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Influence of *Acacia caven* (Mol) coverage on carbon distribution and its chemical composition in soil organic carbon fractions in a Mediterranean-type climate region

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Abstract

The *Acacia caven* (Mol) is one of the most widespread tree species of the Mediterranean-type ecosystem of South America, forming the "Espinal" ecosystem characterized by a complex and heterogeneous structure like savannas. In South-Central Chile, these Espinal ecosystems include 2 million hectares of agricultural and agroforestry soil. We analyzed the effect of *A. caven* (land coverage) on C-distribution and chemical composition of soil organic carbon (SOC) fractions. Two ecosystems with a gradient of *A. caven* vegetation were studied: a well-preserved Espinal (WPE; with 51–80% land coverage) and Degraded Espinal (DE; with less than 25% of land coverage). The soil under the trees was physically fractionated by wet sieving to obtain light (>212 µm; LF), intermediate (53–212 µm; IF) and heavy (<53 µm; HF) fractions of SOC. The SOC fractions were analyzed by using Fourier-transform infrared spectroscopy (FTIR), natural abundance of ^{13}C relative to ^{12}C ($\delta^{13}C$) and Nuclear Magnetic Resonance Spectroscopy of ^{13}C (^{13}C NMR) techniques. The results indicate that the *A. caven* coverage in the Espinal ecosystem affected the distribution (dry mass of each fraction) and C content of SOC fractions, decreasing both parameters in the more degraded ecosystem (DE), especially in the most labile fractions (LF and IF). Increases in $\delta^{13}C$ value in the profiles of soils, due microbial isotopic discrimination were observed for IF and HF fractions, but not for LF fractions. The SOC fractions showed important chemical structural differences, while the LF fraction was the most reactive fraction (with more carboxylic groups), followed by IF and HF fractions, in consecutive order. The chemical composition of SOC fractions was affected by the *A. caven* coverage. In ecosystems with less land coverage increase of aromaticity and decrease of aliphaticity in LF and IF fractions was noted.

Keywords: Degraded ecosystems; Chemical functional groups; ^{13}C analysis; ^{13}C NMR solid state; FTIR spectroscopy

1. Introduction

The use of physical fractionation in studies of soil organic carbon (SOC) turnover has increased over the past two decades, suggesting that the biological process and the substrate availability for decomposition depend not only on the substrate's intrinsic chemical nature but also, and maybe the most importantly, on the nature of its association with the soil's mineral component (Christensen, 2001). It has been shown that land use and management, climate, and soil texture influence both organic matter content and its composition (West and Post, 2002), where the term 'composition' describes the nature and content of functional groups (e.g. carboxylic, phenolic) present within the organic material. The composition of organic materials contained in soil is controlled by two factors: the chemical composition of the initial organic inputs and the type and magnitude of decomposition processes. Process type is controlled by the kinds of organism present in soil and their metabolism; while process magnitude is regulated by the soil's

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environmental conditions (e.g. soil temperature, water content, pH and redox potential) and the protection offered to the organic materials affected by inorganic matrix interaction (Baldock et al., 1992).

The soil's organic matter is quantitatively and qualitatively characterized using spectroscopic techniques such as nuclear magnetic resonance (NMR), Fourier-transform infrared (FTIR), electron paramagnetic resonance (EPR), ultraviolet–visible (UV–Vis), and fluorescence. These methods present a number of advantages: they are nondestructive, requiring only small amounts of sample; they are procedurally simple and do not require elaborate special sample preparation; and they provide valuable information on molecular structures and chemical properties of SOC (Stevenson, 1994).

Acacia caven (Mol) is a member of a widespread genus in regions with a Mediterranean-type climate in the southern hemisphere (e.g. Chile and Australia) and in other areas where agroforestry systems are based on legume trees such as the Chaco region (northern Argentina, central Paraguay and southern Bolivia). *A. caven* is also one of the most widespread tree species of sub-tropical South America and is found between the latitudes 18° and 36° S and from the Atlantic to the Pacific Oceans. In Chile, the abundance of this specie (anthropogenic formation) is due to the degradation of the native forest. Intensive soil use based on annual crops has allowed the *A. caven* invasion of the sclerophyllous forest, forming the present predominant ecosystem characterized by a complex, heterogeneous structure like savannas, with both herbaceous and woody strata. These *A. caven* dominated areas are actually known as the "Espinal ecosystem", occupying an area of 2 million hectares (Ovalle et al., 1999).

The soil covered by *A. caven* in these ecosystems has direct relationship with the intensity of soil use and the number of years since conversion from native forest, i.e. areas with less land surface coverage by *A. caven* show a greater intensity of soil use (Ovalle et al., 2006), and biological degradation (Muñoz et al., 2007a) and strong diminution of C content (Muñoz et al., 2007b).

The authors of the present study hypothesize that the amount of land coverage by *A. caven* influences the SOC fraction distribution and its chemical composition. The objectives are to: a) determine the carbon (C) distribution in different SOC fractions in *A. caven* ecosystems with different land surface coverage; and b) characterize the structural and functional properties of SOC fractions using a combination of FTIR, $\delta^{13}C$ and ^{13}C NMR techniques.

2. Materials and methods

2.1. Site and soil sampling

The Espinal ecosystems are located in the dry lands of the Mediterranean-type climate region, specifically in the rural area of Cauquenes (35°58′S; 72°17′W) of South-Central Chile. The landscape is characterized by complex slopes that vary from slightly undulated (2 to 8% slope) to strongly undulated (9 to 20% slope). The average precipitation in this zone is 695 mm year^{-1}, with 5 months of summer drought. The average altitude is 170–180 m above sea level (Santibáñez and Uribe, 1993).

Table 1
Soil characteristics of Espinal ecosystems

Ecosystem	Soil depth (cm)	SOC (%)[a]	Bulk density (g cm^{-3})[b]
WPE	0–5	3.5	1.19
	5–10	1.9	1.44
	10–20	1.5	1.48
	20–40	0.8	1.50
DE	0–5	1.9	1.34
	5–10	1.1	1.5
	10–20	0.9	1.53
	20–40	0.5	1.56

[a] Dry combustion.
[b] Cylinder method.

The Cauquenes Series (fine, mixed, active, mesic Ultic Palexeralf) is formed in situ from strongly weathered granite rocks and has clay–loam to clay texture throughout the profile, increasing the clay content from 39 to 59% (0 to 115 cm of depth), with clay translocation in Bt1 and Bt2 layers and the presence of quartz in the profile. Kaolinite is the predominant mineral. These soils have an average of 42% of base saturation and a pH of 5.8; good drainage and an abundant presence of fine and medium pores (CIREN, 1994; Stolpe, 2006).

The detail of Espinal ecosystems is described in Muñoz et al. (2007a). Two sites with different *A. caven* land surface coverage were selected: a well-preserved ecosystem (WPE; 51–80% soil cover, 909 ± 154 trees ha^{-1}) and a degraded ecosystem (DE; less than 25% soil cover, 375 ± 130 trees ha^{-1}). On the average, the trees were 30–60 years old and 2.7 m tall. Livestock in the area is mainly ovine, with an average stocking rate of two sheep ha^{-1} year^{-1}. There are also some areas dedicated to bovine and ovine production.

Soil characteristics are presented in Table 1. SOC was determined by dry combustion and bulk density by using the cylinder method on undisturbed soil samples. Soil sampling was performed in the ecosystems under the canopy of *A. caven* at the beginning of spring (August–September, 2003). Four representative sub-sites were sampled in each one of the ecosystems. At each sub-site, replicated soil samples were taken by selecting two trees, and at each tree a soil sample was collected beneath the tree canopy at a distance equal to approximately half of its canopy ratio (mean canopy diameter = 2.2 m). All soil samples from each site were taken at four depths (0–5, 5–10, 10–20 and 20–40 cm).

2.2. SOC fractionation

The SOC fractionation procedure used was modified from Balesdent et al. (1991) in which the soil was mechanically dispersed, followed by a physical separation through wet sieving. Briefly, 50 g of air-dried soil and 10 small glass balls (6-mm diameter) were placed in 180 ml of distilled water and shaken in a rotator agitator (REAX 2, Heidolph Instrument, Schwabach, Germany) at 50 cycles per minute for 16 h, causing the mechanical rupture of soil macroaggregates. Then, the soil was wet sieved through 53 and 212 μm stainless steel sieves thereby separating three fractions of organic matter: a) light fraction (LF, above 212 μm) that was separated from the sand by flotation