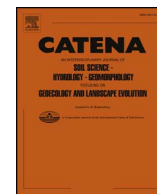




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Seasonal evolution of soil organic matter, glomalin and enzymes and potential for C storage after land abandonment and renaturalization processes in soils of NE Spain

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ABSTRACT

Rates of recovery of soil organic matter (SOM) in abandoned fields of Mediterranean Spain are affected by spontaneous succession in the vegetation, the occurrence of periodic wildfires and lack of forest management. Soil organic matter has a relevant role together with the renaturalization process of shallow soil under vines (V) and olive groves (OL), cork oak (S) and pine (PI) trees, pasture (PR), Cistus (MC) and Erica (MB) scrub in abandoned areas of NE Spain that are sensitive to fire. Physical, chemical, biological and biochemical properties of the soil determined season by season warned against its fragility. Pyrolysis-GC products showed in general moderate to strong positive and negative correlation with soil organic carbon (OC), easily extractable glomalin (EE-GRSP) and total glomalin (GRSP), β -glucosidase and protease, which strengthens the hypothesis that both less and more recalcitrant SOM fractions might be inferred and so there is a scale of potential carbon storage in the environments studied.

Recently abandoned V and OL soil had small OC contents (mean 2.51 ± 0.25 and 15.26 ± 1.39 g kg⁻¹) and GRSP (mean 1.04 ± 0.22 and 2.84 ± 0.53 g kg⁻¹) and large contents of aromatic compounds. By contrast, PR and MB soil had large OC (mean 36.24 ± 0.75 and 37.66 ± 2.38 g kg⁻¹) and GRSP (mean 4.85 ± 0.87 and 3.88 ± 0.76 g kg⁻¹) content and smaller contents of aromatic compounds. This suggested a renewal of active OC in older soil. In fact, EE-GRSP and GRSP of more organic soil were positively correlated with the mineralization indices N/O (Furfural/Pyrrrole) and O/Y (Pyrrrole/Phenol) from active organic compounds ($P < 0.05$ and $P < 0.01$ respectively), and negatively correlated ($P < 0.05$) with the humification index B/E3 (Benzene/Toluene) from recalcitrant organic compounds. Principal component analysis (PCA) identified those environments where soil renaturalization is better. Our findings might indicate the potential for carbon storage in different abandoned shallow soil environments under renaturalization in Mediterranean climate conditions.

1. Introduction

Soil renaturalization implies the recovery of an ecological role by environments which have been under stress caused by land-use change including land abandonment. The dynamics of soil organic matter are essential to this process and may be a useful indicator of the recovery (Dalal et al., 2011). Changes in organic matter pools result from the balance between carbon inputs from biota and carbon losses through decomposition of labile organic compounds related to fast to medium carbon turnover in soil (Heimann and Reichstein, 2008), which affects

soil carbon storage. After land-use change and abandonment in many parts of the Mediterranean region, the spontaneous recolonization by vegetation of large areas has been regarded as the earliest sign of soil renaturalization (Vaccari et al., 2012). However, this process might last decades and is the result of complex biophysical and biochemical interactions. The soil of abandoned land in the Mediterranean region is often degraded because of frequent wildfires that set-back the natural succession of vegetation. In fact, after complete abandonment, in few years fire may largely and severely expand through areas previously functioning as firebreaks. Independently of abandonment time,

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recurrent fire interrupts the fragile equilibrium of renaturalization process affecting both plants and soils (Pardini et al., 2004).

This decreases the soil organic matter content (SOM) and limits the short-term capacity for regeneration (Spanos et al., 2005). In these conditions other soil properties such as the structural stability of aggregates and infiltration rates might be affected by the decline in SOM, which increase soil compaction and water erosion, respectively. Consequently, the recovery of organic matter content and profile development might be delayed, especially in shallow soil with little clay (Dunjó et al., 2004). The monitoring of soil organic carbon (OC) and composition is, therefore, paramount and might contribute to the elucidation of OC dynamics and soil renaturalization.

Recently, Emran et al. (2012b) observed that OC and glomalin (GRSP) pools increased in the oldest abandoned soils in NE Spain resulting in a more stable structure. Further investigations on the same soils (Gisbert et al., 2013) showed that the relations between OC, GRSP and enzyme activity were the most appropriate properties to express SOM dynamics because labile and stable organic compounds coexist.

The GRSP (glomalin related soil protein) is a glycoprotein produced by endomycorrhizal fungi described by Wright and Upadhyaya (1996) and defined as a major carbon pool in soil (Rillig et al., 2001), contributing to the physical stability of soil because of its hydrophobic properties. According to Rillig et al. (2003) the relation between glomalin and the stability of soil aggregates in water was reported to apply better to soil in which organic material was the main binding agent. The same authors showed glomalin to be less effective in improving soil structure where the soil contains carbonates (probably the main binding agents), which might compete with glomalin for soil microsites.

Rillig (2004) suggested that large glomalin concentrations might partially seal the soil pore system and slow down the penetration of water into aggregates. This implies that large glomalin carbon content might contribute to OC preservation, which would be of importance especially in abandoned sandy soil. In such soil, OC fractions have a dominant role in the formation of stable crumb structure together with soil renaturalization (Marinari et al., 2007).

The turnover of organic inputs and native SOM is still poorly understood. Site-specific factors such as vegetation, land use and climatic seasonality might control SOM composition, and so affect its persistence and or degradability. Methodological constraints also hinder elucidation of the complex chemical composition and distribution of SOM. The humic substances in soil have been largely recognized as complex polymeric organic compounds of high molecular weight (polyphenols, proteins, active enzymes, lipids and polysaccharides). Piccolo's (2002) hypothesis on this topic suggested that an apparent large molecular size might arise from aggregation of small molecules held together by weak chemical forces, and improved understanding of the size and type of humic substances. Nevertheless, prediction of SOM dynamics remains uncertain (von Lütow et al., 2006). Schmidt et al. (2011) suggest that soil contains considerably more carbon than the atmosphere or terrestrial vegetation, but the reasons why SOM may persist for a long time or even decompose readily remain poorly understood.

In this study pyrolysis-gas chromatography (Py-GC) was used to explore the composition of the organic matter in abandoned soil. The Py-GC is a fast and reproducible method able to analyse native SOM in soil samples with no prior chemical manipulation, and chemical transformations of SOM in natural conditions can be determined. Stewart (2012) discussed the value of the technique and explained how it uses thermal fragmentation of large molecules into smaller units to obtain a soil molecular fingerprint. The pyrolysis products identified might originate from lignin, polysaccharides, lipids, proteins and other sources such as antioxidants, i.e. polyphenolic compounds that can interrupt the oxidative reaction of SOM degradation, as suggested by Schlichting et al. (2013).

There is no evidence of previous investigations on the chemical composition of SOM in the soil studied in the Cap de Creus Peninsula,

NE Spain. Therefore, we hypothesized that SOM dynamics would be illustrated better by recording the seasonal variation in its OC, glomalin, enzyme activity and products of Py-GC, and by establishing their relationships with the progress of renaturalization of the soil. The aim was to elucidate the potential for carbon storage of the soil after the land has been abandoned.

2. Materials and methods

2.1. Site description

The characteristics of the study area are reported in Emran et al. (2012a) and (2012b). It is located at the Cap de Creus Peninsula, northeast Spain and occupies approximately 30 km² with altitudes ranging from 65 to 320 m above sea level. It is a typical mid-mountain Mediterranean ecosystem covered by old terraced soils. The average annual rainfall is around 450 mm concentrated in spring and autumn, and the temperature ranges between 35 °C in summer and – 5 °C in winter with mean annual values of 16 °C. The tramuntana wind reaches speeds of 100 km h^{–1} often causing fire propagation along abandoned land. The soil mainly formed on Palaeozoic slates is shallow and is classified as a Xerorthent Lithic (Keys to Soil Taxonomy, 2010) with an A, R profile development. The terraced soils were mainly exploited for wine and oil production during many decades and then progressively abandoned due to plant diseases and mechanization of agriculture. Now, 85% of the old terraced land is abandoned and spontaneously colonized by Mediterranean scrub vegetation. Because of frequent fires, the scrub areas are mainly dominated by *Cistus monspeliensis* (more affected by fire) or *Erica arborea* (less affected by fire). However, plant species and density is changing according to periodic wildfire occurrence. The remaining surfaces has stands of cork oak and pine trees (5%), pasture (5%) and recently abandoned vines and olive groves (5%). Seven soil environments were selected within the area representing the diversity of cover: (V) recently abandoned terraced soil under vines (*Vitis vinifera* L.); (OL) olive groves (*Olea europaea* L.); (S) cork oaks (*Quercus suber* L.); (PI) pines (*Pinus halepensis* Mill.); (PR) pasture; (MC) *Cistus monspeliensis* scrub repeatedly affected by fire; (MB) *Erica arborea* scrub not affected by fire since 1984. The soils were all formed on the same parent material and changed in properties according to perturbation by fire or natural succession of vegetation. An area of approximately 0.5 was considered representative of each abandoned soil environment. Physiographical and pedological characteristics are listed in Table 1.

2.2. Soil physical analyses and sampling

Field measurements were done season by season from winter 2010 to autumn 2011. Three determinations per season (on about day 15 of each month, for example December 15th, January 15th, February 15th, for winter) were made at random in each of the soil environments over an area of 0.5 ha of the following properties: bulk density (BD) and soil moisture (SM) by the core method (Forster, 1995). Similarly, for each date at least four soil samples were taken accurately at a depth of 0–10 cm (at the same sampling points as the field determinations) for subsequent laboratory analyses. Soil samples from each soil environment were air-dried, pooled to obtain a composite sample for that date, crushed and sieved to < 2 mm. Consequently, there were three samples per season and a total of 84 soil samples. Texture was determined by Robinson's pipette (Eijkelkamp Agriresearch Equipment, Giesbeek, The Netherlands) and water holding capacity (WHC) was obtained according to Forster (1995).

2.3. Soil chemical analyses

Soil pH, organic carbon (OC) and total nitrogen (TN) contents (Selecta Pro-Nitro, Barcelona, Spain) were determined according to

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