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ORIGINAL ARTICLE

Land use impact on chemical and spectroscopical characteristics of soil organic matter in an arid ecosystem

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Abstract Soil organic matter (SOM) storage and composition in ecosystems may undergo change as a result of long-term livestock and soil cultivation, particularly in arid environments. In this work, we evaluated the alterations produced in both the quantity and quality of SOM due to productive management systems. The impact of land use change on SOM, dissolved and hot water-extractable carbon (DOC and HWC), humic substances (HS), humic acids (HA), fulvic acids (FA) and the infrared and visible spectroscopy of HS were studied at three productive sites: total and selective clearings with livestock (TC livestock and SC livestock), total clearing with irrigated agriculture (TC agriculture), and an undisturbed site located in central-western Argentina. The SOM content was higher at the undisturbed and TC agriculture sites. DOC varied among the study sites only during the dry season, while HWC decreased during the wet season, clearly indicating the lability of this fraction. The concentrations of HS, HA, and FA were reduced (50–75 %) by land use change, with the HS composition determined by infrared spectroscopy reflecting a high quantity of polysaccharides in TC agriculture, while the E_4/E_6 ratio (UV–vis) presented low values at the undisturbed site, indicating a high degree of condensation of aromatic substances. In conclusion, (a) the conversion of native woodlands to livestock systems favored soil C losses, (b) the highest SOM storage recorded in TC agriculture may reflect a greater residue accumulation at the soil surface and (c) the combination of different techniques provided a very good insight into the status of soil degradation.

Keywords Land use · Soil organic matter · Spectroscopical characteristics · Arid ecosystem · Argentina

Abbreviations

SOM	Soil organic matter
DOC	Dissolved organic C
HWC	Hot water-extractable C
HS	Humic substances
HA	Humic acids
FA	Fulvic acids
TC livestock	Total clearing with livestock
SC livestock	Selective clearing with livestock
TC agriculture	Total clearing with irrigated agriculture

Introduction

Land use and agricultural management practices are likely to be affect by human interventions, which may produce important changes in the quantity and quality of soil organic matter (SOM) and consequently have an impact on

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C and N storage (Ghani et al. 2003). It is well known that the conversion from forest to other systems of land uses modifies the C cycle (Sharma et al. 2014), with the rate of soil C losses depending on both the production and the management systems, among other factors (Sharma et al. 2014). In contrast, sustainable land use systems can help in soil C sequestration to reduce the emission of CO_2 (Li et al. 2007), which is important because the increased level of CO_2 in the atmosphere is recognized as one of the most relevant environmental issues of this century (Kumar and Nair 2011; Aweke et al. 2014). To date, virtually all the bibliography concerning soil C sequestration in arid and semi-arid ecosystems has been mainly focused on utilizing the amount of SOM as the sole measure of the ecosystem performance in atmospheric CO_2 reduction. However, in these ecosystems, where the primary biomass production is limited and meteorological events are unpredictable and erratic, the most reliable descriptors should be related to SOM stability (Miralles et al. 2012).

In fact, SOM is the key component of soil as it is the principal source/sink of C in terrestrial ecosystems and has a strong influence on the physical and chemical soil characteristics (Vergnoux et al. 2011). Therefore, the amount of C stored in soil depends on the balance between the input of C from litter or crop residue decomposition and the C losses occurring through biological activities (Abril and Noe 2007). In addition, SOM affects the main processes that take place in soil, such as microbial activities, nutrient release, erosion protection, and the promotion of biological activity, with it also being responsible for the sustainability of many agroecosystems (Masciandaro and Ceccanti 1999; Morán Vieyra et al. 2009; Mujuru et al. 2013). Thus, SOM study is important because allows to evaluate the consequences of replacing the original vegetation on fragile soils, such as in arid ecosystems (Aranda and Oyonarte 2005). In this way, SOM could be used as an indicator of soil degradation due to its productive use (Vergnoux et al. 2011).

There is a wide range of both humic and non-humic compounds in SOM (Prentice and Webb 2010), including a labile fraction with aliphatic substances of low molecular weight (acids, carbohydrates, lipids, etc.) (Marinari et al. 2010), with its fraction components having a rapid turnover rate in the soil and may be easily used as a substrate by soil microorganisms (Ghani et al. 2003; Marinari et al. 2010). The SOM is also composed of a stable fraction of high molecular weight humic substances (HS) (Bayer et al. 2002; Spaccini et al. 2006; Papini et al. 2011; Vergnoux et al. 2011; Vázquez et al. 2013), which are complex and heterogeneous macromolecules and constitute one of the most important components of SOM (Muscolo et al. 2013). HS are produced by both microbial activity and chemical reactions that take place during the decomposition and transformation of litter (Francioso et al. 2002; Spaccini et al. 2006; Muscolo et al. 2013) and are highly resistant to biodegradation due to their strong association with the soil mineral phase. In fact, this is the most stable fraction of SOM (Chen et al. 2007; Bardy et al. 2008).

The HS can be separated into fulvic and humic acids on the basis of their solubilities. Fulvic acids (FA) are soluble in both alkali and acid, whereas although humic acids (HA) are soluble in alkali, they precipitate in acid (Vergnoux et al. 2011; Abril et al. 2013). Accordingly, HA are more polymerized and aromatized than FA, and consequently, the fulvic/humic acid ratio indicates the degree of SOM maturity and the potential mobility of C in the soil system (Aranda and Oyonarte 2006; Guimarães et al. 2013). The SOM pools (labile and stable fractions) are more sensitive indicators of the fertility and of the soil degradation due to productive use than the total SOM content (Vityakon 2007), because labile and stable components are highly dependent on management practice and land use.

Nowadays, many techniques are available to evaluate the quality of SOM components, including UV–vis and Fourier transform infrared spectroscopy (FT-IR), among others (Carletti et al. 2010; Giovanela et al. 2010; Mao et al. 2011; Gezici et al. 2012; Guimarães et al. 2013). These are valuable tools for the characterization of SOM and its components and also to evaluate soil humification processes. Within this context, some numerical indexes derived from these techniques have been proposed in the literature, which have been useful for evaluating the degree of humification in HS extracted from organic materials of diverse origins (Aranda et al. 2011; Miralles et al. 2012). Both FT-IR and UV–vis allow identifying the effects of land use and cropping systems on the humification degree of SOM and also reveal the relative composition and changes in the functional organic C groups throughout the soil.

Arid and semi-arid ecosystems are present in all continents and occupy a great extension of the total land surface (30–40 % approximately) (Bonino 2006; Miralles et al. 2012). In these ecosystems, there exists a delicate balance between the C sequestrated and the biodegradation, which can be easily affected by human activity (Miralles et al. 2012). Over the last 50 years, the arid zones in the central region of Argentina have been turned into areas with agriculture and livestock. For this reason, the reduction of forest in the arid Chaco of Argentina has been associated with the expansion of the agricultural frontier (Bonino 2006). These new cleared areas have been habilitated for extensive livestock systems and high-tech irrigated agriculture with many crop sequences (Zak et al. 2004). Therefore, the analyses of soil quality in arid zones has gained attention in recent years due to environmental issues related to soil degradation (desertification) and the sustainable production considerations of different management systems (Duval et al. 2013). Although there is information available about SOM and HS characteristics in arid regions (Almendros et al. 2005; Aranda and Oyonarte 2005; Abril et al. 2013), few studies have focused on the relationship between the quantity and quality of SOM and its components as surrogated descriptors for evaluating the sustainability of productive management.

In the present study, our objective was to evaluate the changes produced in both the quantity and quality of SOM fractions due to different productive management systems in an arid environment in soils recently habilitated for livestock and agriculture. The understanding of these processes is key for the formulation of criteria for sustainable management and for making management decisions that can reduce the risk of desertification in vulnerable areas with similar characteristics to those studied in this work. In addition, an improved knowledge of SOM characteristics will provide new insights into help determine the factors that control the whole process of humification, which is still awaiting clarification.

Materials and methods

Study area

The study was conducted in a western arid region of Cordoba province (Argentina) in Chancaní Reserve (31°20′S, 65°28′W) and in surrounding areas with similar topographic, environmental and soil conditions (Bonino 2006) (Fig. 1). The climate is warm, highly seasonal, with high temperatures in summer and mild winters (26 and 12 °C means, respectively) and a pronounced dry season (Bonino 2006). The mean annual precipitation in this area is approximately 500 mm (Abril et al. 2013), with 70 % of the rainfall being concentrated in summer (November to March). The dominant soils are Entisols, generally classified according to Soil Taxonomy as mollic Ustifluvent alluvial, loam bulk of neutral pH (Abril et al. 2013). The original or climax vegetation corresponds to the Arid Chaco region, with a predominance of *Aspidosperma quebracho-blanco,* xerophytic woody plants and summer grasses (Abril et al. 2013).

Sampling design

In the study area, we selected four sampling sites: an undisturbed site in a sector of 100 ha in Chancaní Natural Forest Reserve and three neighboring productive sites on the Alamo farm, which had all been cleared in 2004 under different soil management situations in a disturbance gradient (Table 1). Our sampling design took into consideration that the analyzed situations were unique in terms of their management history. Therefore, no true replicates were available (Hurlbert 1984). The soils characteristics were similar in all situations: pH, texture and salinity (means of 7.55, Sandy-loam and 1053 µS cm^{-1}, respectively). As the soil samples were collected from the similar environment with the same management history, then the major differences observed depended only on the characteristics of the production or management system after 2004. At each site, three composite soils samples (15 sub-samples, 0–20 cm deep) were taken randomly on two sampling dates: during the dry season (winter-2011) and the wet season (summer-2012). These samplings were carried out within a week of each other during both seasons. Soil samples were air-dried for 24 h, sieved through a 2 mm mesh, and stored at 4 °C until being processed.

Chemical and biological analyses

The following parameters of each soil sample were analyzed: (a) total soil organic matter (SOM) content, using the wet method of Walkley and Black (Nelson and Sommers 1996); (b) dissolved organic C content (DOC), by extraction of 10 g of soil adding 30 mL of distilled water and centrifuging for 20 min at 3000 rpm (Zhang et al. 2006); (c) hot water-extractable C (HWC), by extraction of 10 g of soil, adding 30 mL of distilled water, incubating for 16 h at 80 °C and centrifuging for 20 min at 3000 rpm according to Zhang et al. (2006) and (d) HS, by fractionation following the same method to obtain the HA and FA fractions, based on the solubility in acid and alkali (Marinari et al. 2010).

The respiratory activity of soils (CO_2 emissions) was determined in situ. These measurements were taken on the same day over a period of 24 h through airtight chambers, with the CO_2 emissions being measured with a gas detector according to Abril and Noe (2007).

Fourier transform infrared spectroscopy

Aliquots of HS in solution were air-dried using a rotary evaporator for spectroscopic analyses. Pellets were obtained by applying a pressure of 10,000 kg cm^{-2} for 2 min to a mixture of 1 mg HS and 200 mg KBr of spectroscopic grade (Chen et al. 2007; Agnelli et al. 2008; Fernandez-Getino et al. 2010). The FT-IR spectra of each sample (acquired between a range of 400 year–4000 cm^{-1}) were measured with a spectral resolution of 2 cm^{-1}, with 24 scans being averaged to reduce the noise. Spectra were registered at room temperature and recorded using a FT-IR Bruker IFS 28 spectrophotometer, normalized and processed with Opus Spectroscopy Software.

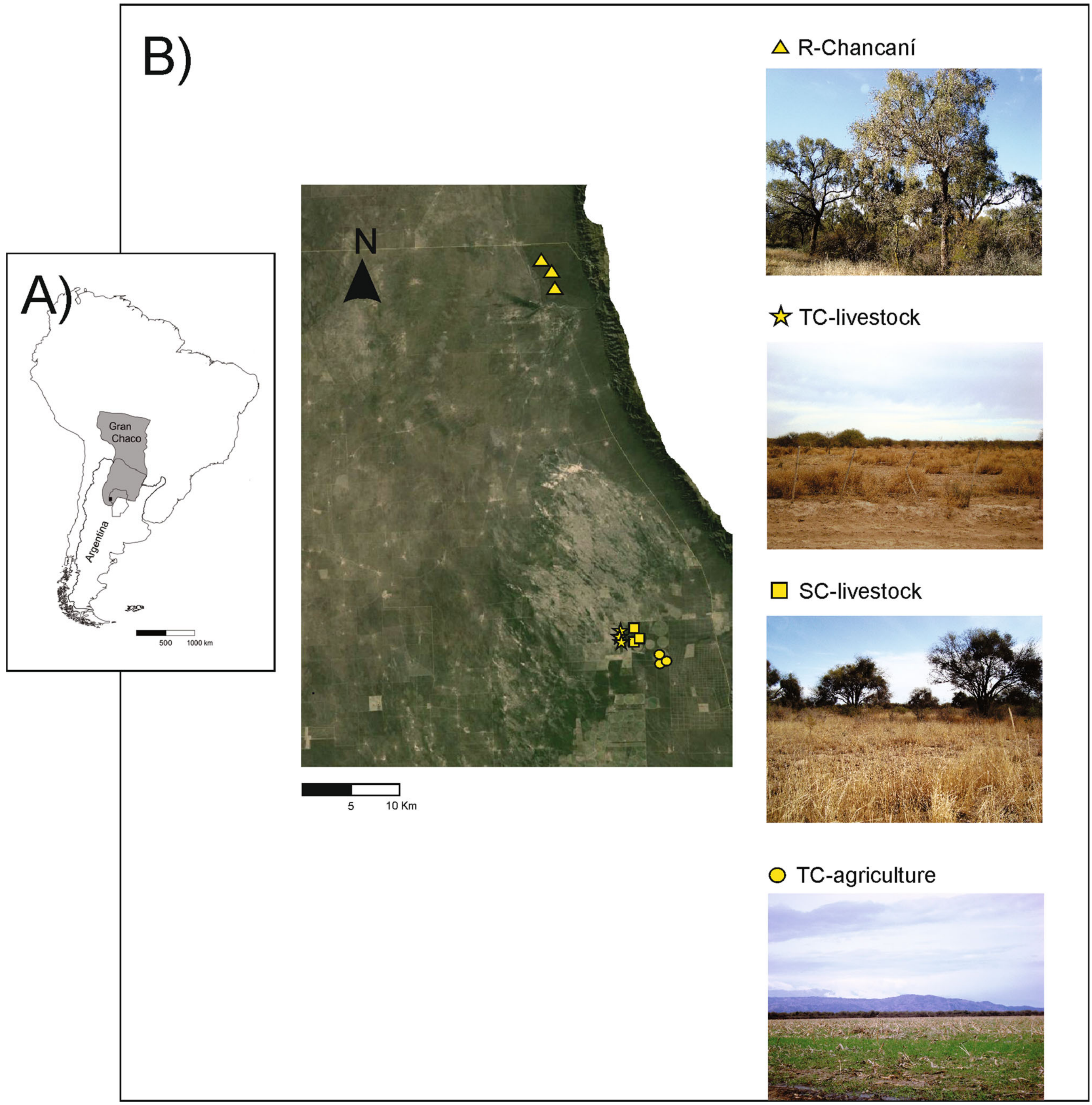

Fig. 1 Map of study site locations. **a** The map shows the area represented by the Gran Chaco forest in Southern South America (*in gray*), the framed area corresponds to Córdoba province in central Argentina and the study area in the southern portion of the Gran Chaco region (*in black*). **b** Detail o the study area showing the locations of the sampling plots

UV–visible spectroscopy

A Shimadzu UV-240 apparatus was used to obtain the E_4/E_6 ratio (at absorbances of 465 and 665 nm of the visible spectra) (Miralles et al. 2012). The HS solutions (obtained with 1 g of soil and 80 mL of NaOH (0.5 mol L^{-1}) were mixed by mechanical stirring for 2 h. After this procedure, all the solutions were left to stand for 24 h under refrigeration at 4 °C and the supernatant was recovered by centrifugation at 3000 rpm for 30 min. Finally, the absorbance of the HS was measured in the aqueous solution (supernatant) (Zbytniewski and Buszewski 2005; Miralles et al. 2012).

Table 1 Management practices in different sites of Arid Chaco of Córdoba, Argentina

	R-Chancaní	TC livestock	SC livestock	TC agriculture
Clearing characteristics	No	Total with extensive livestock	Selective with extensive livestock (30 % tree cover)	Total Crop sequence: maize/wheat/potato
Productive management	No	*Cenchrus ciliaris* Pasture sowed	*Cenchrus ciliaris* Pasture sowed	No-till: in maize and wheat Biannual conventional tillage: potato
Irrigation	No	No	No	Sprinkling irrigation
Fertilization	No	No	No	Potato: 200 kg N ha^{-1} and 33 kg S ha^{-1}

R-Chancaní Chancaní natural forest reserve, *TC livestock* total clearing with livestock, *SC livestock*, selective clearing with livestock, *TC agriculture* total clearing with irrigated agriculture

Calculations and statistical analyses

The following parameters were calculated from the soil data: CMI (carbon mineralization index): C–CO$_2$/C-SOM; humification index HI: HA/FA (Abril and Noe 2007; Vergnoux et al. 2011; Guimarães et al. 2013).

To assess the effects of land use at each site, the data were examined using the analysis of variance (ANOVA) and Fisher's test (LSD) to obtain the respective least significant differences between means at $p < 0.05$. The normality of the distributions was corroborated using the Shapiro–Wilks test, and differences between seasons for each parameter were tested using a paired t test ($p < 0.05$). A principal component analysis (PCA) and Pearson's correlation were performed to examine relationships and patterns between the analyzed data. All statistical analyses were performed using the Infostat software for windows (Di Rienzo et al. 2013).

Results and discussion

Quantitative impact on SOM pools under different land use systems

Total carbon content

It is widely accepted that in arid zones the productive use of soil results in SOM loss (Almendros et al. 2005; Abril and Noe 2007). In our study, the total SOM content varied from 19.80 to 57.20 g kg^{-1} being higher in undisturbed soils (R-Chancaní) and the TC agriculture site in both sampling seasons (Table 2). The conversion of forest to cropland or livestock has been reported to produce the destruction of soil structure and an increased mineralization of organic matter, which is no longer physically protected within the aggregates from microbial decomposition leading to loss of SOM (Islam and Weil 2000). However, in our case, cultivation did not cause any depletion in the total SOM content compared to undisturbed soils. This appears to be contradictory, since the TC agriculture site is plowed every 2 years because sowing potatoes causes aggregates to break and results in an increase in the proportion of microaggregates, silt and clay-sized particles in the soil (Six et al. 2000; Lal 2005). Nevertheless, it is important to remark that this crop is irrigated and fertilized, which might mask the SOM loss and the effect of tillage due to an increment of labile pool (Panettieri et al. 2013) causing an increase in C returning to the soil (Paul et al. 1991). In fact, the labile pool increases quickly due to plowing and reacts to changes in soil practices, but also this rise can be exhausted very rapidly by biological oxidation in soil (Sommer et al. 2011). Related to this, several studies have demonstrated that some soil properties depend on the amount of organic matter accumulated in different fractions much more than on the total SOM content (Hevia et al. 2003). Because of the large pool size, SOM changes slowly for the same management practices (Sainju et al. 2012) and its content does not allow cultivate sites to be distinguished from undisturbed sites. However, various pools of SOM are usually more sensitive to changes in land use than the total soil C (Six et al. 2002). Our results demonstrated that systems with clearing for livestock had a significant reduction (from 42 to 63 %) of the SOM content during the dry season, and also during the wet season (from 12 to 37 %), suggesting that livestock has a high impact in terms of a reduction in SOM (Table 2).

Labile carbon fractions

Dissolved organic C has been proposed as an indicator of the C available to soil microorganisms, in spite of the fact that the factors controlling its concentration and bioavailability are not well understood (Lundquist et al. 1999; Zhang et al. 2006). The DOC varied among the study sites during dry season with TC agriculture presenting the

Table 2 Soil organic matter and fractions of the soil studied at 0–20 cm depth

Sites	SOM (g kg^{-1})		DOC (mg kg^{-1})		HWC (mg kg^{-1})		HS (g kg^{-1})		FA (g kg^{-1})		HA (g kg^{-1})	
	D	W	D	W	D	W	D	W	D	W	D	W
R-Chancaní	53.80 a	40.20 a	256.00 b	250.78	3056.61 a†	1305.33 a†	16.90 a	10.60 a	5.90 a	4.80 a	10.90 a	5.80 a
SC livestock	31.20 b	35.10 ab	205.40 b	182.02	664.11 b	698.06 b	5.60 c	3.40 c	2.00 b	2.50 b	3.40 c	0.90 b
TC livestock	19.80 c	25.20 b	142.65 c	156.72	518.79 b	480.73 b	3.80 c	2.80 c	2.10 b	1.40 b	1.80 c	1.40 b
TC agriculture	57.20 a	40.60 a	457.18 a	255.45	4341.75 a†	1639.36 a†	9.90 b	7.10 b	2.20 b	2.80 ab	7.80 b	4.30 a

Each value is the mean of three composite samples with different letters indicating statistically significant differences among sites, LSD test ($n = 3$; $p \leq 0.05$)

SOM soil organic matter, *DOC* dissolved organic carbon, *HWC* hot water-extractable carbon, *HS* humic substances, *FA* fulvic acids, *HA* humic acids, *D* dry season (winter), *W* wet season (summer), *R-Chancaní* Chancaní natural forest reserve, *TC livestock* total clearing with livestock, *SC livestock* selective clearing with livestock, *TC agriculture* total clearing with irrigated agriculture

† Indicates significant differences between seasons for each sampling site ($p < 0.05$)

highest values, while the lowest values were observed in TC livestock (Table 2). This is in agreement with some other authors (Marinari et al. 2010; Benbi et al. 2015), who observed that DOC was unable to discern the effect of management on semi-arid or arid soils.

The correlation between the DOC and SOM contents showed that the DOC concentration increased linearly in the top soil with increasing SOM content ($R^2 = 0.80$; $p \leq 0.002$). This concurs with Zhang et al. (2006), who found high correlations between DOC and SOM at both undisturbed and cultivated sites.

During HWC extraction, the DOC, microbial biomass, soluble soil carbohydrates, and amines are all extracted from soil (Ghani et al. 2003). In our study, HWC varied in both seasons with the pattern: R-Chancaní = TC-agriculture > SC-livestock = TC-livestock (Table 2). HWC represents the most easily degradable fraction of SOM and has therefore been suggested as the most appropriate stability indicator of SOM to reflect the land use effects (Schulz 2004). Differences in the HWC fraction in soils under differing management systems indicate different patterns of root exudation between crop residues or litter and also the amount and type of C input in the soil (Campbell et al. 1999; Benbi et al. 2015). As the content of HWC was significantly higher at the TC agriculture site than at the other livestock sites, this increases the possibility that the greater total SOM was due to the input of a large amount of labile residues during harvesting and plowing.

HWC revealed a completely different behavior to that of DOC, allowing sites cleared for livestock to be distinguished from the undisturbed site in both sampling seasons. The decrease in HWC during the wet season clearly indicated the lability of this fraction due to leaching and/or microbial degradation. In the dry forests of central Argentina, the high content of HWC can be a result of both the low deposition of litter (due to the low primary productivity and high presence of perennial species) and weather conditions (high temperatures and very contrasting dry-wet cycles), which promote pulses of decomposition (Abril and Noe 2007; Abril et al. 2013).

Recalcitrant carbon fractions

The HS compositions showed some significant changes as a result of the presence of different types of productive management, which also involved changes in the type of vegetation (Aranda and Oyonarte 2005). HS revealed the following pattern: R-Chancaní > TC-agriculture > SC-livestock = TC-livestock in both sampling seasons (Table 2), with the stable SOM (HS) corresponding to approximately 17–20 % of SOM, which is in agreement with data found by Abril et al. (2013) in surrounding areas in the Arid Chaco of Córdoba. However, the values reported in our study are lower than those mentioned in other arid and semi-arid zones (34 % in the Spanish desert: Aranda and Oyonarte 2005, and 40 % in the African savannas: Almendros et al. 2005).

In our study, the FA and HA losses showed different patterns. The undisturbed site (R-Chancaní) presented 50 % more FA content compared with the other productive sites. However, the analysis of the HA suggested different C patterns of accumulation at the studied sites. The TC agriculture site lost approximately 34–40 % of its recalcitrant component (HS) compared to the undisturbed site (Table 2). In contrast, sites with clearing for livestock lost approximately 68–80 % of HS compared to the undisturbed site during both the dry and wet seasons. These results concur with most related which have reported a reduction in SOM and in its fractions when forest is converted to other land uses (Navarrete and Tsutsuki 2008; Guimarães et al. 2013). The fact that the livestock sites lost the greatest proportion of the recalcitrant component of SOM is due to the stability of HS in soils being related to the regular addition of organic matter, which in turn determines the formation of stable humus forms. Therefore, even the minimal alterations in total C input, management and soil quality (which in turn affect breakdown rates) can affect the C dynamics in different systems (Guimarães et al. 2013).

Ratios involving humic substance fractions

The relationships found between different components of HS can be interesting when studying the effects of land use or soil management on soil quality. The ratio between humic and fulvic acids (HI: HA/FA) reflects the mobility of soil organic C (Guimarães et al. 2013), with a higher or lower degree of humification, being related to the C content and aromaticity of HA (Aranda and Oyonarte 2005). In this study, the HI varied from 0.57 to 3.59, with the highest value at the TC agriculture site occurring during the dry season (Table 3). The high values (more aromaticity) recorded imply a greater degree of humification and the accumulation of a smaller proportion of FA, which may be explained by the increase in the oxidative burst of SOM due to the mechanical disruption associated with the impact induced by the production management (Miralles et al. 2012). This oxidative process begins by attacking the more labile fractions of the recalcitrant SOM (FA). In fact, the values found here for the TC agriculture site were higher than those obtained in other arid/semi-arid environments, which only varied from 1.22 to 2.10 (Aranda and Oyonarte 2005).

CO_2–C emissions and C mineralization index

In both sampling seasons, the CO_2 emissions were higher at the TC agriculture site, with the CO_2 emissions increasing by more than twice during wet season at all sites (Table 3). This increase in CO_2 emissions in the wet season can be explained by the effect of precipitation and temperature increase (means of 17 °C in winter vs. 32 °C in summer) (Rochette and Angers 1997), as these cause a rise in the biological activity of the soil.

The high CO_2 emissions at the TC agriculture site may have resulted from the practice of moldboard plowing of the soil. Indeed, Rochette and Angers (1997) reported that plowing increased CO_2 emissions during tillage due to the degassing of soil CO_2. In addition, the incorporation in the fall of fresh maize residues increased the CO_2 losses compared with a non-tilled control. Thus, management practices that contribute to increase the relative rate of decomposition of soil C and plant residues cause greater net soil respiration (Rochette and Angers 1997; Paustian et al. 2000).

The C mineralization index (CMI) varied among the studied sites in both sampling seasons. In the dry season, the highest values were observed at productive sites, while the lowest value was found at the undisturbed site. In contrast, during the wet season, the highest value occurred at the TC livestock site and the lowest at the undisturbed site. In addition, the CMI varied between sampling seasons for all study sites (Table 3). Thus, the CMI was a sensitive indicator of the productive impact and was also useful to establish the differences between the productive management systems. Values of CMI near unity indicate a balance between the mineralization/humification processes in the soil (whereas those less than one indicate a tendency to accumulate SOM with values greater than one revealing a tendency for SOM loss).

The CMI at the undisturbed site had a value of approximately one (equilibrium), while at the productive sites (especially during the wet season) the CMI rose sharply to values greater than one due to the high CO_2 emissions related to the available SOM content and optimal conditions for microbial degradation (temperature and moisture). Therefore, during the wet season (summer), a major net loss of SOM occurred due to the predominance

Table 3 Soil respiration, C mineralization index and humic substance index of the soil studied at 0–20 cm depth

Sites	Soil respiration (mg CO_2/soil g^{-1} day^{-1})		CMI		HI (HA/FA)	
	D	W	D	W	D	W
R-Chancaní	0.16 b†	0.37 c†	0.79 b†	0.98 d†	2.00 ab	1.21 a
SC livestock	0.12 b†	0.73 b†	1.09 ab†	2.76 c†	1.75 b	0.57 b
TC livestock	0.14 b†	0.63 b†	1.15 a†	8.85 a†	1.03 b	1.19 a
TC agriculture	0.49 a†	1.07 a†	1.12 a†	3.60 b†	3.59 a†	1.81 a†

Each value is the mean of three composite samples with different letters indicating statistically significant differences between sites, LSD test ($n = 3$; $p \leq 0.05$)

CMI C mineralization index, *HI* humification index, *HA* humic acids, *FA* fulvic acids, *D* dry season (winter), *W* wet season (summer), *R-Chancaní* Chancaní natural forest reserve, *TC livestock* total clearing with livestock, *SC livestock* selective clearing with livestock, *TC agriculture* total clearing with irrigated agriculture

† Indicates significant differences between seasons for each sampling site ($p < 0.05$)

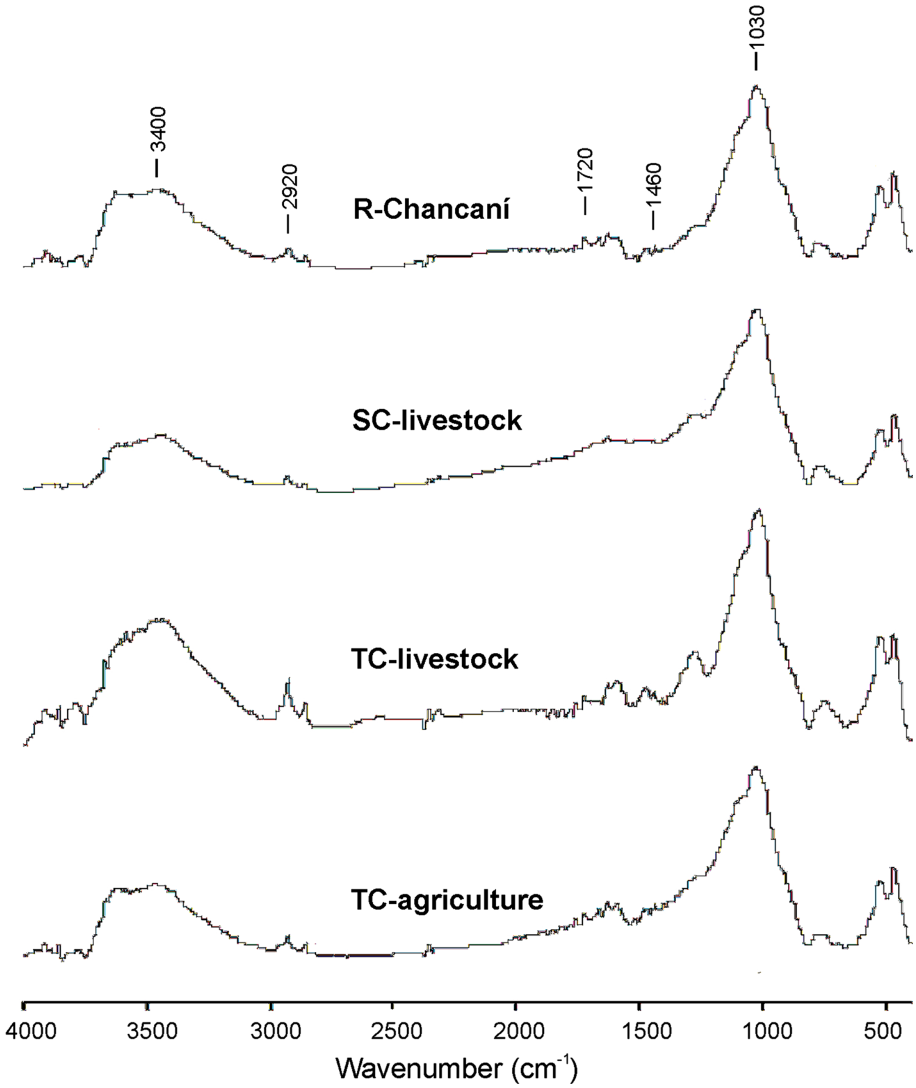

Fig. 2 Normalized IR spectra of HS of the soil studied at 0–20 cm depth

of mineralization of the C soil, probably favored by the high moisture and temperature.

Qualitative impact on SOM pools for different land use systems

Infrared spectroscopy of HS

The assignment of the principal absorption bands in the infrared spectra was based on various studies (Smith 1999; Canellas et al. 2001; Simeoni et al. 2003; González Pérez et al. 2004; Brunetti et al. 2007; Fernández-Getino et al. 2010; Giovanela et al. 2010; Aranda et al. 2011; Moraes et al. 2011; Polak et al. 2011; Gezici et al. 2012). In this study it was possible to observe the same general pattern in the IR of all the HS studied, thus suggesting similar chemical structures (Fig. 2). In the fingerprinting region below 1000 cm^{-1}, assignments to concrete functional groups are more complicated due to the absorption of impurities from the HS.

Taking into account the assignments reported above, these bands can be checked as descriptors for the proportion of: OH groups (I_{3400}: relative intensity of the band at 3400^{-1}), alkyl groups (I_{2920}: means of the relative intensity of the band at 2920^{-1}), carboxylic acid groups (I_{1720}: means of relative intensity of the band at 1720^{-1}), aliphatic groups (I_{1460}: means of relative intensity of the band at 1460^{-1}) and carbohydrate-like structures (I_{1030}: means of relative intensity of the band at 1030^{-1}) (Miralles et al. 2012) (Table 4). Our semi-quantitative data from the IR spectrum peak intensities supported some of the above results, such as:

(a) Concerning the O-containing functional groups, all spectra revealed an unspecific 3400 cm^{-1} stretching band for H-bonded O–H groups (I_{3400}). A great homogeneity during the dry season was observed,

Table 4 IR band intensities of HS from dry and wet seasons of the soil studied at 0–20 cm depth

Infrared band (wavenumber cm^{-1})										
Sites	I_{3400}		I_{2920}		I_{1720}		I_{1460}		I_{1030}	
	D	W	D	W	D	W	D	W	D	W
R-Chancaní	1.16 (0.31)	0.38 (0.08)	0.52 (0.12)	0.20 (0.05)	1.38 (0.14)	0.00	0.89 (0.23)	1.98 (0.40)	0.70 (0.06)	0.96 (0.32)
SC livestock	1.32 (0.56)	1.83 (0.34)	0.55 (0.09)	0.83 (0.20)	1.29 (0.19)	0.00	0.90 (0.10)	1.99 (0.35)	0.67 (0.12)	0.45 (0.07)
TC livestock	1.14 (0.44)	0.65 (0.10)	1.08 (0.39)	0.73 (0.23)	1.42 (0.11)	0.00	0.75 (0.17)	1.98 (0.55)	0.34 (0.05)	0.39 (0.09)
TC agriculture	1.12 (0.25)	1.02 (0.15)	0.62 (0.15)	1.07 (0.45)	1.40 (0.22)	0.00	0.75 (0.08)	1.99 (0.25)	1.59 (0.85)	0.85 (0.21)

Absorption units in full-scale normalized spectra

Each value is the mean of three composite samples

Standard error determined for $n = 3$ ($p < 0.05$ in brackets)

I_{3400} relative intensity of the band at 3400^{-1}, I_{2920} relative intensity of the band at 2920^{-1}, I_{1720} relative intensity of the band at 1720^{-1}, I_{1590} relative intensity of the band at 1590^{-1}, I_{1460} relative intensity of the band at 1460^{-1}, I_{1030} relative intensity of the band at 1030^{-1}, *D* dry season (winter), *W* wet season (summer), *R-Chancaní* Chancaní natural forest reserve, *TC livestock* total clearing with livestock, *SC livestock* selective clearing with livestock, *TC agriculture* total clearing with irrigated agriculture

whereas during the wet season, a quantitative reduction in the proportion of OH groups (I_{3400}) at the undisturbed site (R-Chancaní) occurred (Table 4).

(b) The absorption in I_{2920} is attributed to the asymmetric and symmetric C–H stretching of methyl and methylene groups of aliphatic skeleton and has been used to estimate the aliphatic content of the samples (Aranda and Oyonarte 2005; Giovanela et al. 2010). In the present study, the TC livestock and TC agriculture sites showed a prominent peak with a relative intensity higher than at other sites in both the dry and wet seasons. In contrast, the other sites presented a greater homogeneity for aliphacity (Aranda and Oyonarte 2005) (Table 4). This result is very relevant because there are few studies that have evaluated the spectroscopic changes in HS due to land use at different seasons.

(c) The presence of carboxylic groups was also shown by FT-IR spectra through bands assigned to the stretching of $C = O$ bonds of acid, ketones and aldehyde compounds (signal at 1700–1720 cm^{-1}) (Table 4). This region of the spectrum presented the most representative bands during the dry season with the band intensities being similar among the different studied sites (Table 4).

(d) Bands detected in the range 1480–1444 cm^{-1} corresponded to the bending vibration of the deformation of (CH) aliphatic groups (CH_2 and CH_3) (Giovanela et al. 2010) (Table 4). In both, the dry and wet seasons, the bands presented similar intensities between the studied sites, although the dominant band in this region of the spectrum was found during the wet season (Table 4).

(e) Finally, the signal at around 1080–1030 cm^{-1} has been previously assigned to C–O stretching of polysaccharide or polysaccharide-like structures (Giovanela et al. 2010).

The higher relative intensities of these bands in the FT-IR spectra of the TC agriculture site may have been related to the decomposition of cellulose, which is also found in higher plants that enter the soil during plowing (Giovanela et al. 2010). In contrast, the livestock sites showed small peaks and the lowest intensity in this spectrum region (Table 4).

UV–vis spectroscopy

The mean values obtained for E_4/E_6 (ratio of the absorbance at 465 and at 665 nm) and $\Delta \log K$ coefficient are shown in Table 5, which varied between 3.81–5.94 and 2.98–6.85 in the dry and wet seasons, respectively.

The lowest values of these parameters were obtained at the R-Chancaní site during both sampling seasons. For the TC livestock site, the highest values were found in the wet season and the coefficient values $\Delta \log K$ was around 0.67, following the similar E_4/E_6 pattern. These results are in agreement with the values found for HS at the R-Chancaní site, suggesting a higher maturation of HS at this site than the others (Aranda and Oyonarte 2006; Miralles et al. 2007; Giovanela et al. 2010; Miralles et al. 2012).

Table 5 UV–vis spectroscopic properties of humic substances of soil studied at 0–20 cm depth

Sites	E_4/E_6^a		Δ log K^b	
	D	W	D	W
R-Chancaní	3.81 b	2.98 c	0.57	0.54
SC livestock	4.75 a	4.76 b	0.68	0.65
TC livestock	5.94 a	6.85 a	0.75	0.72
TC agriculture	4.12 a	4.60 b	0.70	0.70

Each value is the mean of three composite samples with different letters indicating statistically significant differences between sites, LSD test ($n = 3$; $p \leq 0.05$)

R-Chancaní Chancaní natural forest reserve, *TC livestock* total clearing with livestock, *SC livestock* selective clearing with livestock, *TC agriculture* total clearing with irrigated agriculture

[a] $E_4/E_6 = \text{Abs}_{465\ \text{nm}}/\text{Abs}_{665\ \text{nm}}$

[b] $\Delta \log K = \log \text{Abs}_{465\ \text{nm}}/\log \text{Abs}_{665\ \text{nm}}$

Comparatively, all the productive sites presented high values for this ratio, revealing a lower degree of aromaticity and condensation, and thereby indicating a relatively high presence of aliphatic structures (Aranda and Oyonarte 2005; Miralles et al. 2007, 2012).

Multivariate analysis

Table 6 Summary of the PC analysis for SOM components

Eigenvectors	PC1	PC2
SOM	0.35	0.12
HS	0.36	−0.14
HA	0.37	−0.10
FA	0.18	−0.45
DOC	0.30	0.35
HWC	0.05	0.54
HI	0.15	0.35
$C\text{–}CO_2$	0.31	0.22
CMI	−0.31	0.14
E_4/E_6	−0.32	0.12

SOM soil organic matter, *HS* humic substances, *HA* humic acids, *FA* fulvic acids, *DOC* dissolved organic carbon, *HWC* hot water-extractable carbon, *HI* humification index (HA/FA), *C–CO$_2$* CO$_2$ emissions, *CMI* C mineralization index, *E$_4$/E$_6$* ratio absorbance 465 nm/absorbance 600 nm, *PC* principal component

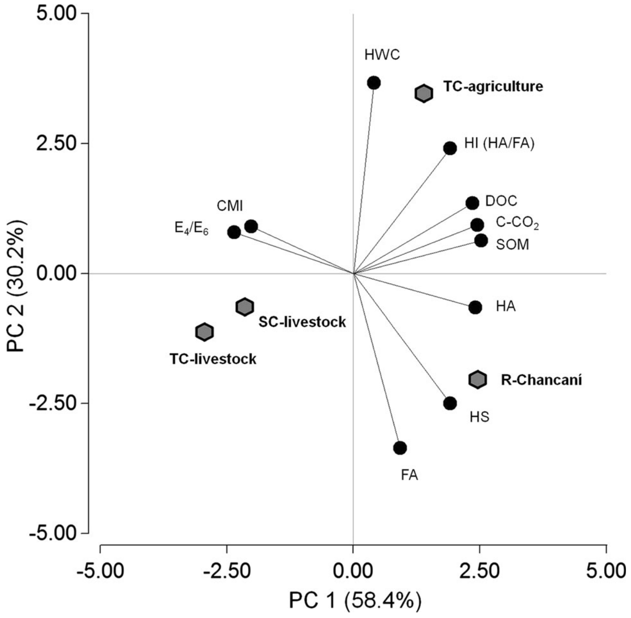

Fig. 3 Principal component analysis (biplot showing variable loadings as lines pointing to the direction of increasing value for the variables, and sample scores shown as symbols). *SOM* soil organic matter, *HS* humic substances, *HA* humic acids, *FA* fulvic acids, *DOC* dissolved organic carbon, *HWC* hot water-extractable carbon, *HI* humification index (HA/FA), *C–CO$_2$* CO$_2$ emissions, *CMI* C mineralization index, *E$_4$/E$_6$* ratio absorbance 465 nm/absorbance 600 nm, *PC* principal component, *R-Chancaní* Chancaní Natural Forest Reserve, *TC livestock* total clearing with livestock, *SC livestock* selective clearing with livestock, *TC agriculture* total clearing with irrigated agriculture

The principal component analysis (PCA) constructed from all the variables analyzed showed that the first two components may explain 88.6 % of the total variation. The first component (PC1) accounted for 58.4 % of the variation with higher weights for SOM, HS and HA, with the second component (PC2) explained 30.2 % of the total variance with the greatest weight for the HWC (Table 6). Moreover, the PCA clearly separated the R-Chancaní and TC agriculture sites from the both livestock sites (TC livestock and SC livestock) (Fig. 3). In addition, the undisturbed site was positively associated with the recalcitrant fraction (HS, HA and FA content), while TC agriculture site was positively associated with the labile fraction (HWC) (Fig. 3; Table 2). This separation is expected, since the undisturbed site showed the higher values of litter compared to the productive sites (Abril et al. 2005). It is widely know that the amount of litter deposited have a great influence on the proportion and stability of SOM and its components (Egli et al. 2007; Abril et al. 2013). Thus, the association between HWC and TC agriculture can be explained by the input of labile residue during plowing (Abril et al. 2013). Furthermore, both livestock sites were associated with higher CMI and E_4/E_6 index and lower quantity of total (SOM), labile (HWC) and recalcitrant carbon (HS, FA and HA) compared to the other sites (TC agriculture and R-Chancaní) (Fig. 3; Table 2). Similarly, a recently study done in Gran Chaco revealed that historic logging and grazing decreased SOM content, but increased CO$_2$ release per soil organic carbon unit (Conti et al. 2016).

Conclusions

- The combination of quantitative and qualitative methods provided a very good insight into the status of soil degradation due to different productive management systems in arid regions.
- The quantity and quality of SOM was differentially affected by the type of land use regime: compared to the undisturbed site (R-Chancaní), livestock regimes decreased SOM quantity, while agriculture regime decreased SOM quality, principally through increasing the labile carbon fraction.
- The clearing for livestock caused the most negative short term changes. However, the TC agriculture was probably the most unstable system in the long term, due to stable SOM being masked by an increase in the labile component. Further, studies about the effects of this type of management on the physical characteristics of the soil should now be carried out considering factors such as aggregates and stability. It should be noted that when these sites lose profitability, they are abandoned, resulting in the total loss of soil fertility and desertification.
- Summing up, our results indicate that this approach could be used worldwide to evaluate both the short- and long-term impact of various productive practices on soils of arid ecosystems, which would allow management guidelines to be established. Changes in the chemical and structural properties of soil humic substances suggest that the arid ecosystem is sensitive to different soil uses.

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