

ORIGINAL ARTICLE

Effects of fire on soil organic matter in northern Amazonian forest fragments

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ABSTRACT

Forest fires incorporate pyrogenic organic matter into the soil, affecting the characteristics of soil organic matter (SOM) due to its high aromaticity, increasing its renewal time. However, the factors that control the concentration of pyrogenic organic matter and its chemical composition and structure are still little known. Forest fragments dispersed in a savanna matrix of the northern Brazilian Amazon are frequently impacted by fires, which can affect the composition of SOM within the fragments. The aim of this study was to analyse the chemical composition of SOM in the border and interior of six forest fragments in the Roraima savanna, in the northern Brazilian Amazon. Soil samples were collected at 10-cm intervals up to 1 m in depth at the border and in the interior of each fragment. Soil organic material concentration was determined with 10% HF solution and its elemental composition, thermogravimetric index, and ¹³C CPMAS NMR spectroscopic analysis were determined. There was no significant difference in the aromaticity index between border and interior. The concentration of alkyl C structures between border (22 to 25%) and interior (19 to 29%) indicated the occurrence of medium-intensity fires in the study area. The thermogravimetric analysis showed no significant difference in the thermal stability of SOM between border and interior. Our results showed no pronounced difference in SOM quality up to 1 m depth between the border and the interior of the evaluated forest fragments, indicating that this compartment is stable throughout the fragments.

KEYWORDS: forest fires; aromaticity index; elemental composition; FTIR

Efeitos do fogo sobre a matéria orgânica do solo em fragmentos de floresta no norte da Amazônia

RESUMO

Incêndios florestais incorporam matéria orgânica pirogênica ao solo, afetando as características da matéria orgânica do solo (MOS), devido a sua alta aromaticidade. Porém, os fatores que controlam a composição química e a estrutura da matéria orgânica pirogênica ainda são pouco conhecidos. Fragmentos florestais dispersos em uma matriz de savana na Amazônia setentrional brasileira são frequentemente impactados por incêndios, que podem afetar a composição da MOS nos fragmentos. O objetivo deste estudo foi analisar a composição química da MOS na borda e no interior de seis fragmentos florestais situados na savana de Roraima, norte da Amazônia brasileira. Amostras de solo foram coletadas em intervalos de 10 cm até 1 m de profundidade na borda e no interior de cada fragmento. A concentração da MOS foi determinada com solução de HF a 10% e sua composição elementar, índice termogravimétrico e análise espectroscópica de ¹³C CPMAS RMN foram determinados. Não houve diferença significativa no índice de aromaticidade entre borda e interior. A concentração de estruturas alquil C entre a borda (22 a 25%) e o interior (19 a 29%) indicou a ocorrência de incêndios de média intensidade na área de estudo. A análise termogravimétrica não mostrou diferença significativa na estabilidade térmica da matéria orgânica do solo entre a borda e o interior. Nossos resultados não mostraram diferença pronunciada na qualidade da MOS até 1 m de profundidade entre a borda e o interior dos fragmentos florestais avaliados, indicando que este compartimento é estável ao longo dos fragmentos.

PALAVRAS-CHAVE: incêndios florestais; índice de aromaticidade; composição elementar; FTIR

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INTRODUCTION

Soil organic matter (SOM) represents a biochemically active environmental compartment that has an impact on primary production and biodiversity (Knicker *et al.* 2006). Quality and quantity of SOM are especially affected under fire events in regions with high fire recurrence during dry and hot periods (Vallejo-Villata *et al.* 2019), especially in Amazonian forests which have been constantly marked by episodes of intense fire (Aragão *et al.* 2018; Marengo *et al.* 2016). Fire and anthropogenic disturbances can potentially affect the carbon pools of SOM in the Amazon region (Fearnside and Barbosa 1998). During forest fires, vegetation and litter also undergo changes such as condensation and cyclization of organic structures, forming cyclic molecules (Almendros *et al.* 2003).

The effects of forest fires on SOM can vary widely depending on factors such as fire intensity and duration, and the amount and flammability of biomass added to the soil (Zimmerman *et al.* 2017; Gerke 2019). An additional intrinsic fire effect on SOM is the immediate decrease in microbial biomass on the soil surface due to the death of most living organisms at temperatures between 50 and 120 °C (Vazquez *et al.* 1993; Neary *et al.* 1999). Several studies addressed the effects of fire on the quality of SOM, mainly in relation to heat-induced transformations of lignocellulosic materials (Knicker *et al.* 1996; Kuhlbusch and Crutzen 1996; López-Martín *et al.* 2018). On the other hand, pyrogenic organic material behaves as an essential carbon reservoir in the soil due to its high aromatic nature, which reduces decomposition and enables long residence time in the soil, while being slowly degraded by microbial activity or due to the recurrence of fire events (López-Martín *et al.* 2018). Microbial attack on the aromatic carbon in the carbonized material leads to a concomitant increase in carboxylic groups (De la Rosa *et al.* 2018).

The effects of fire episodes on soil organic material vary with the type of ecosystem, geographical conditions, fire frequency and intensity (Roscoe *et al.* 2000; Cerri *et al.* 2004). In anthropogenic forest fragments (e.g. resulting from deforestation) or originated from paleoclimatic events (e.g. in a savanna matrix), SOM may vary due to the border effect resulting from environmental differences between the matrix and the interior of the fragment (Schröder and Fleig 2017; Bae and Ryu 2021; Barros and Fearnside 2016). Although forest fragments dispersed in Amazonian savannas may have similar soils (Feitosa *et al.*, 2016), distinctions in vegetation structure and species composition between border and interior of fragments (Santos *et al.* 2013) can lead to differences in the characteristics of the organic matter pool mediated by fire intensity (Biddulph and Kellman 1998). The effects of fire on quality of SOM in forest fragments is little studied in fragments of seasonal forest dispersed in savanna matrices in

the northern Brazilian Amazon (Knicker *et al.* 2005a; Leal *et al.* 2019).

Most savanna areas in the northern Brazilian Amazon are located in the state of Roraima (Sanaiotti *et al.* 2002; Miranda *et al.* 2003). This landscape is regionally known as *Lavrado* (Barbosa *et al.* 2007), and is part of a large ecosystem of open areas occupying parts of Brazil, Guyana and Venezuela, covering an area of ~68,000 km² (Barbosa and Campos 2011). Roraima savannas are part of the Brazilian Amazon Biome, occupying over 40,000 km² (Barbosa *et al.* 2005), and contain natural fragments of seasonal forest (paleoclimatic forest islands) dispersed throughout the entire forest-savanna mosaic of the Branco-Uraricoera-Tacutu river basin (Santos *et al.* 2013). Due to edaphoclimatic conditions, the Roraima savannas experience an extreme water deficit in periods of drought, facilitating the spread of anthropogenic fires due to the accumulation of dry biomass on the soil (Couto-Santos *et al.* 2014). Therefore they are frequently affected by intense fire (Barbosa and Fearnside 2005a), affecting above-ground biomass and the manner of incorporation of carbon into the soil (Barbosa and Fearnside 2005b).

Forest fragments cover approximately 30% of the Roraima savanna (Barbosa *et al.* 2010). In drier years, the fire sweeps the forest fragments completely, when the fragments lose part of their crown cover and become more exposed to drying of litter and understory vegetation. In any fire event, the fragments are impacted by understory fire, and their borders tend to be more affected than the interior (Santos *et al.* 2013). The stronger effect of fires on the border of the fragments has been related to the drier and rapidly combustible plant material that permeates the borders (Biddulph and Kellman 1998). Soil pyrogenic carbon stock in these seasonal forests is higher than 3.4 Mg ha⁻¹ (Turcios *et al.* 2016), which thus hold an immense carbon pool with a potentially distinct chemical composition due to differences in the structure and species composition of the combustible plant material between the border and interior of the fragments.

This study aimed to evaluate the chemical composition of SOM from forest fragments in an area in the Roraima savanna where fire episodes are frequent and severely affect the borders and interior of forest fragments to provide an approximation of the relative abundance of carbon functional groups (aromatic, carboxylic and alkylic) that can be used as indicators of changes in the structure of SOM impacted by fire.

MATERIAL AND METHODS

Study area

The study was carried out in Project PANA I (*Projeto de Assentamento Nova Amazônia I*), a rural settlement in the Roraima savanna. The study area (03°04'15"N, 60°48'44"W) approximately 440 km² is located 35 km northwest of Boa

Vista, the capital of Roraima, northern Brazil (Figure 1). Annual rainfall ranges from 1,500 to 1,700 mm and mean temperature is 27.8 ± 0.6 °C (INMET 2018), with a Aw climate (Köppen classification), typical of the savanna areas of the northern Brazilian Amazon (Barbosa 1997).

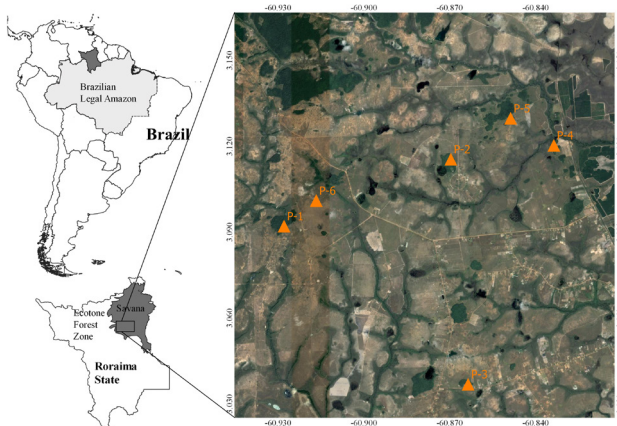


Figure 1. Location of six forest fragments dispersed in a savanna matrix (*Lavrados de Roraima*) in Roraima state, northern Brazil. This figure is in color in the electronic version.

We sampled six forest fragments, ranging between 2 and 60 ha located in a landscape of low relief (-90 m a.s.l) on Oxisols with a bulk density ranging from 1.24 g cm^{-3} in the superficial layers to 1.63 g cm^{-3} in the deepest layers (Feitosa *et al.* 2016).

Sampling design

The fragments were sampled between December 2013 and February 2014. To assess the quality of SOM in each fragment, soil samples were collected at equidistant intervals along a transect crossing the fragment, totalling two border points and two points in the interior of the fragment. At each point, samples were taken along a 1-m vertical profile at depths of 0-10, 10-20, 20-30, 30-40, 40-50, and 90-100 cm using a soil auger (Eijkelkamp, Giesbeek, Netherlands). The two border samples and the two interior samples were pooled, forming two composite samples (border and interior) for each fragment.

Granulometric analysis

The size distribution of soil mineral particles in the samples followed Almeida *et al.* (2012). The procedure aims to break the soil aggregates and the individualization of particles using mechanical and chemical energy, to form a stabilized suspension, and the quantification of the size fractions. The larger fractions (coarse sand and fine sand) were separated by sieving, while the smaller fractions (silt and clay) were separated by sedimentation of particles in the suspension, according to Stokes' law. The larger fractions were quantified by weighing, and the smaller fractions by the pipette method following Embrapa (1997).

SOM concentration and elemental analysis

In order to concentrate SOM, 5 g were taken from each composite soil sample and were treated with 30 mL of 10% (v/v) hydrofluoric acid (HF) solution under mechanical agitation for 2 hours and then centrifuged for 10 min at 3,000 rpm (Gonçalves *et al.* 2003). After the separation of the supernatant, the procedure was repeated five times until the residue turned dark in color. The remaining sediment was washed three times with deionized water, the pH of the last wash being around 4.0. SOM_{HF} was obtained after drying the samples in an oven at 60 °C for 24 hours, after which the samples were weighed.

Carbon (C) and nitrogen (N) concentration was determined in duplicate for each sample by dry combustion, and the C/N ratio was calculated before and after treatment with HF (C/N_{HF}). To evaluate preferential losses of C and N by the 10% HF solution, the R factor was calculated according to equation (1) (Dick *et al.* 2005; Potes *et al.* 2010).

$$R = (\text{C/N}_{\text{soil}}) / ([\text{C/N}_{\text{HF}}]) \quad (1)$$

FTIR spectroscopic analysis

The SOM_{HF} samples (border and interior) of each fragment were analyzed by Fourier transform infrared spectroscopy (FTIR) (Shimadzu FTIR 8300) on KBr pellets (1 mg sample:100 mg KBr) using 32 scans and a resolution of 4.0 cm^{-1} within the range of 4,000 to 400 cm^{-1} . The absorption bands were attributed according to Tan (1996). We calculated the aromaticity index ($I_{\text{C=C}}/I_{\text{C-H}}$), which informs about the degree of saturation of the organic material (Chefetz *et al.* 1996). The index relates the absorption intensity around $1,640 \text{ cm}^{-1}$, which indicates the presence of aromatic groups, with that at $2,920 \text{ cm}^{-1}$, which indicates the presence of aliphatic groups (Dick *et al.* 2008a).

The intensity value was obtained after adjusting the general baseline of the spectrum at three to four points (approximately at $3,800, 1,750, 980$ and 500 cm^{-1}). To measure the intensity, a baseline between $1,696$ and $1,530 \text{ cm}^{-1}$ was established for aromatic groups and between $3,000$ and $2,800 \text{ cm}^{-1}$ for aliphatic groups. Prior to the analysis, the samples were vacuum-dried at 40° C for 24 hours. The analysis of the FTIR spectra was performed using OriginLab 9.0 software.

^{13}C -NRM CP/MAS spectroscopy

The ^{13}C nuclear magnetic resonance analysis of the SOM_{HF} samples (^{13}C -NMR CP/MAS spectra) was carried out on a Bruker DSX 200 (50.3MHz) spectrometer using a 7 mm OD zirconium rotor with Kel-F caps (6.8 kHz), with a contact time of 1ms, 90° 1H pulse width of $6.6 \mu\text{s}$ and pulse delay between 200 and 300 ms. Depending on the signal to noise ratio, 4,800 to 1,100 scans were accumulated and a 100 Hz linewidth was employed.

Chemical shifts were reported about the tetramethylsilane scale (= 0 ppm), which was adjusted with glycine (carboxyl C = 176.04 ppm), and their respective assignments were made according to Knicker and Ludeman (1996): (0–45 ppm), alkyl C; (45–60 ppm), O/N-alkyl C; (60–110 ppm), O-alkyl C; (110–140 ppm), aromatic C; (140–160), O-Aryl C; (160–185 ppm), carboxyl C, and (185–220 ppm), carbonyl C. The relative proportion (%) of the signal of each functional group was obtained by integrating the respective spectral region with the MestreNova software. The following indices were calculated, relating the respective areas: degradability ratio (alkyl C/O-alkyl C) (Baldock *et al.* 1997): (0–45 ppm)/(45–100 ppm); carbonization (aromatic C/alkyl C), which describes the degree of biomass carbonization (Knicker *et al.* 2006): (110–160 ppm)/(0–45 ppm).

For this analysis, the border and interior samples for each depth layer of the six fragments were pooled into one composite border and one composite interior sample. The SOM_{HF} ¹³C NMR spectra were obtained at three depths (0–10, 40–50, 90–100 cm). The low C concentration in the 90–100 cm layer of the interior sample (Table 1) led to a high signal/noise spectrum, and therefore the relative distribution of C functional groups from this sample was not considered in the discussion of results.

Thermogravimetric analysis

Thermogravimetric analysis (TA Instruments, TGA-Q50) of SOM_{HF} was performed under an oxidizing atmosphere, employing 5 to 10 mg of SOM_{HF} of each sample. The initial weight was stabilized at 30 °C and the heating ramp was 20 °C min⁻¹ to 950 °C. The thermal decomposition curves were divided into regions according to the decomposition of different structures (Crittter and Airoidi 2006). The thermostability of the SOM_{HF} samples was determined by the mass loss ratio in the 420–600 °C interval to the 105–420 °C interval ($M_{p_{420-600}}/M_{p_{105-420}}$). The thermogravimetric index (TGI) indicates the proportion between less and more thermolabile structures. Considering that thermolability is inversely related to chemical recalcitrance, higher values of the TGI represent higher chemical recalcitrance of the SOM structure (Benites *et al.* 2005).

Statistical analysis

The difference between border and interior samples from all depth layers for C and N concentrations, and particle size (silt, clay and sand) were tested with one-way ANOVA at $P < 0.05$. Data normality of the variables was assessed with the Shapiro-Wilk test. The thermogravimetric data were compared between border and interior for all depth layers with one-way ANOVA at $P < 0.05$. TGI, alkyl C/O-alkyl C and aromatic C/alkyl C ratio samples were compared with a paired t-test ($P < 0.05$). All analyses were performed with

the softwares R (R core team) (ExpDes package; Ferreira *et al.* 2021) and GraphPad Prism.

RESULTS

Granulometry, C and N concentration and effect of demineralization

There was no significant difference between border and interior samples in sand, clay and silt concentration, as well as C and N concentration (Tables 1, 2). C/N decreased with depth in both border and interior samples and ranged overall between 13 and 9, with the highest values in the surface layer (Table 1). C/N_{HF} varied from 3.6 to 12.7 in border, and from 3.9 to 9.3 in interior samples. The R-values ranged from 0.3 to 1.0, indicating preferential losses of N during the treatment (Table 1).

Chemical composition of SOM

The FTIR spectra of SOM_{HF} showed the same pattern in the border and interior (Figure 2). We identified a broadband at 3,377 cm⁻¹, due to -OH stretching, two bands at 2,922 cm⁻¹ and 2,855 cm⁻¹, due to the aliphatic C-H stretching, and other bands at 1,722 cm⁻¹, attributed to the C=O stretching of carboxylic groups, 1,647 cm⁻¹, resulting from the C=C stretching of the aromatic groups, 1,566 cm⁻¹, due to deformation of the N-H and C=N stretching, 1,375 cm⁻¹, due to aliphatic C-H, 1,244 cm⁻¹, due to C-O stretching and OH deformation of carboxylic groups, a band of low intensity around 1,070 cm⁻¹, due to C-O stretching of carbohydrates, and at 1,034 cm⁻¹, resulting from Si-O vibrations of inorganic material that was not removed by HF treatment. The FTIR relative intensity values for each functional grouping are available in the Supplementary Material (Table S1). Particularly in border samples below 10 cm and interior samples below 30 cm, the contribution of the inorganic group is relevant, as indicated by the “shoulder” to the right of the 1,074/1,070 cm⁻¹ band (Figure 2).

The aromaticity index ranged from 3.3 to 4.5 in the border and from 2.2 to 5.6 in the interior samples, tending to increase with depth (Table 1). The predominant groups in the ¹³C NMR spectra were O-alkyl-C (N-O-alkyl + O-alkyl C + di-O-alkyl C), decreasing proportionally with depth in the border samples (50 to 41%) and increasing in the interior samples (43 to 53%) (Table 3; Figure 3). The alkyl C groups were the second most abundant (22 to 29%), followed by total aromatic groups (aryl-C + O-aryl) (15 to 18%) and carboxylic groups (8 to 12%).

In the spectrum of the 0–10-cm layer, there was a signal in the region of 151 ppm (Figure 3), which was assigned to the O-aryl groups, indicating the presence of lignin derivatives. The marked signal in the 50 ppm region can be attributed to methoxyl (Gerzabeck *et al.* 2006). In the border samples, the

Table 1. Carbon (C) and nitrogen (N) concentration and C/N ratio in whole soil before (C/N) and after treatment with HF ($[C/N]_{HF}$), R index, and aromaticity index ($I_{C=C}/I_{C-H}$) in soil sampled at the border and in the interior of six forest fragments at 10-cm intervals along a 1-m depth profile. Values are the mean followed by the standard deviation in parentheses.

Depth (cm)	C (%)	N (%)	C/N	C_{HF} (%)	N_{HF} (%)	C/N_{HF}	R	$I_{C=C}/I_{C-H}$
Border								
0-10	1.58 (0.08)	0.26 (0.01)	13 (0.16)	4.50 (1.25)	0.63 (0.01)	7.1 (1.20)	0.5	3.3
10-20	1.19 (0.28)	0.28 (0.01)	13 (1.57)	3.70 (1.20)	0.82 (0.00)	4.5 (0.70)	0.3	3.9
20-30	0.72 (0.01)	0.06 (0.00)	12 (0.21)	2.66 (0.86)	0.21 (0.00)	12.7 (1.50)	1.0	4.5
30-40	0.57 (0.00)	0.09 (0.00)	11 (0.08)	1.82 (0.26)	0.50 (0.01)	3.6 (1.10)	0.3	4.3
40-50	0.47 (0.03)	0.07 (0.00)	11 (0.63)	1.61 (0.20)	0.37 (0.00)	4.4 (0.52)	0.3	4.1
90-100	0.29 (0.01)	0.03 (0.00)	9 (0.19)	0.93 (0.12)	0.17 (0.00)	5.5 (0.81)	0.4	4.5
Interior								
0-10	1.56 (0.03)	0.12 (0.01)	13 (0.25)	4.60 (1.32)	0.63 (0.03)	7.3 (1.40)	0.6	2.2
10-20	0.90 (0.05)	0.07 (0.00)	12 (0.31)	3.49 (1.16)	0.82 (0.03)	4.3 (0.44)	0.3	3.9
20-30	0.62 (0.01)	0.05 (0.00)	11 (0.01)	1.96 (0.71)	0.21 (0.00)	9.3 (1.03)	0.7	5.2
30-40	0.55 (0.06)	0.05 (0.00)	11 (0.74)	1.71 (0.68)	0.50 (0.01)	3.4 (0.90)	0.3	4.2
40-50	0.51 (0.05)	0.05 (0.00)	10 (0.73)	1.45 (0.56)	0.37 (0.00)	3.9 (0.94)	0.3	5.4
90-100	0.37 (0.02)	0.02 (0.00)	10 (0.63)	0.95 (0.14)	0.17 (0.00)	5.6 (0.80)	0.4	5.6

Table 2. Chemical and physical properties of the soil at different depths along vertical profiles from the border and interior of six forest fragments in the Roraima savanna, Northern Brazilian Amazon. Values are the average of six composite soil samples followed by the standard deviation in parentheses.

Attribute	Soil depth (cm)					
	0-10	10-20	20-30	30-40	40-50	90-100
Border						
pH	5.46 (0.43)	5.24 (0.38)	5.09 (0.36)	5.03 (0.30)	5.01 (0.32)	5.20 (0.34)
Ca ²⁺ (cmol _c dm ⁻³)	2.85 (1.22)	1.80 (0.90)	1.30 (0.74)	1.03 (0.62)	0.93 (0.45)	0.70 (0.43)
Mg ²⁺ (cmol _c dm ⁻³)	1.12 (0.49)	0.76 (0.46)	0.62 (0.20)	0.58 (0.19)	0.60 (0.26)	0.66 (0.28)
K ⁺ (cmol _c dm ⁻³)	1.33 (1.01)	0.66 (0.63)	0.27 (0.12)	0.25 (0.12)	0.21 (0.09)	0.28 (0.37)
Al ³⁺ (cmol _c dm ⁻³)	0.06 (0.11)	0.11 (0.15)	0.13 (0.15)	0.15 (0.16)	0.15 (0.17)	0.06 (0.10)
P ³⁺ (cmol _c dm ⁻³)	11.02 (5.72)	6.55 (2.90)	4.67 (3.66)	2.23 (1.28)	1.56 (1.46)	0.30 (0.66)
SB (cmol _c dm ⁻³)	5.29 (2.28)	3.22 (1.43)	2.19 (0.90)	1.86 (0.70)	1.75 (0.60)	1.61 (0.95)
SOM (g kg ⁻¹)	35.13 (6.68)	24.04 (5.11)	17.34 (5.57)	14.43 (4.55)	10.88 (2.79)	5.96 (2.97)
Sand (%)	69.60 (7.60)	66.94 (6.55)	63.18 (6.01)	59.36 (9.18)	54.32 (9.48)	46.37 (10.87)
Silt (%)	11.22 (4.35)	11.77 (4.57)	12.48 (6.78)	12.59 (5.74)	14.59 (8.90)	16.01 (5.27)
Clay (%)	19.19 (4.51)	21.29 (4.68)	24.34 (5.71)	28.06 (6.19)	31.09 (6.42)	29.29 (6.84)
Interior						
pH	5.51 (0.28)	5.31 (0.33)	5.20 (0.35)	5.11 (0.39)	5.14 (0.39)	5.25 (0.36)
Ca ²⁺ (cmol _c dm ⁻³)	3.00 (1.02)	1.89 (0.68)	1.21 (0.29)	0.99 (0.32)	0.93 (0.32)	0.86 (0.26)
Mg ²⁺ (cmol _c dm ⁻³)	1.00 (0.26)	0.76 (0.29)	0.68 (0.23)	0.59 (0.26)	0.64 (0.28)	0.57 (0.15)
K ⁺ (cmol _c dm ⁻³)	1.24 (1.10)	0.41 (0.29)	0.29 (0.08)	0.24 (0.10)	0.21 (0.10)	0.22 (0.12)
Al ³⁺ (cmol _c dm ⁻³)	0.03 (0.03)	0.06 (0.03)	0.08 (0.07)	0.09 (0.07)	0.09 (0.06)	0.05 (0.12)
P ³⁺ (cmol _c dm ⁻³)	14.74 (12.22)	9.85 (5.94)	7.95 (5.41)	4.96 (2.46)	4.75 (2.58)	4.16 (2.37)
SB (cmol _c dm ⁻³)	5.23 (1.94)	3.06 (1.10)	2.18 (0.50)	1.82 (0.58)	1.78 (0.54)	1.52 (0.34)
SOM (g kg ⁻¹)	38.91 (12.22)	22.65 (4.24)	14.99 (2.15)	11.50 (3.44)	9.90 (2.76)	9.09 (8.21)
Sand (%)	69.92 (6.48)	65.29 (6.90)	61.51 (8.40)	57.88 (8.89)	54.78 (9.42)	47.17 (10.37)
Silt (%)	11.26 (4.15)	12.88 (4.09)	11.96 (2.58)	11.93 (3.18)	13.15 (4.94)	14.23 (6.44)
Clay (%)	18.81 (4.81)	21.84 (5.01)	26.53 (7.17)	30.19 (7.26)	32.08 (5.85)	30.27 (6.28)

Ca = calcium; Mg = magnesium; K = potassium; Al = aluminum; P = phosphorus; SB = sum of bases; SOM = soil organic matter.

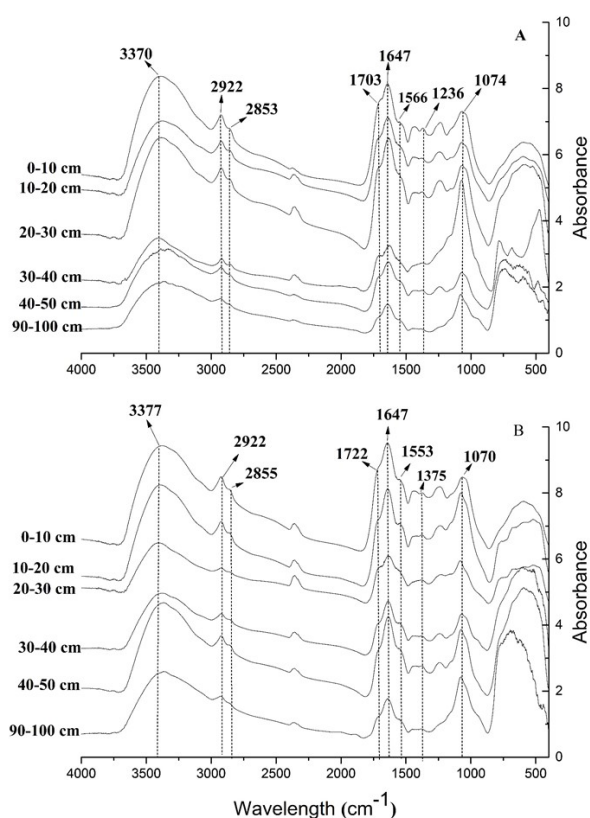


Figure 2. FTIR spectra of soil organic matter after 10% HF treatment (SOM_{HF}) at different soil depths in the border (A) and interior (B) of forest fragments in the savannas in the state of Roraima, northern Brazilian Amazon. For this analysis, the samples of all six fragments were pooled for one composite sample of border and one of interior soil for each depth layer of the 1-m profile.

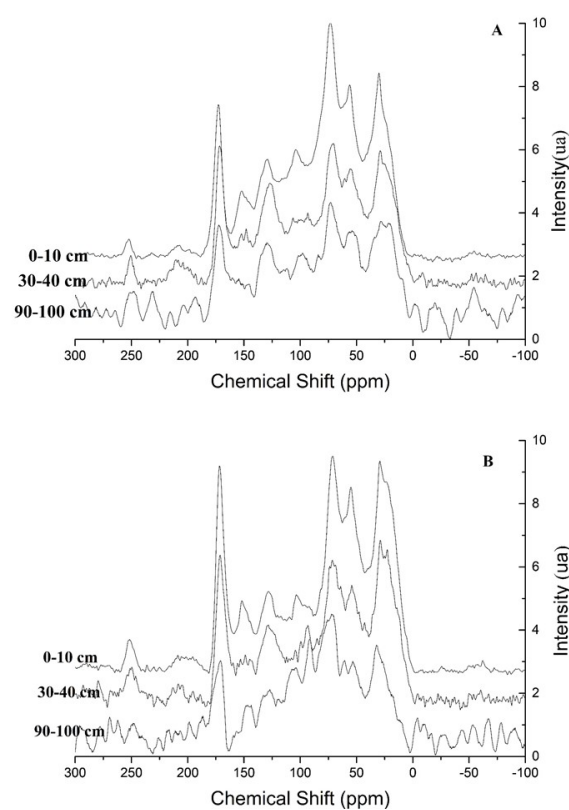


Figure 3. ^{13}C NMR CP / MAS spectra and distribution of C functional groups in HF-treated soil organic matter (SOM_{HF}) at three representative depths of border (A) and interior (B) soil profiles of six forest fragments in an area of savanna in the northern Brazilian Amazon. For this analysis, the samples of all six fragments were pooled for one composite sample of border and one of interior soil for each depth layer of the 1-m profile.

Table 3. Proportion of carbon types (%) determined by CP/MAS ^{13}C NMR in composite soil samples treated with HF at three depths from the border and interior of six forest fragments in an area of savanna in the northern Brazilian Amazon.

Sample	Depth (cm)	Carbon types								Ratios	
		alkyl-C (0-45 ppm)	O-alkyl-N (45-60 ppm)	O-alkyl-C (60-90 ppm)	di-O-alkyl-C (90-110 ppm)	aromatic-C (110-140 ppm)	O-aril (140-160 ppm)	carboxyl-C (160-185 ppm)	carbonyl-C (185-220 ppm)	alkyl-C/O-alkyl-C	arom-C/alkyl-C
Border	0-10	22.3	14.7	26.1	9.4	12.7	5.6	8.3	0.9	0.44	0.82
Border	30-40	22.0	15.4	18.5	10.4	15.4	2.3	10.6	2.4	0.5	0.94
Border	90-100	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Interior	0-10	28.5	16.2	19.7	8	9.4	5.7	11.1	1.4	0.65	0.53
Interior	30-40	29.3	14.7	14.4	9.1	13.2	5.3	12.6	1.5	0.77	0.63
Interior	90-100	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd = not determined; alkyl-C/O-alkyl-C = soil organic matter decomposition index; *arom-C/alkyl-C = carbonization index of soil organic matter

resonance intensity of aromatic groups decreased in the 30-40-cm layer, which was not observed in the interior samples.

On average, the border samples had a higher proportion of O-alkyl C and a lower proportion of alkyl C groups (Figure 3). Consequently, there was no significant difference in the alkyl C/O-alkyl C ratio between the border and interior samples according to the paired t-test, owing to the higher proportion of alkyls (alkyl-C). There was also no significant

difference in the aromatic C/alkyl C ratio between border and interior samples.

SOM_{HF} thermal degradability

Overall, the SOM_{HF} of border and interior samples showed similar thermal decomposition curve (Supplementary Material, Figures S1, S2), with four major temperature intervals (Table 4). The mass loss of up to 1.17% for $T \leq 105$ °C corresponds to the loss of hydration water (Crittler

and Airoidi 2006). In the second interval of 105-230 °C, the highest values were observed in the superficial layers (0-30 cm) in both border and interior samples (0.37% and 0.45%, respectively). Mass loss in the following intervals (up to 2.26% for 230 °C < T < 420 °C; up to 1.94% for 420-600 °C, and up to 99.5% for ≥ 650 °C) indicated that, after treatment with HF, the samples were predominantly constituted of inorganic material.

Table 4. SOM_{HF} mass loss (Mp %) at four temperature ranges, temperature residue (> 650°C) and thermogravimetric index (TGI) of soil samples from the border and interior of six forest fragments in the Roraima savanna (northern Brazil). Values of Mp % are the mean and the standard deviation (in parentheses). TGI was calculated as the mass loss at the 4th interval / 2nd + 3rd intervals.

Depth (cm)	Temperature range (°C)					TGI
	30-105	105-230	230-420	420-600	Residue > 650	
Interior						
0-10	0.21 (0.01)	0.21 (0.01)	2.26 (0.22)	1.55 (0.30)	95.91 (1.11)	0.61
10-20	0.11 (0.00)	0.13 (0.01)	1.08 (0.33)	1.06 (0.26)	97.60 (2.20)	0.87
20-30	0.80 (0.02)	0.11 (0.00)	0.95 (0.30)	0.76 (0.12)	98.11 (3.82)	0.72
30-40	0.09 (0.00)	0.10 (0.00)	0.94 (0.28)	0.80 (0.52)	98.07 (3.24)	0.77
40-50	0.08 (0.00)	0.11 (0.00)	1.02 (0.41)	0.88 (0.46)	97.91 (4.32)	0.77
90-100	0.01 (0.00)	0.04 (0.00)	0.30 (0.30)	0.15 (0.00)	99.50 (4.81)	0.44
Border						
0-10	0.02 (0.00)	0.03 (0.00)	0.29 (0.01)	0.23 (0.03)	99.45 (2.01)	0.72
10-20	0.10 (0.00)	0.16 (0.04)	1.31 (0.14)	1.23 (0.26)	97.20 (0.90)	0.84
20-30	0.24 (0.01)	0.21 (0.13)	1.72 (0.20)	1.94 (0.42)	95.89 (1.02)	1.01
30-40	1.17 (0.02)	0.18 (0.04)	1.38 (0.32)	1.52 (0.38)	96.73 (1.70)	0.97
40-50	0.07 (0.00)	0.08 (0.00)	0.76 (0.04)	0.65 (0.24)	98.44 (2.81)	0.77
90-100	0.02 (0.00)	0.03 (0.00)	0.29 (0.02)	0.17 (0.01)	99.49 (3.92)	0.53

The TGI tended to increase with depth, indicating an increase of thermostability, as seen by thermogravimetric analysis for the 40-cm depth (Table 4), and no statistical difference was observed between border and interior samples according to the paired t-test.

DISCUSSION

This is the first study analyzing the effect of fire on SOM quality in forest fragments of the Roraima savannas that considered the edge effect. The concentrations of C and N in our samples are consistent with those of weathered soil in the Amazon region (Reis *et al.* 2018) and are typical for well-humified SOM, while the lowest values observed at around 1-m indicate enrichment of N compounds of microbial origin in deeper layers (Hanke and Dick 2017). The low C/N ratio observed may also be related to the degradation of pyrogenic organic matter influenced by high precipitation and temperature, as also recorded in subtropical cambisols affected by fires (Potes *et al.* 2012), due to the solubilization of protein nitrogenous compounds of microbial origin (Rumpel *et al.*

2002, 2019). The observed R-values were generally acceptable both for border and interior samples, as only for 0.7 > R > 1.0 the preferential losses of C or N are relevant (Dick *et al.* 2006).

The increase of the aromaticity index with depth in both border and interior samples was similar to that observed in subtropical lithic entisols affected by fires, which was related to a dilution effect on the soil surface by the input of non-burned vegetation residues (Potes *et al.* 2010). In subtropical oxisols under native vegetation, the gradual increase in the aromaticity of organic matter up to a depth of 1 m was attributed to the dispersion of aromatic compounds originated from ancient burning events, which functionalized over time, favoring their migration along the profile (Dick *et al.* 2005). The high precipitation and temperature at our study site likely promoted the carboxylation of aromatic structures, and their migration along the profile was favored by the sandy soil texture and intense rainfall. The functionalization of aromatic structures resulting from vegetation burning may occur within a relatively short period after the fire event (Knicker *et al.* 2013).

The generally larger proportion of functional groups (O-alkyl C) in the border samples, where fire impact is more frequent and intense compared to the interior, is indicative of higher lability and easily combustible material at the border, as observed for other tropical and subtropical oxisols (Gonçalves *et al.* 2003). Therefore, our results indicate that the preservation of biochemically labile structures (such as carbohydrates) in well-drained soils on the border of the fragments is more related to the protection of SOM by organo-mineral interactions with iron and aluminum oxides than to the type of vegetation. The proportion of alkyl C groups related to lignin, suberin and cutin-type structures was higher in the interior samples, probably due to the presence of more lignified and slow combustion materials (e.g., tree trunks and bark).

The lower proportion of aromatic groups in our study compared to other soils subjected to annual burning (Knicker 2006; Leal *et al.* 2019), is possibly due to the enhanced decomposition of aromatic groups by soil microbiota in the hot and humid climate of the region (Knicker 2006). The high percentage of aromatic structures (aromatic-C) found in the border samples also shows that organic matter on the border is less labile than the slower burning material in the interior of the fragments. This finding is in agreement with Knicker *et al.* (2008b), who found a higher proportion of O-alkyl C structures in areas subjected to recent burning.

The mass loss during the thermal degradation of SOM in the range of 105-230 °C is related to more labile structures, such as carboxyl groups, alkyl and O-alkyl C structures (Rosa *et al.* 2005; Critter and Airoidi 2006). The oxidation of organic matter at low temperatures (e.g., < 350 °C) is related to the loss of the more labile (less biologically stabile) fraction of SOM (Schaiedung *et al.* 2017). Recent studies

(Katsumi *et al.* 2016; Miao *et al.* 2016) and the publication of a first methodological postulate (DIN standard, 19539) to determine biologically labile and stable structures of SOM in mineral soils revealed the presence of biologically labile SOM in solid samples, including soils, being thermally oxidized at temperatures below 400 °C (TOC 400) (DIN Standards Committee Water Practice 2015).

The third temperature interval of the thermal degradation curve (230-420 °C) leads to the decomposition of more complex aliphatic structures than those degraded at lower temperatures, while in the fourth interval (420-600 °C), the loss of mass corresponds to structures with high thermal and biological stability, such as aromatic structures (Potes *et al.* 2012; Leal *et al.* 2015). Above 600 °C, the resulting inorganic material is probably composed of sand-sized quartz particles that resisted the treatment for the duration employed, and/or neo-precipitated silicates during HF treatment (Dick *et al.* 2008b; Potes *et al.* 2010; Leal *et al.* 2015). Alkyl organic structures and oxygen and nitrogen-containing functional groups decompose at temperatures below 400 °C, while more complex structures are more resistant to thermal degradation and their presence causes mass loss at higher temperatures (Crittter and Airolidi, 2006). In general, pyrogenic organic matter suffers the greatest mass loss at temperatures above 500 °C, and more condensed structures decompose at temperatures above 650 °C. (Hsieh and Bugna 2008).

CONCLUSIONS

Our results are the first to show the variability in the quality of SOM in the natural forest fragments in the Roraima savanna of the northern Brazilian Amazon, which are often impacted by understory fire. The aromaticity index increased with soil depth, due to the percolation and functionalization effect of aromatic compounds. The organic matter in these soils often affected by fire is easily decomposed due to the high proportion of O-alkyl C groups, such as carbohydrates. Regarding the chemical composition of the SOM, the border effect up to 1 m in depth was not pronounced, showing that this compartment tends to be stable throughout the fragments.

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SUPPLEMENTARY MATERIAL (only available in the electronic version)

Silva *et al.* Effects of fire on soil organic matter in northern Amazonian forest fragments

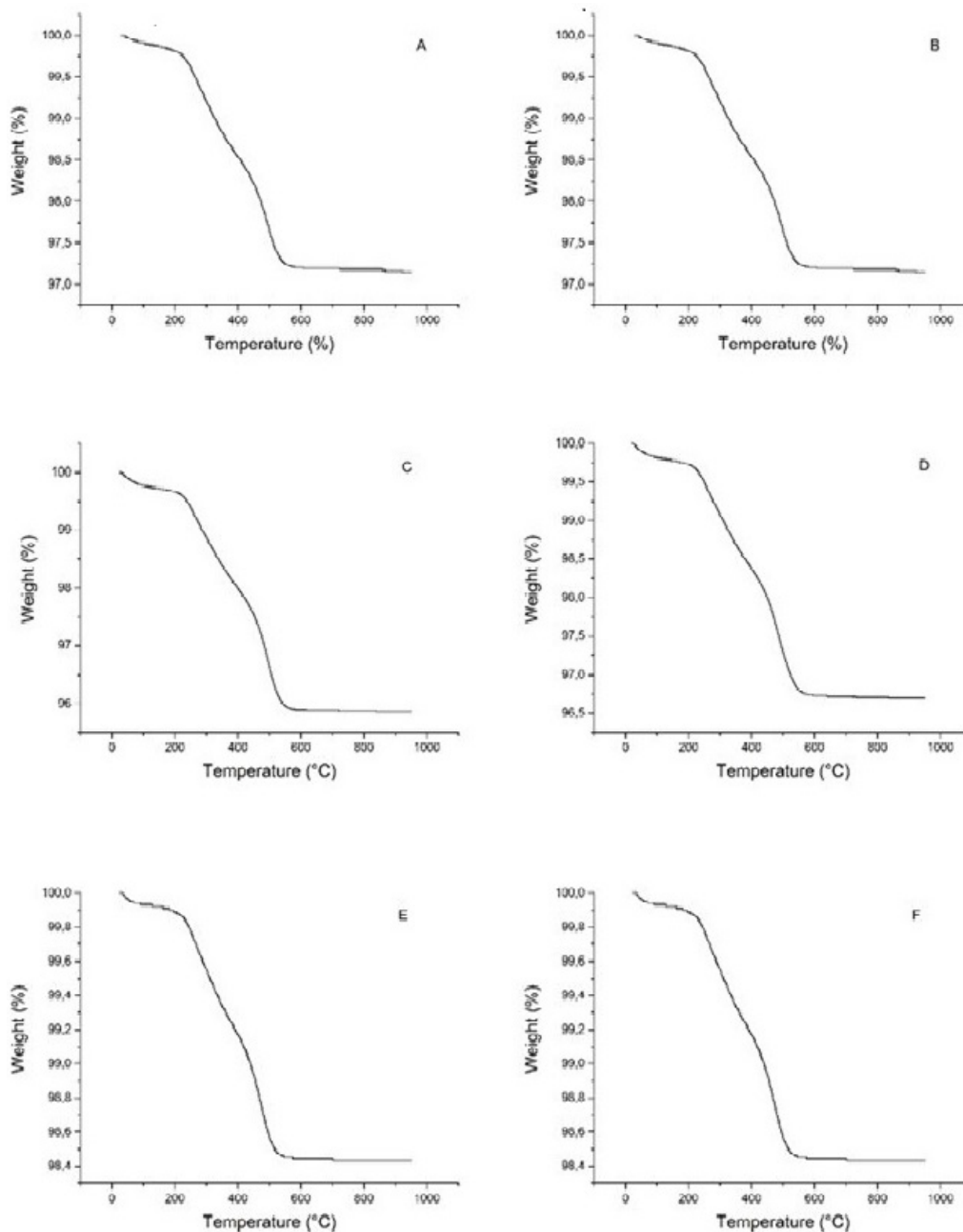


Figure S1. Thermogravimetric analysis (TGA) diagrams of soil samples from the border of six forest fragments in the northern Brazilian Amazon at different depths. A – 0-10; B – 10-20 cm; C – 20-30 cm; D – 30-40 cm; E – 40-50 cm; F – 90-100 cm. For this analysis, soil samples of each depth for the border and interior of each of six forest fragments were pooled into one overall composite border sample and one overall composite interior sample.

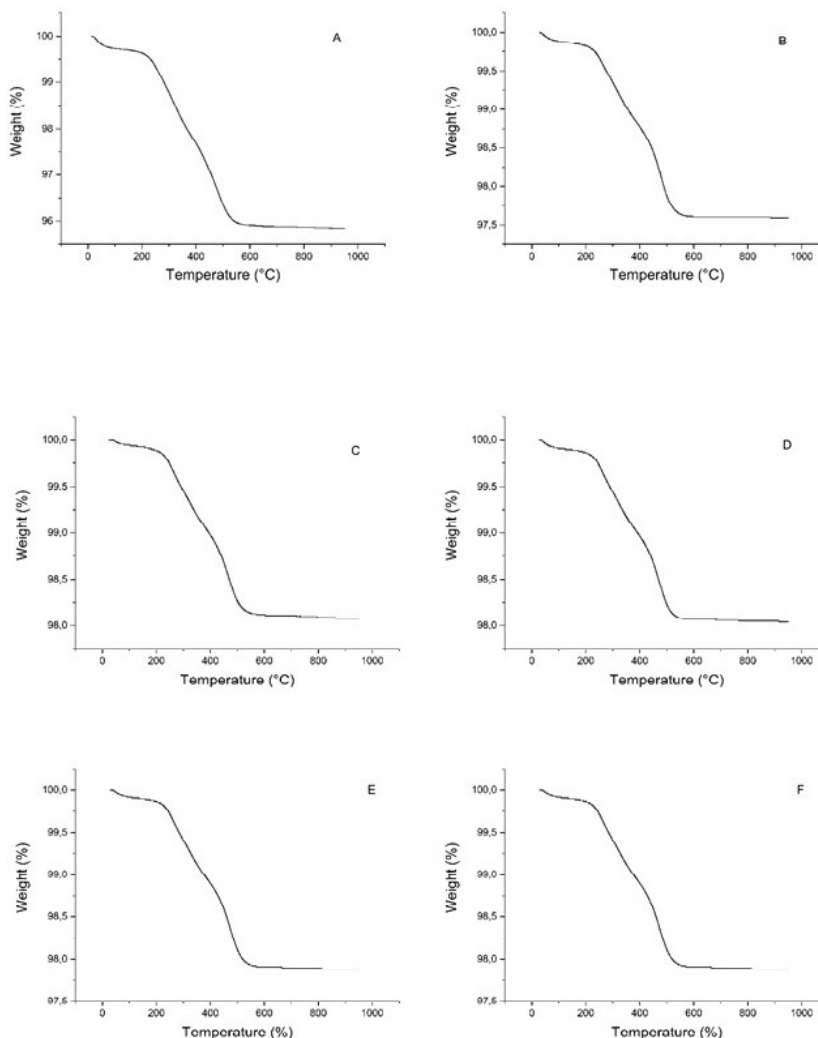


Figure S2. Thermogravimetric analysis (TGA) diagrams of soil samples from the interior of six forest fragments in the northern Brazilian Amazon at different depths. A – 0-10; B – 10-20 cm; C – 20-30 cm; D – 30-40 cm; E – 40-50 cm; F – 90-100 cm. For this analysis, soil samples of each depth for the border and interior of each of six forest fragments were pooled into one overall composite border sample and one overall composite interior sample.

Table S1. Fourier transform infrared (FTIR) spectral relative intensities (RI) of soil organic matter in samples from the border and interior of six forest fragments located in an area of savanna in the northern Brazilian Amazon. Samples were taken along 1-m depth profiles. For this analysis, soil samples of each depth for the border and interior of each of six forest fragments were pooled into one overall composite border sample and one overall composite interior sample.

Location in the fragment	Depth (cm)	RI ₂₉₂₂	RI ₁₇₀₅	RI ₁₆₆₄	RI ₁₅₄₈	RI ₁₂₂₇	RI ₁₀₇₇
Border	0-10	7.41	22.96	24.44	10.37	11.85	18.52
Border	10-20	6.15	18.46	23.85	14.62	14.62	18.46
Border	20-30	5.19	18.52	25.19	15.56	12.59	19.26
Border	30-40	3.95	13.16	17.11	7.89	5.26	51.32
Border	40-50	6.41	19.23	26.28	11.54	10.90	22.44
Border	90-100	6.45	15.32	29.03	12.10	2.42	32.26
Interior	0-10	6.34	21.13	14.08	14.08	11.27	18.31
Interior	10-20	6.20	17.05	24.03	10.08	12.40	26.36
Interior	20-30	4.42	18.58	23.01	13.27	13.27	24.78
Interior	30-40	6.52	17.39	27.17	13.04	8.70	23.91
Interior	40-50	5.81	13.95	31.40	13.95	6.98	24.42
Interior	90-100	4.35	13.04	24.35	10.43	5.22	40.00