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Chemical Composition and Stocks of Soil Organic Matter in a South Brazilian Oxisol under Pasture

Graciele S. Santana,[a] Deborah P. Dick,*,[b] Michely Tomazi,[c] Cimélio Bayer[a] and Aino V. A. Jacques[d]

[a]Department of Soil Science, [b]Institute of Chemistry, and [d]Department of Forage, Plants and Agrometeorology, Federal University of Rio Grande do Sul (UFRGS), Bento Gonçalves Av., CP 7712, 91540-000 Porto Alegre-RS, Brazil

[c]Embrapa Agropecuária Oeste, CP 449, 79804-970 Dourados-MS, Brazil

Este estudo investigou a composição química e distribuição da matéria orgânica do solo (SOM) em compartimentos de Oxissolo sob pastagem nativa sem queima há 41 anos (NP), pastagem nativa sem queima há oito anos (BP), pastagem nativa em solo com calcário e adubado, sem queima há 41 anos (AP), e mata nativa (NF). Os estoques de carbono (C) e nitrogênio (N) no solo e nos compartimentos físicos foram determinados e a composição química da SOM foi investigada por espectroscopia de infravermelho com transformada de Fourier (FTIR) e análise termogravimétrica. Entre os ambientes sob pastagem, AP apresentou maiores estoques de C e de N no solo e nas frações leves. A fração pesada de BP apresentou maior índice de aromaticidade, o que pode ser devido à presença de carbono pirogênico. O sistema AP apresenta uma alternativa sustentável para sequestrar carbono em comparação com as práticas de queima da vegetação em sistemas de pastagens nativas no sul do Brasil.

This study evaluated the chemical composition and distribution patterns of soil organic matter (SOM) of Oxisol under native pasture without burning for the last 41 years (NP), native pasture without burning for the last eight years (BP), native pasture in soil amended by liming and fertilization and without burning for the last 41 years (AP), and native forest (NF). Stocks of carbon (C) and nitrogen (N) in the whole soil and in physical pools were determined and SOM composition was investigated by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis. Among the pasture environments, AP presented the greatest C and N stocks in soil and in the light fractions. The heavy fraction of BP presented the greatest aromaticity index, and this can be related to the presence of pyrogenic carbon. Concerning soil carbon accumulation, AP represents a sustainable alternative in relation to the practice of vegetation burning in the management of native pastures in southern Brazil.

Keywords: physical pools, soil amendment, pasture burning, chemical recalcitrance

Introduction

In the last ten years, concern about global warming, which is caused by increasing emissions of greenhouse gases (GHG) from anthropogenic activities, is growing among the scientific communities. In Brazil, GHG emissions due to the change of land use and because of agriculture represent approximately 75, 91 and 94% of the total Brazilian emissions of CO_2, CH_4 and N_2O, respectively.[1]

Deforestation in the tropics usually causes a reduction of around 30% in soil carbon (C) stocks when crops are introduced and about 12% when the forest area is converted into grassland.[2] However, tropical and subtropical pastures, either native or cultivated, have a great potential to accumulate C below ground when they are adequately managed.[3] The high C input and the protection of soil organic matter (SOM) promoted by perennial grassland show the importance of pastures in C sequestration. This effect is related to the extensive root system of grasses, which allows efficient cycling of nutrients and greater soil aggregation.[4] The accumulation of C provided by pasture

*e-mail: debby.dick@gmail.com

depends on the soil type and on the intensity of applied management practices, such as grazing intensity and pressure, dry forage cutting, irrigation, soil amendment and vegetation burning. Improvement of pastures by use of conservation management practices in tropical pastures (Brazil) has promoted an increase of soil C stocks at a rate of 0.61 Mg C ha^{-1}.[5] In these works, C stocks increase was assigned to a higher forage production as the result of a good soil fertility status.

Burning of vegetation is a common practice employed either to clear the field,[5] or to promote the re-growth of vegetation after winter in subtropical regions.[6] Vegetation burning usually promotes an immediate increase of soil nutrient availability after burning. However, in general, up to 90 days after the fire this effect ceases and nutrient concentration in soil tends to decrease if no further soil amendment is performed. Additionally, overgrazing may have a higher impact on C accumulation in pasture environments than fire or the type of forage species.[7]

Different land uses also affect the distribution of SOM in different soil physical pools. Influence of management systems on the composition of SOM physical pools was observed by several studies, and these pools, especially the free light fraction (FLF), are highly sensitive to land use and soil management.[8,9] Among the lighter fractions, the occluded light fraction (OLF) shows longer mean residence time in soil, mainly due to its physical protection within the aggregate.[10] In the case of the introduction of cropland on a grassland or in a forest area, the SOM decomposition of the OLF is promoted by the disruption of the aggregate.[11] The fraction associated with soil mineral particles (heavy fraction, HF) is considered the most stable, with a higher mean residence time in the soil, which is generically assignable to three stabilization mechanisms: biochemical recalcitrance, physical protection promoted by soil aggregation and organo-mineral interaction.[12]

The chemical composition of SOM in physical pools is also an important factor governing its dynamics in the environment. Concerning vegetation burning, a lower content of biochemically labile SOM and a higher association of N in more stable organic forms were observed in frequently-burned pasture in comparison with the unburned environment in a Mediterranean soil.[13] Moreover, in a tropical soil (Cerrado region, Brazil), charred material was identified in the OLF, but according to the authors this material is readily degraded in the soil as soon as the aggregate is disrupted by soil disturbance.[14]

In previous studies, the influence of different pasture managements on soil chemical characteristics of a highland subtropical Oxisol was observed. The improvement of soil nutrient content by the application of fertilizer and liming promoted the increase of forage production in comparison with the non-amended environment.[6] Moreover, the most recently fire-affected environment presented lower forage productivity and different forage species comparing to the environment not affected by fire in the last 41 years.[15] Nevertheless, information about the effect of pasture management on SOM dynamics in highland soils is still scarce. Therefore, aiming to shed some light on the impact of pasture managements on the SOM stocks and its chemical composition in subtropical environments, this study determined C stocks in the soil and in the physical pools of a highland Oxisol from Southern Brazil under different pasture managements. The chemical composition of SOM and its thermostability were investigated by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). For comparison, soil samples from a native forest in the same region were also analyzed. This study focused on the 0-5 cm layer, since frequent vegetation burning of pastures affects mainly the surface layer.[16]

Experimental

Study area and soil sampling

The study area is located at André da Rocha City, Rio Grande do Sul State (28º38'S and 51º34'W), Brazil, at about 900 meters above sea level. The climate is mesothermal with an annual mean temperature of 14.1 °C and rainfall of 2470 mm year^{-1}.[17] The soil is classified as a Rhodic Ferralsol (FAO) with heavy clayey soil texture in the 0-5 cm layer (90 g kg^{-1} sand, 300 g kg^{-1} silt and 610 g kg^{-1} clay). The studied environments, whose main characteristics are summarized in Table 1, consist of native pasture without mowing and burning for the last 41 years and grazed with an average of 1.2 livestock ha^{-1} yr^{-1} (NP), native pasture without mowing and burning for the last 8 years and grazed with an average of 0.5 livestock ha^{-1} yr^{-1} (BP), native pasture without burning for the last 41 years, grazed with an average of 1.2 livestock ha^{-1} yr^{-1} and amended by liming and fertilization in the last 17 years (AP) and native forest (NF). After 24 years of ceasing fire, the AP environment received a total of 8 Mg ha^{-1} of lime and 10 kg N ha^{-1}, 60 kg P ha^{-1} and 30 kg K ha^{-1} in the first 7 years. Afterwards, fertilization maintenance was performed when necessary for a period of 10 years until soil sampling. All pasture environments have been subjected to biennial burning immediately after the winter (September) for at least the past 100 years before ceasing fire, and belong to local farmers. The grazing was conducted either in a rotational manner or as continuous grazing depending on the time of the year.

The native vegetation represents a transition zone between grassland and *Araucaria* sp forest. The dominant species in each environment are: NP-*Sorghastrum* spp., *Paspalum notatum* F1 and *Eringium horridum* Malme; AP-*Paspalum paniculatum* and *Paspatum notatum*; BP-*Piptochaetium montevidense*, *Andropogon selloanus* (Hack) and *Schizachirium tenerum* Nees.[18]

In each environment, within an area of 150 m × 150 m, three sites were selected for field replications and a pit of 50 × 50 × 50 cm deep was opened in each site. The chosen sites were representative of each environment and were located at the same slope position. Disturbed soil samples from the 0 to 5 cm layer of the three inner walls of each pit were collected resulting in a composite sample (3 samples per pit) in each field of about 2 L. Prior to soil sampling the above ground vegetation residues (forest floor and grassland) were removed. Soil samples (three field replicates) were air dried and ground in order to pass a 2.0 mm sieve. Some chemical and physical characteristics of the soil are given in Table 1.

Soil organic carbon and nitrogen stocks

Total C and N contents were determined by dry combustion (975 °C) in triplicate (Perkin Elmer 2400) and the C/N weight ratio was calculated. The C content was assigned exclusively to SOM, because all soil samples were carbonate free.

The stocks of total soil organic carbon (C_{soil}) and of total soil nitrogen (N_{soil}) (Mg ha^{-1}) were calculated following the procedure of Gatto *et al.,*[19]

$$C_{soil} \text{ or } N_{soil} = (Conc \times \rho_b \times T)/10 \qquad (1)$$

Here, C_{soil} or N_{soil} is the total soil organic carbon or total soil nitrogen stocks (Mg ha^{-1}), Conc is the element concentration (g kg^{-1}), ρ_b is the field bulk density (g cm^{-3}) and T is the thickness of the soil layer (cm). The bulk density of the soil under native pasture (NP) was used as a reference for the calculations of C stocks of all environments.[20]

SOM density fractionation

The density fractionation of SOM was performed according to Conceição *et al.*,[21] with soil samples < 2.0 mm. Approximately 10 g of air-dried soil were placed in a 100 mL centrifuge tube containing 80 mL of sodium polytungstate (SPT) solution with density of 2.0 g cm^{-3}. The tube was closed with a rubber stopper and gently inverted five times to release the FLF located between aggregates. The suspension was centrifuged at 2000 *g* during 90 minutes and the supernatant containing the FLF was filtered under vacuum in a 0.45 μm glass fiber filter (Whatman GF/A, 0.45 μm), having been previously weighed. The material on the filter was washed with distilled water, followed by a 0.01 mol L^{-1} CaCl$_2$ solution to remove the SPT, and finally by distilled water (200 mL) to remove the remaining CaCl$_2$. The filtered SPT solution was returned to the tube containing precipitated soil, and the suspension was sonicated (Sonics Vibra-Cell VC 750) at 630 J mL^{-1} to break up aggregates, and consequently release the OLF. After soil dispersion, the suspension was centrifuged and filtered as performed with the FLF. The residual soil (HF) remaining in the tube after the separation of the light fractions was washed with distilled water (200 mL) and with 0.01 mol L^{-1} CaCl$_2$ solution. The separated fractions were oven-dried at 50 °C, weighed and ground. The contents of C and N of the light fractions (FLF and OLF) were determined by dry combustion. After subtracting the weight of the filter, the C and N stocks (Mg ha^{-1}) of the FLF and OLF were calculated, following the procedure also applied to the whole soil. The complete

Table 1. Soil properties of the 0-5 cm layer of the Oxisol, C/N ratio of the vegetation and annually produced dry matter of the environments: native pasture without burning for the last 41 years (NP), native pasture without burning for the last 8 years (BP), native pasture on amended soil (AP) and native forest (NF)

Site	pH H$_2$O	C/N[a] veg.	BD[b] / (g cm^{-3})	P[c] / (mg kg^{-1})	Ca	Mg	K	Al	CEC[d]	DM[e] / (kg ha^{-1})
							Exchangeable ion			
							(cmol$_c$ kg^{-1})[f]			
NP	4.60	22	1.25	4.57	2.77	2.13	0.73	2.63	8.26	9,555
BP	4.70	62	1.23	4.47	1.30	1.17	0.32	4.93	7.72	3,665
AP	4.90	n.d.	1.36	15.0	8.57	5.37	0.42	0.80	15.15	9,148
NF	4.20	18	1.07	9.50	2.43	0.97	0.24	5.53	9.17	n.d.

[a]C/N veg: C/N ratio of the dried vegetation (Dick *et al.*, 2008); [b]BD: bulk density; [c]P, available P estimated by Mehlich-1; [d]CEC: effective cation exchange capacity; [e]DM: Mean annual dry matter production until 2001 (Heringer and Jacques, 2002), [f]cmol$_c$: centimol of charge; n.d.: not determined.

removal of SPT from the HF is not always attained, and this fraction may remain contaminated by this reagent. Therefore, the contents of C and N contained in the HF were determined by the difference between the element content in the soil and the respective content in the two light fractions. The SPT extract after sonication showed a light yellow color indicating the presence of soluble organic compounds from the soil. Here, we assumed that these compounds were adsorbed onto the clay fraction and therefore they are included in the calculation of C content of the HF.

10% hydrofluoric acid treatment

Prior to the FTIR (Shimadzu FTIR 8300) and to the TG analyses, the SOM physical fractions were treated with 10% (v/v) hydrofluoric acid solution.[22] This treatment concentrates the organic fraction and avoids the interference of the inorganic matrix in the spectra and thermograms. The analyzed soil samples contain kaolinite and goethite,[15] which absorb in the same infrared spectral region and decompose in the same temperature range (30 to 700 °C)[23] as the organic fraction. The loss of organic carbon in surface horizons of Oxisols due to the hydrofluoric acid treatment can be as high as 40%, but the obtained results have shown that this loss does not show a significant preference for any carbon group.[24] Following the procedure adopted by Duguy and Rovira,[16] we reasoned that no major changes in the chemical characteristics occurred due to the hydrofluoric acid treatment.

Infrared spectroscopy analyses of SOM

The concentrated organic matter was analyzed in duplicate by FTIR in KBr pellets (1 mg sample: 100 mg KBr) using 32 scans and a resolution of 4 cm^{-1}, in the range from 4000 to 400 cm^{-1}. The absorption band attributions were made following Tan,[23] and an aromaticity index (I_{1630}/I_{2920}) was calculated[25] that relates the intensity of the 1630 cm^{-1} absorption band to that of the 2920 cm^{-1}. The intensity value (I) was obtained from the equipment software, after establishing a baseline between 1696 and 1530 cm^{-1} and between 3000 and 2800 cm^{-1}, respectively. The relative absorbance intensities (RI) of the main peaks were also calculated,[26] dividing the corrected intensity of a distinct peak (e.g., around 2920, 1720, 1630, 1540, 1455 and 1045 cm^{-1}) by the sum of the intensities of all studied peaks and expressing them as percentage. The parameters, in units of cm^{-1}, for the determination of a given peak intensity were: Base1/peak/Base2 3000/2920/2800; 1800/1720/1700; 1700/1630/1500; 1560/1540/1490; 1500/1455/1400 and 1190/1045/900.

Thermogravimetric analysis

The thermodecomposition curves of FLF, OLF and HF, previously treated with 10% hydrofluoric acid solution, were obtained in a thermogravimetric analyzer (TGA-Q50 TA Instruments) with 5 to 10 mg sample over static air. The initial weight was stabilized at 45 °C and a heating curve was obtained with a heating rate of 20 °C min^{-1} up to 105 °C, with a holding time of 5 min, followed by heating at 10 °C min^{-1} up to 700 °C. The thermodecomposition curves were divided into four regions according to the weight loss during heating: 1st region = 45-105 °C; 2nd region = 105-350 °C; 3rd region = 350-650 °C; 4th region = 650-700 ºC. The quotient of the weight loss between the 3rd region and that of the 2nd region was calculated and defined as a thermogravimetric index (TGI).[27] This index enables the comparative evaluation of the thermal stability of the SOM, and, in comparative studies, a higher TGI value (higher thermal stability) can be related to a higher proportion of chemical recalcitrant structures, which decompose above 450 °C.[16]

Data analysis

The results of soil C and N stocks, density fractionation, FTIR relative intensities and TGA data were evaluated by descriptive data analysis based on one mean standard error.

Results and discussion

Soil C and N stocks

Soil C stocks in the 0-5 cm layer varied between 27 and 38 Mg C ha^{-1} among the sites and the smallest values were found in the NP and BP environments (Table 2). The lower C stock under BP, comparing to AP, suggests that ceasing fire for 8 years without further soil amendment eliminates any possible benefit on C accumulation as it was observed on recently and frequently fire affected environments.[28-30]

The greatest soil C stock of pasture environments occurred in AP (Table 2), where the value surpassed that of BP by approximately 11 Mg C ha^{-1}. In comparison with NP, the C stock did not differ, although the amended soil pasture tended to store a higher amount of soil C than the non-managed pasture (NP) of approximately 6 Mg C ha^{-1}. Again, the reported higher forage production in the AP site, in comparison with BP (Table 1), accounts most probably for its greater soil C stocks, since soil amendment, besides promoting the growth of the root system, also results in a greater input of above ground residues. The effect of a high

shoot dry matter production, assigned mainly to a good fertility status, on soil C accumulation has been verified on a Brazilian Oxisol in pasture.[3]

Similar to C stocks behavior, the smallest N stock among the pasture environments was found in BP, while the greatest was observed in AP (Table 2), confirming the effect of soil amendment in promoting SOM storage in grasslands.

The soil C stock found under NF was greater than that in the NP and in the BP environments (Table 2) as was expected for a forest environment.[2,5] However, no difference in C stocks was observed between NF and AP.

The C/N ratio in the whole soil varied between 16 and 18 and did not differ within the studied environments.

Table 2. C and N stocks and C/N ratio in bulk soil and in physical pools and proportion of soil C stock contained in a given physical fraction of the 0-5 cm layer of an Oxisol under native pasture without burning for the last 41 years (NP), native pasture without burning for the last 8 years (BP), native pasture on amended soil (AP) and native forest (NF)

Site	Carbon / (Mg ha^{-1})	Nitrogen / (Mg ha^{-1})	C/N ratio	$C_{fraction}/C_{soil}$ / %
		Soil		
NP	30.3 (5.31)*	1.77 (0.31)	17.3 (3.00)	–
BP	26.7 (2.78)	1.42 (0.04)	18.8 (1.66)	–
AP	37.8 (4.98)	2.13 (0.23)	17.8 (2.22)	–
NF	37.9 (1.66)	2.44 (0.76)	16.3 (3.72)	–
		Free light fraction (FLF)		
NP	3.18 (1.08)	0.19 (0.06)	17.1 (0.64)	10 (4)
BP	2.24 (0.92)	0.08 (0.02)	27.8 (6.07)	8 (4)
AP	6.98 (0.90)	0.39 (0.04)	18.0 (0.54)	18 (4)
NF	11.5 (4.20)	0.90 (0.38)	12.9 (0.63)	30 (10)
		Occluded light fraction (OLF)		
NP	3.38 (0.39)	0.24 (0.04)	14.4 (1.06)	11 (2)
BP	3.09 (0.05)	0.16 (0.01)	19.2 (1.57)	12 (1)
AP	4.66 (0.71)	0.34 (0.07)	14.0 (0.87)	13 (3)
NF	6.36 (0.15)	0.39 (0.06)	16.6 (2.33)	17 (1)
		Heavy fraction (HF)		
NP	23.7 (5.56)	1.35 (0.22)	17.8 (4.01)	78 (6)
BP	21.3 (3.70)	1.18 (0.04)	18.1 (2.60)	80 (5)
AP	26.1 (5.66)	1.40 (0.19)	18.6 (2.99)	69 (7)
NF	20.0 (2.62)	1.14 (0.31)	18.7 (6.38)	53 (9)

Values are means (n=3) and one standard deviation.

C and N stocks in SOM physical pools

Among the pasture environments, C stocks contained in the HF accounted for 69% of soil C in AP and to 80% in BP (Table 2). Proportion of clay-associated or mineral-associated soil organic carbon, reported for the surface layer of non-disturbed environments on subtropical and tropical Brazilian areas, vary between 58 and 90%.[31,32] The C_{FLF}/C_{soil} proportion showed a broader variation (8 to 18%) than C_{OLF}/C_{soil} (around 12%) and the highest C_{FLF}/C_{soil} value was verified for AP (Table 2). The relative uniform values observed for C_{OLF}/C_{soil} may be an indicator of the stability of this fraction regardless of the pasture management. According to Buurman and Roscoe,[14] the OLF in undisturbed Cerrado area (Brazil) tends to present a slower decay than the FLF. In fact, Marín-Spiotta,[33] verified that the FLF of tropical pastures has a shorter mean residence time than the respective OLF.

Concerning the absolute values, C stocks in both light fractions were larger in the AP than those found in the respective fractions of NP and BP (Table 2). No differences of C stocks in physical fractions were observed between these two environments, and the C stocks found for the HF of the three pasture environments did not differ either. These results show that the comparatively higher soil C stock in the AP environment is due to the higher C stock in both light fractions.

Regarding the C stocks in the HF, the result was not unexpected because, due to its high mean residence time in soils, this fraction shows low sensitivity with respect to changes in the management.[13,34]

Among all studied environments, the largest proportion of C contained in both light fractions was found under NF, which also showed the greatest stocks of C_{FLF} and C_{OLF} (Table 2). The enrichment of light fractions under forest may be related to the chemical composition of the forest litter, which consists in great part of structures more resistant against biological degradation (e.g., lipids and aliphatic chains)[35] in comparison with the grassland environment. In contrast, grasslands are composed of more degradable compounds in comparison with forest vegetation, contributing to accumulation of the colloidal SOM in the HF.[33]

The N stocks in both light fractions of the pasture environments decreased in the order AP > NP > BP (Table 2), highlighting the low content of N-containing groups in grass species developed in fire-affected pastures. In fact, in the BP environment, a preferential development of N-poor species over warm-season grasses and legumes had been observed earlier.[18] The N depletion in the FLF and OLF of BP was confirmed by their high values of C/N ratio in comparison with that of the two other pasture environments (Table 2). These results are in line with the high C/N ratio determined for the vegetation from the BP environment (62) in comparison with the other studied environments ($18 \leq C/N \leq 22$) from a previous study of the area.[15] In the native forest, the N stocks were high in both light fractions. The C/N ratio values in the HF did not differ among the environments.

SOM chemical composition of the physical pools

Regardless of the environment, the spectra of the same fractions exhibit the same FTIR pattern and therefore only one example for each fraction is given in Figure 1. The main identified absorption bands and their respective assignments are: a broad band around 3405 cm^{-1} due to stretching of OH groups (bonded and non-bonded); two bands at 2920 and 2850 cm^{-1} due to aliphatic C–H vibrations of aliphatic methyl and methylene groups; a band around 1720 cm^{-1} due to C=O stretching of COOH groups; a peak around 1643 and 1635 cm^{-1} due to C=C stretching of aromatic groups; a shoulder at 1543 cm^{-1} due to N–H bending of amide II; weak bands around 1400 cm^{-1} due to C–H aliphatic groups; a broad band at 1260 cm^{-1} due to C–O stretching and OH bending from COOH; and a peak at 1040 cm^{-1} due to C–O stretching of carbohydrates. The contribution of the Si–O stretching band, which generally occurs at 1030 cm^{-1},[36] to the intensity of the 1040 cm^{-1} peak should not be ignored. Nevertheless, this contribution should not be relevant because the heavy fraction, which presented the greatest residues at T >700 °C and therefore the greatest ash content (Table 4), also presented the lowest values for the relative intensity at 1045 cm^{-1} (Table 3). The spectra of the HF (Figure 1) showed a prominent peak at around 2300 cm^{-1}, assigned to the absorption of CO$_2$ from the surrounding air and whose intensity was not included in the calculation of the relative intensities.
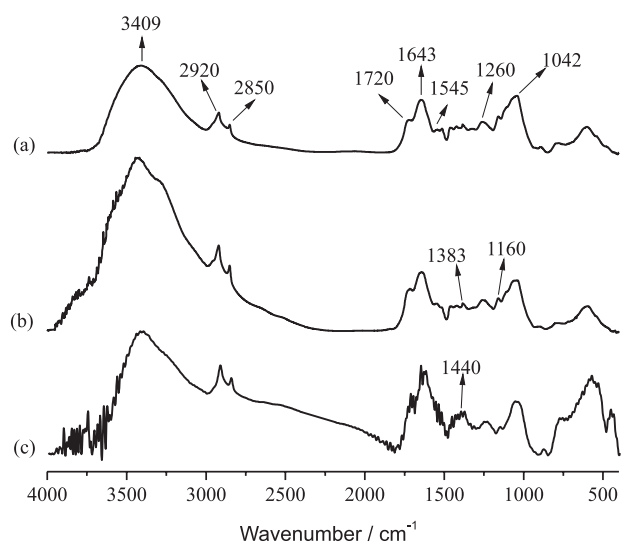

Figure 1. FTIR spectra of the free light fraction (a), occluded light fraction (b) and heavy fraction (c) of the 0-5 cm layer of an Oxisol under native pasture without burning for the last 41 years (NP) treated with 10% hydrofluoric acid.

The absence of a prominent peak around 1440 cm^{-1}, due to asymmetric axial stretching of carboxylate anion

of COO$^-$ groups, and of the band at 1245 cm^{-1} confirm the presence of non-dissociated COOH groups and exclude a relevant contribution of the C=O symmetric stretching of carboxylate groups to the 1630 cm^{-1} region. In fact, the hydrofluoric acid treated samples were washed with distilled water and dried at pH < 4.0, assuring the protonation of carboxylate groups.

The FLF presented larger RI$_{2920}$ and smaller RI$_{1630}$ values in the BP environment than in the NP (Table 3). The lower aromaticity of SOM in the FLF under BP was confirmed by the lowest value found for the aromaticity index I$_{1630}$/I$_{2920}$. Furthermore the smallest value for RI$_{1540}$ in the FLF and in the OLF corroborates the impoverishment of N in the two light fractions in BP, reflecting the influence of the vegetation species as it was already discussed by the C/N ratio. The OLF under BP also presented a higher proportion of carbohydrates (RI$_{1045}$) than in the other environments. Differently, in the HF the value for RI$_{2920}$ was smaller and that for RI$_{1630}$ was larger in BP than in the other pasture environments, resulting in the largest I$_{1630}$/I$_{2920}$ index found in the present study. One possible explanation for this result may be the contribution of pyrogenic carbon in this fraction that still remained after 8 years of ceasing fire, but this assumption needs further investigation. Golchin *et al.*[37] observed, in a burnt grassland, a considerable amount of aromatic carbon in the occluded fractions and they suggested that aromatic charcoal was concentrated in these fractions.

The chemical composition of the SOM in AP differed from that in the NP only in the FLF, where the proportion of carboxylic groups (RI$_{1720}$) tended to be higher and carbohydrates lower (Table 3). The FLF in forest presented a higher proportion of aromatic groups, leading to a high value for I$_{1630}$/I$_{2920}$. In both light fractions, the lowest proportion of carbohydrate was observed between the studied samples. These results are probably related to the quality of the litter found in forest, that tends to contain higher proportion of lignin and tannins and a lower proportion of carbohydrates than the grassland litter.[33] In general, when going from the FLF to the OLF and to the HF, the SOM tends to get enriched in aromatic structures (RI$_{1630}$ and I$_{1630}$/I$_{2920}$ increase) and depleted in carbohydrates as expected for the humification process.[38]

Thermodegradation behavior of the SOM in physical pools

The thermograms, which showed the same pattern within the samples, were divided into four main temperature regions, selected according to the sample decomposition behavior (Figure 2). For T < 105 °C the weight loss varied between 5 and 10% (Table 4) and corresponds to the loss of water from the organic matter.[41] Between 105 and

Table 3. FTIR indexes RI_{2920}, RI_{1720}, RI_{1630}, RI_{1540}, RI_{1455}, RI_{10450} and I_{1630}/I_{2920} of the 0-5 cm layer of an Oxisol under native pasture without burning for the last 41 years (NP), native pasture without burning for the last 8 years (BP), native pasture on amended soil (AP) and native forest (NF)

Site	Relative intensity / %						I_{1630}/I_{2920}
	RI_{2920}	RI_{1720}	RI_{1630}	RI_{1540}	RI_{1455}	RI_{1045}	
				Free light fraction (FLF)			
NP	18.4 (0.79)	7.78 (1.98)	22.2 (2.24)	8.30 (0.88)	9.95 (0.35)	33.3 (0.18)	1.21 (0.07)
BP	21.9 (1.80)	9.62 (1.90)	17.8 (0.42)	6.52 (1.26)	10.6 (0.91)	33.5 (2.70)	0.81 (0.09)
AP	19.1 (2.64)	11.4 (2.58)	22.4 (3.84)	7.50 (1.37)	10.6 (1.81)	29.0 (0.72)	1.17 (0.04)
NF	18.8 (1.24)	11.3 (0.17)	27.7 (2.06)	7.88 (2.00)	10.9 (0.02)	23.3 (1.50)	1.47 (0.01)
Mean	19.6 (1.98)	10.0 (2.13)	22.5 (4.21)	7.55 (1.29)	10.5 (0.86)	29.8 (4.60)	1.16 (0.25)
				Occluded light fraction (OLF)			
NP	23.7 (1.89)	10.9 (0.58)	22.1 (0.74)	6.44 (0.99)	10.5 (1.11)	26.4 (1.54)	0.94 (0.11)
BP	24.6 (1.78)	12.3 (0.02)	21.0 (0.69)	3.71 (0.54)	9.36 (0.28)	29.0 (0.30)	0.85 (0.09)
AP	23.4 (3.56)	9.83 (0.59)	22.1 (1.95)	7.46 (0.15)	9.55 (0.47)	27.6 (0.40)	0.98 (0.33)
NF	30.0 (4.08)	13.3 (2.78)	23.5 (0.70)	5.01 (2.00)	11.9 (0.09)	16.2 (0.09)	0.79 (0.08)
Mean	25.4 (3.91)	11.6 (1.81)	22.1 (1.48)	5.65 (1.75)	10.3 (1.19)	24.8 (5.43)	0.89 (0.16)
				Heavy fraction (HF)			
NP	16.6 (2.00)	12.9 (3.32)	26.4 (1.14)	8.3 (2.13)	13.3 (0.35)	22.6 (4.24)	1.60 (0.22)
BP	13.5 (2.95)	12.3 (2.58)	28.4 (2.58)	7.8 (2.21)	15.4 (2.58)	22.1 (1.84)	2.17 (0.66)
AP	16.2 (0.97)	11.7 (0.72)	26.9 (3.05)	9.7 (0.94)	12.5 (3.03)	23.1 (0.72)	1.67 (0.29)
NF	15.9 (1.55)	11.4 (0.60)	29.8 (0.26)	9.1 (2.94)	12.1 (1.34)	21.7 (0.37)	1.88 (0.17)
Mean	15.6 (1.98)	12.2 (1.76)	27.9 (2.13)	8.7 (1.80)	13.3 (2.10)	22.4 (1.85)	1.83 (0.38)

Values are means (n=3) and one standard deviation.

650 °C two main decomposition regions were identified (as indicated by the change in the declivity of the thermo degradation curve, Figure 2).

The FLF from the pasture environments presented the greatest weight loss in the second temperature interval (105-350 °C) (Table 4), indicating the predominance of more thermo-labile groups, such as alkyl and O-alkyl structures and carboxylic groups and even some alkyl-aromatic groups.[39,40] In the OLF the weight loss in the second and in the third temperature interval was similar, while in the HF the weight loss in the 350-650 °C interval tended to be greater than in the 105-350 °C range. The third temperature interval is generally attributed to the decomposition of less thermolabile structures such as lignin and other polyphenols.[41]

The TGI gives the proportion between the less to more thermolabile structures. Considering that the thermolability is inversely related to the chemical condensation, higher values of TGI represent a higher chemical condensation of the SOM structure.[27]

The TGI in the pasture environments increased from FLF < OLF < HF, and this result correlates with the observed increase of the aromaticity index obtained from the FTIR results. In the HF of the pasture environments a difference between TGI values was identified. The largest values observed in the BP and AP environments could be related to a preservation of pyrogenic carbon structures (BP) and to a possible SOM stabilization through organo-mineral complexes (AP). Nevertheless, this hypothesis was not supported by our previous results and it needs further investigation.

The residual mass at T > 650 °C (residue) is composed mainly of an inorganic matrix that was not removed by hydrofluoric acid treatment and remained as oxides (such as SiO_2, Al_2O_3 and Fe_2O_3) after the combustion.[42] The eventual formation of condensed organic structures due to an incomplete combustion should not be discarded, even though it does not affect the obtained TGI values.

The fractions from the NF showed a different behavior regarding the thermodecomposition: in all three fractions the weight loss in the third interval was larger than in the second one. As verified for the pasture environments, the TGI increased from FLF < OLF < HF, but for a given fraction the value found for NF was always larger than in a pasture environment. These results may be explained with the chemical composition of the litter on the forest floor, which is richer in lignin than that produced in grasslands.[35]
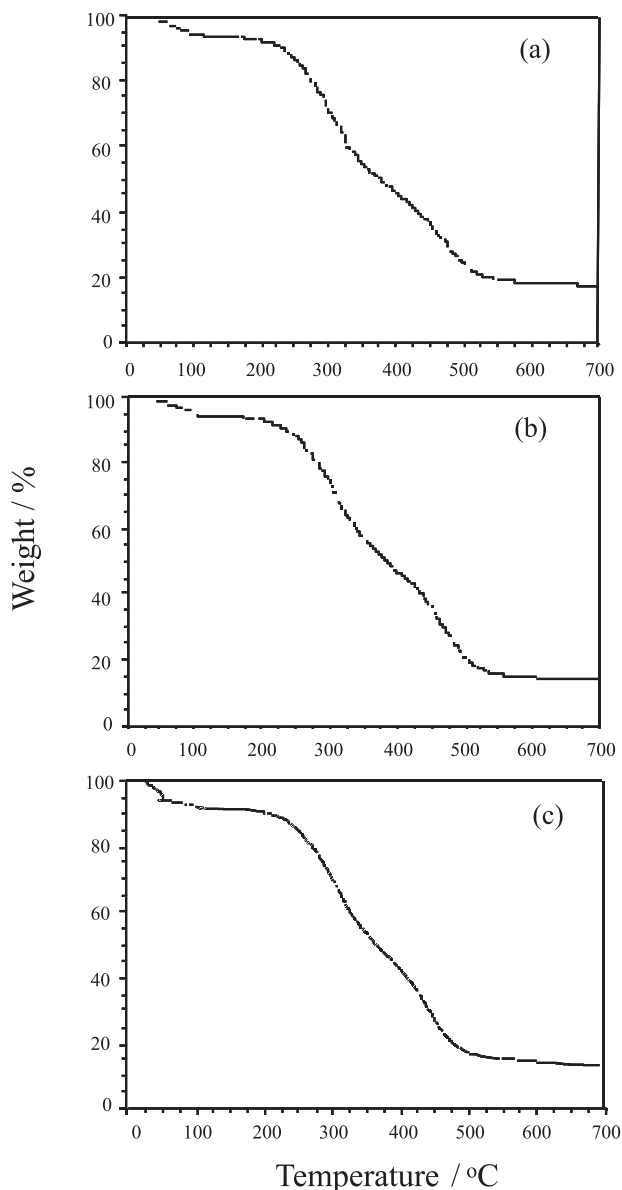
Figure 2. Examples of the TGA curves obtained from the free light fraction (a), occluded light fraction (b) and heavy fraction (c) of the 0-5 cm layer of an Oxisol under native pasture without burning for the last 41 years (NP) treated with 10% hydrofluoric acid.

Table 4. Mass loss in three temperature intervals, residual mass for T > 650 °C and TGI of physical pools treated with hydrofluoric acid, of the 0-5 cm layer of an Oxisol under native pasture without burning for the last 41 years (NP), native pasture without burning for the last 8 years (BP), native pasture on amended soil (AP) and native forest (NF)

Sites	ΔT / °C				TGI[a]
	45-105	105-350	350-650	T > 650 °C	
	Mass loss / %			Residue / %	
Free Light Fraction (FLF)					
NP	8.8 (0.0)	40 (1.7)	33 (0.7)	18 (2.2)	0.8 (0.1)
BP	9.6 (0.9)	43 (0.8)	34 (0.4)	14 (1.0)	0.8 (0.0)
AP	10 (0.0)	40 (0.6)	34 (0.0)	16 (0.6)	0.9 (0.0)
NF	5.3 (0.2)	38 (0.3)	39 (0.7)	18 (0.8)	1.0 (0.0)
Mean	8.4 (0.3)	40 (0.9)	35 (1.3)	16 (1.1)	0.9 (0.0)
Occluded light fraction (OLF)					
NP	7.8 (0.1)	39 (0.8)	37 (0.5)	15 (1.3)	1.0 (0.0)
BP	9.2 (0.8)	38 (0.1)	38 (0.8)	14 (1.3)	1.0 (0.1)
AP	7.8 (1.6)	39 (1.1)	39 (0.8)	13 (0.4)	1.0 (0.0)
NF	6.0 (0.8)	36 (0.1)	46 (1.7)	12 (1.2)	1.3 (0.0)
Mean	7.7 (0.8)	38 (0.5)	41 (1.0)	13 (1.0)	1.1 (0.0)
Heavy fraction (HF)					
NP	8.4 (1.1)	38 (1.0)	38 (0.3)	14 (0.1)	1.0 (0.0)
BP	6.2 (0.1)	22 (0.5)	29 (0.1)	43 (0.4)	1.3 (0.0)
AP	6.1 (0.1)	24 (0.2)	32 (0.3)	37 (0.5)	1.3 (0.0)
NF	6.3 (0.6)	23 (0.3)	30 (0.7)	40 (1.5)	1.4 (0.1)
Mean	6.7 (0.5)	27 (0.4)	32 (0.6)	34 (0.6)	1.3 (0.0)

[a]Thermo-gravimetric index. Values are means (n=3) and one standard deviation.

system that improves soil quality and promotes carbon sequestration.

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Conclusion

The ceasing of vegetation burning may recover the original SOM stocks after some years, but without any further soil amendment soil C stocks will not increase. The soil use affects the proportion and chemical composition of the SOM in physical pools as was indicated by the higher amounts of FLF and the presence of a more aromatic organic fraction in the forest environment in comparison with the pasture environments. In the specific case of the subtropical Brazilian highlands, soil amendment by fertilizing and liming seems to be a pasture management

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