real power output calorimetrically (North, 1976). The probe output energy was calculated from:

$$P = (m_w c_w + C_{cont}) \, \Delta T \; t^{-1} + Ht,$$

where P is the calculated power (W), m_w is the mass of water (g), c_w is the specific heat of water (4.18 J g^{-1} K^{-1}), C_{cont} is the heat capacity of the container (J K^{-1}), ΔT is the temperature change (K), t is the sonication time (s) and H is the heat loss (J s^{-1}). The heat capacity of the glass beaker (C_{cont}) was determined using the method of mixtures (Morra et al., 1991), according to:

$$C_{cont} = m_1 c_w \left((T_1 - T_2) \, (T_3 - T_2)^{-1} \right) - m_2 c_w,$$

where C_{cont} and c_w are as above and m_1 is the mass (g) of an amount of water heated to T_1 (K), which is added to the beaker that already contained an amount of water m_2 (g) at room temperature (K). The final equilibrium temperature (K) of the water in the beaker is T_3.

The wanted energy output was 300 J ml^{-1} and the corresponding time was calculated from:

$$t = m_s E \; P^1,$$

where t is the sonication time (s), m_s is the mass of soil (g), E is the energy (J g^{-1}) and P is the power output (W).

2.4. Density fractionation of soil

A density fractionation procedure was applied to the topsoils (0–10 cm depth) of the 36 sampled plots. A flow diagram of the method used is provided in Fig. 2. The method follows the concept of Golchin et al. (1994a), who differentiated three degrees of physical protection of OM: FF, non-protected; OF, occluded within aggregates — extractable by sonication; and DF, retained in the dense residual material after sonication.

Briefly, 5 g of soil sample was placed in small centrifuge bottles (50 ml capacity), and 35 ml of NaI at 1.8 g ml^{-1} density were added. The bottles were shaken gently and the floating material, considered as the FF, was then recovered by centrifugation at 8000 g for 30 min at 18 °C, and filtered over a vacuum filter, using a glass fiber filter (Whatman GF/F), by washing with deionized water. The recovered NaI (not mixed with the washing water) was added to the residue remaining in the bottle and the solution was fitted to 1.8 g ml^{-1} density. The bottle was placed in an ice bath and sonicated at 300 J ml^{-1} with a probe-type ultrasonic disintegrator (Branson 450 W).

The floating material, considered as the OF, was recovered by centrifugation and washed in the same way as the FF. The remaining material, considered the DF, was washed with deionized water. All fractions were dried at 40 °C, weighed, ground in a mortar and pestle, and analyzed for C, N and Black carbon contents. Carbonates were analyzed for the whole soils and it was assumed that all carbonates were recovered in the DF. To obtain enough sample to perform analysis, it was necessary to accumulate several replicates of the fractions.2.5. Black carbon analysis.