

# Pedogenesis of high-mountain soils from Serra da Mantiqueira, Brazil<sup>1</sup>

## Pedogênese de solos alto-montanos da Serra da Mantiqueira, Brasil

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**ABSTRACT** - In the Serra da Mantiqueira region the pedogenetic studies contribute to both the understanding of past events and supporting the conservation of natural resources. This study aimed to characterize the soils from the Minas Gerais high-mountains region to evaluate the influence of paleoenvironmental conditions on pedogenesis. Five profiles were selected and characterized for morphological, physical and chemical properties. Isotopic analyses of <sup>13</sup>C were performed in soil samples collected at depths of 10, 20, 30, 40, 50, 60, 80 and 100 cm; except in P2, which was collected up to 60 cm deep. Erratic distribution of the particle-size fractions and C contents highlight the sedimentary nature of the profiles, resulting from the erosive action favored by the relief. High organic C content in subsurface and its accumulation in the surface were observed in the profiles, which suggests the occurrence of the melanization process. In the profiles P2, P4 and P5 (*Cambissolos/ Cambisols*) the brownish color indicates the xanthization process, while in P1 (*Argissolo/ Lixisol*), is highlighted the process of eluviation and illuviation resulting in the increase of clay in subsurface and presence of clay films. In P3 (*Latossolo/ Ferralsol*), the low values of sum of bases, silica removal and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (ki index) values below 1.0 point to the advanced weathering and the allitization process. The variation in the isotopic signature of δ<sup>13</sup>C indicates a drier past condition, with mixed vegetation, with gradual change of vegetation with predominant C<sub>3</sub> photosynthetic pathway. In P1 and P4, the decrease in the contents of δ<sup>13</sup>C in surface results from anthropic action.

**Key words:** Pedoenvironment. Altitude soils. Carbon. Humic horizon.

**RESUMO** - Na região da Serra da Mantiqueira os estudos pedogenéticos podem contribuir tanto para o entendimento de eventos pretéritos como para auxiliar na conservação dos recursos naturais. Este estudo objetivou caracterizar solos de região altomontana de Minas Gerais para avaliar a influência das condições paleoambientais na pedogênese. Cinco perfis foram selecionados e caracterizados quanto aos atributos morfológicos, físicos e químicos. Análises isotópicas de <sup>13</sup>C foram realizadas em amostras de solo coletadas nas profundidades de 10, 20, 30, 40, 50, 60, 80 e 100 cm; exceto em P2, que foi coletado até 60 cm de profundidade. A distribuição errática das frações granulométricas e de C evidenciam a natureza sedimentar dos solos, resultado da ação erosiva condicionada pelo relevo. Nos perfis P2, P4 e P5 (*Cambissolos/Cambisols*) a coloração brunada indica o processo de xantização, enquanto no perfil P1 (*Argissolo/Lixisol*) é evidenciado o processo de eluviação e iluviação, resultando no incremento de argila em profundidade e pela presença de cerosidade. Em P3 (*Latossolo/Ferralsol*) os pequenos valores de soma de bases, remoção de sílica e valores da razão SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (índice ki) inferiores a 1,0 evidenciam o intemperismo avançado e o processo de alitização. Nos perfis verifica-se elevados teores de C orgânico em profundidade e acúmulo superficial, o que sugere a ocorrência do processo de melanização. A variação na assinatura isotópica do δ<sup>13</sup>C indica uma condição pretérita mais seca, com vegetação mista, com mudança gradual de vegetação com via fotossintética predominante C<sub>3</sub>. Em P1 e P4, a diminuição dos teores de δ<sup>13</sup>C em superfície é resultado da ação antrópica.

**Palavras-chave:** Pedoambiente. Solos de altitude. Carbono. Horizonte húmico.

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## INTRODUCTION

Serra da Mantiqueira is one of the oldest and most important mountain complexes in the Southeastern region of Brazil, sheltering significant remnants of the Atlantic Forest biome and representing a large watershed of the Paraíba do Sul and Paraná basins (MODENESI-GAUTTIERI, 2000; PINTO *et al.*, 2015). Besides being considered a region of extreme importance in terms of water, it is also composed of unique and fragile environment that constitutes important refuges for animal and plant life; therefore, it is necessary to better understand the existing resources for its preservation. Among these resources the soils stand out, which contribute to the conservation of water bodies and forest maintenance (FONTANA *et al.*, 2017; MENEZES *et al.*, 2009; PINTO *et al.*, 2015).

In the Serra da Mantiqueira region, where predominates mild air temperatures conditioned by high altitude, the reduction in the rate of decomposition of organic material favors the accumulation and maintenance of soils with high contents of organic matter (OM), commonly found in sparse areas almost always associated with the regions of rugged relief. Thus, the relief shapes associated with the dynamics of water fluxes and OM deposits contribute to variations in soil attributes in different landscape segments (FONTANA *et al.*, 2017).

Some studies report the occurrence of soils with *A húmico* (umbric) horizons associated with *Latosolos* and *Cambissolos* (Ferralsols and Cambisols) (CALEGARI *et al.*, 2013; FONTANA *et al.*, 2017; MARQUES *et al.*, 2011; MODENESI-GAUTTIERI, 2000; PINTO *et al.*, 2015; SILVA; VIDAL-TORRADO, 1999), which may constitute an important relict aspect derived from a unique form of environmental conditions favorable to the accumulation of OM at a great depth and whose maintenance would result from the stability of the surface on which they are and from the formation of organomineral complexes (CALEGARI *et al.*, 2013; FONTANA *et al.*, 2017; MODENESI-GAUTTIERI, 2000; PINTO *et al.*, 2015; SILVA; VIDAL-TORRADO, 1999). According to Calegari *et al.* (2013), the genesis and paleoenvironmental meaning of these soils are not yet fully understood, so they are assumed to be relict soils in landscapes which had a favorable climate for the accumulation of organic carbon.

In studies associated to the reconstruction of vegetation and paleoclimate inference, stable isotopes are important instruments, since they are based on the fact that the isotopic composition varies in a predictable manner, as the element moves through the various compartments of an ecosystem (CALEGARI *et al.*, 2013; COE; CHUENG; GOMES, 2012). Among the isotopes, <sup>13</sup>C is one of the most used in qualitative environmental studies due to the easy methodological procedures and interpretation (COE; CHUENG; GOMES, 2012).

Due to the small relevance of the high-mountain environments in tropical climate regions and the particularities of the soils formed under these conditions, the hypothesis of this study is that, although the soils located in these environments have different degrees of pedogenetic development, similarities can be verified in the properties present in the superficial *A húmico* (umbric) horizons, which may be associated with a possible relict environmental condition. Thus, the aim of this study was to characterize soils of Serra da Mantiqueira for a better understanding of paleoenvironmental conditions and infer about the aspects related to their pedogenesis.

## MATERIAL AND METHODS

### Location and characterization of the study area

The study area is located in the microregion of Itajubá, southern Minas Gerais State, in the Serra da Mantiqueira Complex. The predominant climate is Cwb type, according to Köppen's classification (ALVARES *et al.*, 2013), that is, subtropical highland climate, characterized by mild and humid summers with dry winters and average annual precipitation ranging from 1,550 to 2,800 mm, which under normal conditions, the average concentration of 88% of the total rainfall occurs between September and March and with dry period between April and August (ÁVILA *et al.*, 2014; OLIVEIRA FILHO *et al.*, 2007; PINTO *et al.*, 2015). The average annual temperature is 21 °C, ranging from 27 °C to 13 °C, and can reach values close to 0 °C at the highest altitudes of the area during the most severe winters (OLIVEIRA FILHO *et al.*, 2007; REBOITA *et al.*, 2015; TROUW *et al.*, 2007).

The region is located at the Mantiqueira Province, in the south part of the southern edge of the São Francisco Craton, regionally belonging to the Nappe Socorro-Guaxupé, where tonalitic to granodioritic orthogneisses predominate, rich in hornblende and biotite-hornblende with intercalations of amphiboles, as well as granites and porphyritic granitoids (TROUW *et al.*, 2007). Altitudes in the area range from 780 m, in the bed of the Verde River, to 2,350 m, in the Serra da Mantiqueira, between the peaks of Itaguaré and Marins, the two main geomorphological compartments that make up the relief of the mountains, with surfaces of high altitudes, sloping and dissected, and the hills, with flattened areas and lowered surfaces of lower levels and gentle slope (ÁVILA *et al.*, 2014; SILVA; VIDAL-TORRADO, 1999; TROUW *et al.*, 2007).

The vegetation of the study area is Atlantic forest, where the altitudinal levels of Serra da Mantiqueira are able to alter the physiognomy of the forest communities present (MEIRELES; SHEPHERD; KINOSHITA, 2008). The predominant vegetation is composed of Montane Rain Forest, in the regions at the top of the Serra da Mantiqueira,

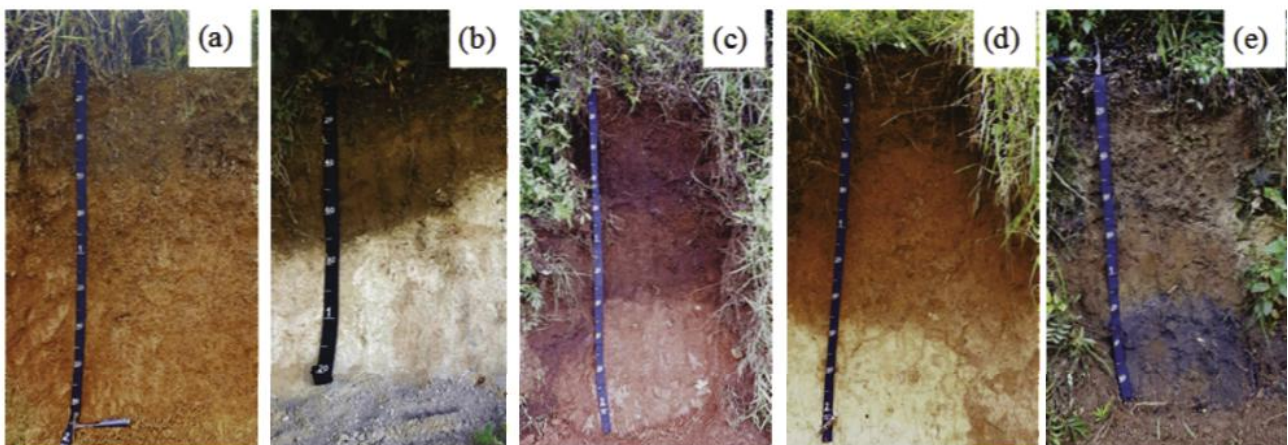
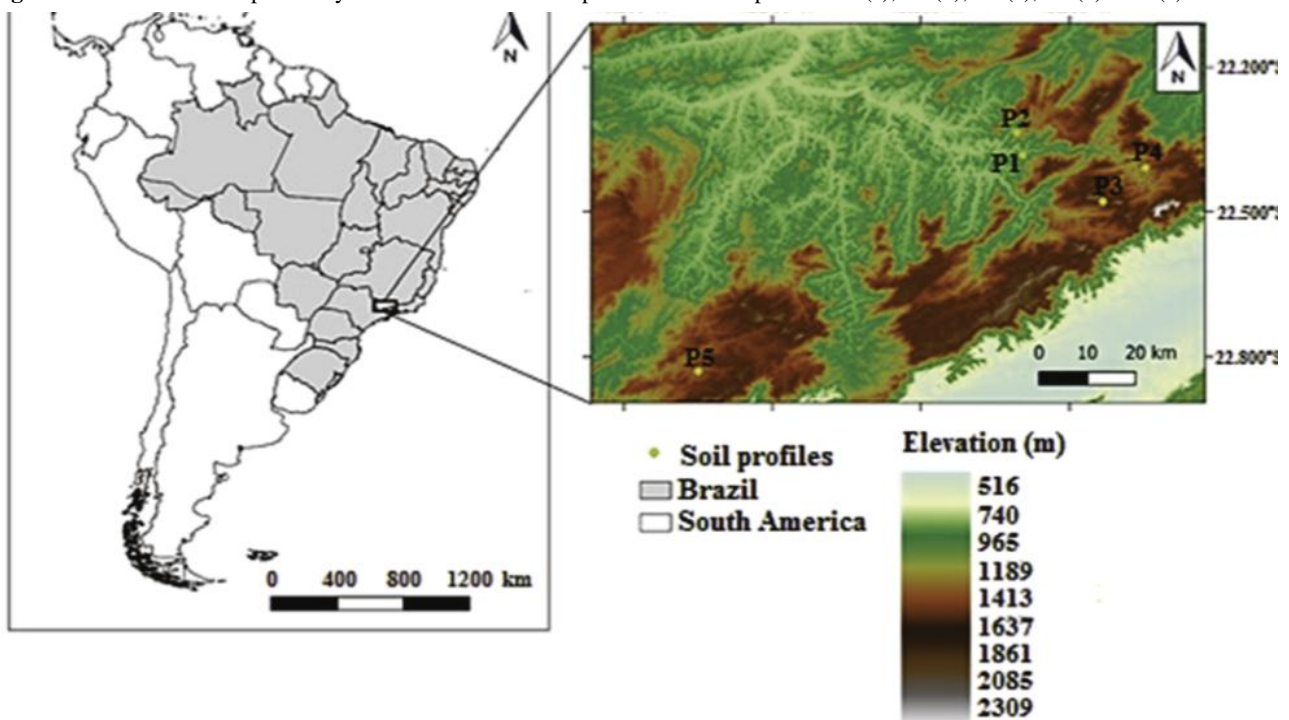
and by high-mountain Ombrophilous Forest (ÁVILA *et al.*, 2014; MEIRELES; SHEPHERD; KINOSHITA, 2008; OLIVEIRA FILHO *et al.*, 2007; SILVA; VIDAL-TORRADO, 1999). The low temperatures promote the appearance of subtropical aspects, such as the occurrence of Araucaria forest and grasslands at high altitudes (MARQUES *et al.*, 2011; MEIRELES; SHEPHERD; KINOSHITA, 2008; MODENESI-GAUTTIERI, 2000; OLIVEIRA FILHO *et al.*, 2007), which characterize abrupt lines of ecotones. The soil classes that predominate in the region are *Argissolos* (Acrisols), *Cambissolos* (Cambisols) and *Latosolos* (Ferralsols), with the presence of histic

and/or *A húmico* (umbric) surface horizons (ÁVILA *et al.*, 2014; OLIVEIRA FILHO *et al.*, 2007; PINTO *et al.*, 2015; SILVA; VIDAL-TORRADO, 1999).

### Soil morphology description, sampling and sample preparation

Five soil profiles were described and sampled according to Santos *et al.* (2015). The altitudes of profiles ranging between 860 and 1,700 m, located in the backslope to shoulder of the landscape and on relief ranging from sloping to steep, as described in Table 1. The distribution and elevation of the relief in the profile collection area is presented in Figure 1.

**Figure 1** - Localization map of study area and distribution of profiles. Photo of profiles P1 (a), P2 (b), P3 (c), P4 (d) e P5 (e)



**Table 1** - General landscape aspects and profile locations in the Serra da Mantiqueira, Minas Gerais, Brazil

Profile	Coordinates	Altitude (m)	Regional relief	General features
P1	22° 22.969' S; 45° 23.677' W	902		Shoulder; pasture
P2	22° 20.162' S 45° 24.432' W	862	Slope varying from 21 to 45%	Backslope; forest vegetation;
P3	22° 28.740' S 45° 13.985' W	1.687		slightly stony and slightly rocky
P4	22° 24.556' S 45° 08.784' W	1.255		Backslope; pasture
P5	22° 43.420' S 46° 02.504' W	1.326	Slope varying from 8 to 20%	Shoulder; forest vegetation

Soil samples were air-dried, ground and sieved through a 2.00-mm-mesh sieve, to obtain the air-dried fine earth (ADFE), from which the physical and chemical analysis were performed.

### Physical and chemical analysis

Particle-size analysis was performed by the pipette method according to Teixeira *et al.* (2017), quantifying the contents of total clay (TC) (dispersed with sodium hydroxide), water-dispersible clay (WDC) (dispersed only deionized water), silt, fine sand, and coarse sand. From the results the silt/clay, fine sand/coarse sand ratios and the clay flocculation index [CFI = TC – WDC) x 100 / TC] were calculated (SOIL SURVEY STAFF, 2014; TEIXEIRA *et al.*, 2017). The textural classes was determined from the soil textural triangle according Santos *et al.* (2015), an adaptation of the classification proposed by the USDA (SOIL SURVEY STAFF, 2014), that have a division of clayey soils into two distinct classes (distinction of clay and heavy clay when clay content is > 600 g kg<sup>-1</sup>).

Soil chemical analyses were performed according to Teixeira *et al.* (2017), being determined: (i) the values of pH<sub>H2O</sub> in soil: solution ratio of 1:2.5 (v/v); (ii) the exchangeable Na and K and the assimilable P extracted with the Mehlich-1 solution, with K and Na being determined by flame photometry and the assimilable P by the photocolometry technique; (iii) exchangeable Ca, Mg and Al extracted with 1 mol L<sup>-1</sup> KCl solution and determined by titration with EDTA solution for Ca and Mg, and with NaOH solution for Al; (iv) potential acidity (H + Al) was determined using 0.5 mol L<sup>-1</sup> calcium acetate extractant solution and also determined by titration with NaOH solution. The results obtained were used to calculate the sum of bases (S), cation exchange capacity at pH 7.0 (T), base saturation (V%), aluminum saturation (m%) and the cation exchange capacity of the clay fraction (CEC<sub>clay</sub>) (TEIXEIRA *et al.*, 2017). Total organic carbon (TOC) contents were quantified from oxidation with potassium dichromate in acid medium and subsequent titration with ammoniacal ferrous sulfate solution (YEOMANS; BREMNER, 1988).

The contents of pedogenetic oxides (Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) were determined by the sulfuric attack method, with iron, titanium and aluminum contents obtained from the filtered extract and silica contents obtained from the residues (TEIXEIRA *et al.*, 2017). Based on the values obtained, the molecular ratios ki (Eq. 1) and kr (Eq. 2) were determined to infer about the degrees of weathering of the soils.

$$Ki = \left( \frac{SiO_2}{Al_2O_3} \right) \times 1.70 \quad (1)$$

$$Kr = \left( \frac{SiO_2 \times 0.60}{Al_2O_3 + (Fe_2O_3 \times 0.64)} \right) \quad (2)$$

Based on morphological, physical and chemical attributes, soil profiles were classified according to the Brazilian Soil Classification System (SiBCS) (SANTOS *et al.*, 2018), and according to the World Reference Base for Soil Resources (WRB) (IUSS WORKING GROUP WRB, 2015).

### δ<sup>13</sup>C isotopic abundance

For the analysis of stable isotopes, soil material was collected at predetermined intervals of 10 cm up to a depth of 60 cm, from which the samples were collected at intervals of 20 cm to a depth of 100 cm, except in P2, due to the lithic contact close to 60 cm from the surface. The isotope ratio was quantified by an isotope ratio mass spectrometer (IRMS) (Delta V Advantage) coupled to an IRMS elemental analyzer (Flash EA 2000), both from Thermo Fisher Scientific (Bremen, Germany), at the Carbon and Nitrogen Biotransformation Research Laboratory (LABCEN) of the Federal University of Santa Maria, Rio Grande do Sul, Brazil. Elemental composition (SOC) was expressed as dry weight percentage, and the isotopic composition (δ<sup>13</sup>C) was measured in relation to the Vienna Pee Dee Belemnite (VPDB) standard, and expressed as parts per thousand (‰, ppt) with a 0.2‰ standard deviation (BOUTTON *et al.*, 1998).

### Statistical Analysis

The dendrogram of hierarchical cluster analysis (HCA) was performed based on the binary grouping according to the degree of dissimilarity between pairs (pair-wise), with single linkages, evaluated by

Euclidean distance (BEEBE; KOWALSKI, 1987). To calculate the dissimilarity between A horizons of all profiles, only the surface horizons were used, and the following variables were analyzed: contents of Al, P and TOC, values of S, T and pH, and clay, silt and sand contents. All statistical procedures were performed in the R version 3.4.3 environment (R CORE TEAM, 2020).

## RESULTS AND DISCUSSION

### Morphological properties

For the profiles, were observed depths ranging from 112 to 237 cm, evidencing the absence of shallow soils and lithic contact close to the surface (Table 2). The soils colors show brown shades, with hues ranging from 5YR to 10YR and predominance of the hue 5YR among the horizons (53%). The values vary between 2 and 7, with a predominance of 4, corresponding to 55%

of the horizons; and chroma ranges from 1 to 7, with predominance of chromas 2 (43%) and 3 (25%) among the horizons. The A horizons are thick and have dark color and its values and chromas are low, usually  $\leq 4$ , which are characteristic of soils of this altitudinal region (BENITES *et al.*, 2003; FONTANA *et al.*, 2017; MARQUES *et al.*, 2011; MODENESI-GAUTTIERI, 2000; PINTO *et al.*, 2015; SILVA; VIDAL-TORRADO, 1999).

Surface horizons show predominance of granular structures due to presence of OM, with moderate to strong degree of development, except in P3, where in the A1 horizon the structure is single grains type. In subsurface, the predominant type of structure between horizons B and BA changes to subangular blocks, with a slight decrease in the degree of development of the structures compared to surface horizons, with predominance of moderate degree and small size. In C horizons, when present, the structures are in single grains (P2) or massive (P4).

**Table 2** - Field morphological attributes of the sampled soils in the Serra da Mantiqueira, Minas Gerais, Brazil

Horizon	Depth (m)	Munsell Color moist	Structure	Clay coating	Textural class
Profile P1					
Ap	0.0 – 0.18	5YR 3/4	mo, fi, gr	-	clay
A1	0.18 – 0.30	5YR 3/2	mo, fi, gr	-	cl
A2	0.30 – 0.56	5YR 3/2	mo, fi, sb	-	cl
BA	0.56 – 0.71	5YR 4/4	mo, fi, sb	we, com	clay
B1	0.71 – 0.97	5YR 4/5	mo, fi, sb	we, com	clay
B2	0.97 – 1.30	5YR 4/7	mo, fi, sb	mo, com	clay
B3	1.30 – 1.74+	5YR 5/3	mo, fi, sb	mo, com	clay
Profile P2					
A1	0.0 – 0.15	7.5YR 4/2	mo/st, me, gr	-	scl
A2	0.15 – 0.27	7.5YR 4/3	mo/st, co, gr	-	sl
A3	0.27 – 0.46	5YR 4/2	mo, co, gr	-	sl
A4	0.46 – 0.61	5YR 4/3	mo, fi, sb	-	scl
Bi	0.61 – 0.76	7.5YR 7/2	we, vf, sb	-	sl
C	0.76 – 1.12+	7.5YR 7/2	single grain	-	sl
Profile P3					
A1	0.0 – 0.20	5YR 3/2	single grain	-	cl
A2	0.20 – 0.41	5YR 3/2	we/mo, me, gr	-	clay
A3	0.41 – 0.63	5YR 3/2	mo, me, gr	-	clay
A4	0.63 – 0.83	5YR 2/2	we/mo, me, gr	-	clay
AB1	0.83 – 1.04	5YR 3/3	mo, me, gr	-	clay
AB2	1.04 – 1.20	5YR 3/4	mo, me, gr	-	clay
AB3	1.20 – 1.33	5YR 3/2	mo, me, gr	-	cl
BA	1.33 – 1.48	5YR 4/3	mo, fi, sb	-	clay
Bw	1.48 – 2.11+	5YR 3/5	mo, fi, sb	-	clay

Continuation Table 2

Profile P4					
A1	0.0 – 0.20	10YR 3/3	mo/st, me, gr	-	ls
A2	0.20 – 0.33	10YR 4/3	mo/st, me, gr	-	sl
A3	0.33 – 0.57	10YR 4/4	mo, me, gr	-	sl
AB	0.57 – 0.71	10YR 4/4	mo, fi, sb	-	sl
BA	0.71 – 0.93	7.5YR 4/3	mo/st, fi, sb	-	cl
B1	0.93 – 1.20	5YR 4/4	mo, fi, sb	-	cl
B2	1.20 – 1.41	5YR 4/4	mo, vf, sb	-	cl
BC	1.41 – 1.53	5YR 4/3	we/mo, vf, sb	-	cl
C1	1.53 – 2.00	10YR 7/6	massive	-	scl
C2	2.00 – 2.37+	10YR 7/4	massive	-	sl
Profile P5					
O	0.0 – 0.09	10YR 4/2	we/mo, vf, gr	-	scl
A1	0.09 – 0.25	10YR 4/2	mo/st, fi + me, gr	-	sl
A2	0.25 – 0.50	10YR 4/2	mo/st, fi + me, gr	-	clay
A3	0.50 – 0.66	10YR 3/2	mo, vf + fi, gr	-	sl
AB	0.66 – 0.82	7.5YR 4/2	mo, vf, gr + mo, vf, sb	-	clay
B1	0.82 – 0.97	7.5YR 4/3	mo, fi, ab + sb	-	clay
B2	0.97 – 1.10	7.5YR 4/2	mo, fi, gr + mo, fi, sb	-	clay
Ab	1.10 – 1.61+	10YR 4/1	mo, fi, gr + we/mo, vf, sb	-	clay

we: weak; mo: moderate; st: strong; vf: very fine; fi: fine; me: medium; co: coarse; gr: granular; ab: angular blocky; sb: subangular blocky; com: common; cl: clay loam; sl: sandy loam; scl: sandy clay loam; ls: loamy sand

Only horizons B of P1 show blocky structures with shiny ped faces, identified in the field as clay films formed mainly due to clay illuviation (BUOL *et al.*, 2011; DORTZBACH *et al.*, 2016a), with development varied from weak to moderate and quantity common. The textural classes are quite variable between horizons and between profiles, with horizons whose texture varies from sandy loam to clay, and 43% of the horizons belong to the clay class, 23% to sandy loam and 20% to clay loam.

### Physical properties

The values of particle size fractions are variable in depth of the profiles. The total sand contents range from 278 to 854 g kg<sup>-1</sup>, with predominance of coarse sand contents to the detriment of fine sand (Table 3). As effect, the values of the fine sand / coarse sand ratio tend to be lower than 1.0. The maximum and minimum of silt contents are 46 and 314 g kg<sup>-1</sup>, respectively, while for the total clay these contents are 74 and 572 g kg<sup>-1</sup>, respectively. The predominance of clay fraction in detriment of silt fraction, also favors values of the silt / clay ratio lower than 1.0, whose average is around 0.7. However, in P2, there are horizons in which the silt contents are higher than clay contents. For the values

of the silt / clay and fine sand / coarse sand ratios, all profiles show an irregular distribution of the values of these ratios in subsurface, which may be an indication of lithological discontinuity. The clay flocculation index (CFI) vary in subsurface, with minimum and maximum values of 2 and 95%, respectively, tending to be highest in the superficial horizons of the profiles P3, P4 and P5. The CFI variation can be due to the nature and degree of pedogenetic development of soils.

The irregular distribution of the silt / clay ratio and fine sand / coarse sand ratio observed in the profiles, in subsurface, are indicatives of the allochthone origin of these soils from colluvial sediments. Similar results were observed by Silva and Vidal Torrado (1999), who associated the lower irregularity of C contents in subsurface with a condition of greater stability of the landscape tops where the studied profiles are located. According to Modenesi-Gauttieri (2000), the colluvial sediments of this region are generally of finer particle-size and have a relatively homogeneous matrix with a better sorted sand fraction. In these profiles, the low values of assimilable P are due, first, to the nature of the parent material, which is naturally poor in total contents of this element (Table 6), as well as to its adsorption to the iron oxide exchange sites (MELO *et al.*, 2015).

**Table 3** - Physical attributes of soils in the Serra da Mantiqueira, Minas Gerais, Brazil

Horizon	Sand			Silt	Clay		CFI %	Silt Clay	Fine sand
	Total	Coarse	Fine		TC	WDC			Coarse sand
----- g kg <sup>-1</sup> -----									
Profile P1									
Ap	376	131	245	203	421	161	63	0.5	1.9
A1	398	142	256	261	341	225	35	0.8	1.8
A2	347	124	223	274	379	269	35	0.7	1.8
BA	302	94	208	272	426	326	31	0.6	2.2
Bt1	278	100	178	172	550	327	42	0.3	1.8
Bt2	355	91	264	73	572	37	94	0.1	2.9
Bt3	294	111	183	215	491	29	94	0.4	1.6
Profile P2									
A1	562	385	177	237	201	53	74	1.2	0.5
A2	623	422	201	197	180	13	93	1.1	0.5
A3	688	536	152	122	190	76	60	0.6	0.3
A4	575	333	242	174	251	76	70	0.7	0.7
Bi	647	416	231	275	78	19	76	3.5	0.6
C	716	473	243	210	74	15	80	2.8	0.5
Profile P3									
A1	418	266	152	196	386	32	92	0.5	0.6
A2	355	218	137	183	462	69	85	0.4	0.6
A3	384	244	140	151	465	88	81	0.3	0.6
A4	385	258	127	154	461	80	83	0.3	0.5
AB1	442	272	170	94	464	156	66	0.2	0.6
AB2	391	229	162	155	454	143	69	0.3	0.7
AB3	413	251	162	300	287	115	60	1.0	0.6
BA	409	243	166	93	498	150	70	0.2	0.7
Bw	381	236	145	146	473	279	41	0.3	0.6
Profile P4									
A1	854	627	227	46	100	9	91	0.5	0.4
A2	573	352	221	157	270	178	34	0.6	0.6
A3	548	330	218	194	258	172	33	0.8	0.7
AB	551	309	242	113	336	142	58	0.3	0.8
BA	427	248	179	190	383	167	56	0.5	0.7
Bi1	424	244	180	244	332	236	29	0.7	0.7
Bi2	439	232	207	165	396	274	31	0.4	0.9
BC	442	241	201	188	370	139	62	0.5	0.8
C1	525	315	210	237	238	130	45	1.0	0.7
C2	566	284	282	314	120	118	2	2.6	1.0
Profile P5									
O	742	668	74	60	198	10	95	0.3	0.1
A1	492	409	83	84	424	147	65	0.2	0.2
A2	429	316	113	145	426	261	39	0.3	0.4
A3	508	405	103	124	368	141	62	0.3	0.3
AB	346	260	86	133	521	394	24	0.3	0.3
B1	420	325	95	156	424	242	43	0.4	0.3
B2	340	258	82	178	482	401	17	0.4	0.3
Ab	411	329	82	125	464	283	39	0.3	0.2

TC = total clay; WDC = Water-dispersible clay; CFI: Clay flocculation index =  $(TC - WDC) \times 100/TC$

### Chemical properties

The pH values range from 3.5 to 5.1, and about 90% of the horizons are classified as extremely acidic ( $> 4.4$ ) (Table 4). Basic cation contents are also considered low in all profiles, with averages for the contents of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^{+}$  of 1.5, 0.9 and  $0.2 \text{ cmol}_c \text{ kg}^{-1}$ , respectively, leading to lower values of sum of bases (S), with minimum and maximum values of 1.01

and  $8.86 \text{ cmol}_c \text{ kg}^{-1}$ , respectively. For base saturation (V%), the minimum and maximum values were 8 and 35%, respectively, and for  $\text{Na}^{+}$  contents, there are no variation between profiles and between horizons, and value are constant and equal to  $0.01 \text{ cmol}_c \text{ kg}^{-1}$ . Aluminum contents range from 0.0 to  $1.5 \text{ cmol}_c \text{ kg}^{-1}$ , resulting in aluminum saturation (m%) values up to 57%, with an average of 24%.

**Table 4** - Chemical attributes of soils in the Serra da Mantiqueira, Minas Gerais, Brazil

Horizon	pH 1:2.5	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^{+}$	$\text{Na}^{+}$	$\text{Al}^{3+}$	$\text{H}^{+}$	S	T	V	m	P $\text{mg kg}^{-1}$	TOC $\text{g kg}^{-1}$
		----- $\text{cmol}_c \text{ kg}^{-1}$ -----						%					
Profile P1													
Ap	3.6	1.3	0.4	0.20	0.01	1.3	14.2	1.91	17.41	11	40	1	37.3
A1	3.6	1.2	0.4	0.18	0.01	1.2	11.5	1.79	14.49	12	40	0	35.6
A2	3.6	3.1	0.3	0.18	0.01	0.3	13.6	3.59	17.49	21	6	0	40.7
BA	3.7	2.5	0.8	0.19	0.01	0.3	8.5	3.50	12.30	28	8	0	20.2
Bt1	3.6	2.2	0.8	0.19	0.01	0.2	8.5	3.20	11.9	27	6	0	22.5
Bt2	3.9	1.5	1.0	0.18	0.01	0.3	8.8	2.69	11.79	23	10	0	27.2
Bt3	4.0	0.9	1.4	0.17	0.01	0.1	9.3	2.48	11.88	21	4	1	29.3
Profile P2													
A1	5.1	4.9	2.7	0.20	0.01	0.0	15.3	7.81	23.11	34	0	5	49.4
A2	4.9	2.5	2.0	0.19	0.01	0.1	10.9	4.70	15.70	30	2	1	22.3
A3	4.4	1.7	1.2	0.19	0.01	0.2	12.4	3.10	15.60	20	6	1	24.5
A4	4.1	1.6	1.1	0.19	0.01	0.2	10.1	2.90	13.20	22	5	1	17.5
Bi	3.9	0.6	0.8	0.20	0.01	0.2	10.7	1.61	12.51	13	8	0	20.5
C	3.5	0.9	0.5	0.18	0.01	0.3	8.9	1.59	10.79	15	16	0	17.7
Profile P3													
A1	3.9	3.9	1.7	0.21	0.01	0.3	15.4	5.82	21.52	27	4	3	51.2
A2	4.0	2.2	1.1	0.19	0.01	0.3	12.3	3.50	16.10	22	8	1	36.4
A3	3.9	1.7	0.8	0.18	0.01	0.8	12.4	2.69	15.89	17	22	1	48.7
A4	3.7	0.6	0.3	0.18	0.01	1.1	11.5	1.09	13.69	8	49	1	34.4
AB1	3.6	0.9	0.3	0.18	0.01	0.8	11.8	1.39	13.99	10	36	1	35.4
AB2	3.5	0.5	0.4	0.20	0.01	0.6	10.5	1.11	12.21	9	34	2	38.8
AB3	3.7	0.7	0.2	0.16	0.01	0.7	8.8	1.07	10.57	10	39	1	40.5
BA	3.7	1.0	0.2	0.20	0.01	0.6	6.0	1.41	8.01	18	28	0	40.2
Bw	3.7	0.7	0.5	0.18	0.01	0.4	5.8	1.39	7.59	18	20	1	25.4
Profile P4													
A1	4.1	3.6	2.4	0.20	0.01	0.2	15.7	6.21	22.11	28	3	9	59.2
A2	4.0	1.4	0.8	0.19	0.01	0.6	11.1	2.40	14.10	17	19	7	30.2
A3	3.8	1.2	0.6	0.17	0.01	1.0	10.0	1.98	12.98	15	33	4	21.9
AB	3.8	1.0	0.7	0.17	0.01	1.1	7.2	1.88	10.18	18	38	2	19.2
BA	3.7	1.1	0.5	0.17	0.01	1.0	8.1	1.78	10.88	16	34	1	15.8
B1	3.7	1.4	0.5	0.16	0.01	0.6	7.7	2.07	10.37	20	22	1	16.2
B2	3.8	1.6	0.6	0.16	0.01	0.5	10.7	2.37	13.57	17	16	1	27.4
BC	3.8	1.3	0.8	0.17	0.01	0.5	8.5	2.28	11.28	20	18	1	11.5



Continuation Table 4

C1	3.9	1.1	0.6	0.17	0.01	0.8	7.7	1.88	10.38	18	30	0	9.7
C2	4.0	1.0	0.8	0.17	0.01	0.7	8.8	1.98	11.48	17	26	0	10.0
Profile P5													
O	4.9	4.8	3.8	0.25	0.01	0.2	15.9	8.86	24.96	35	2	5	90.1
A1	4.2	1.3	1.5	0.18	0.01	0.8	12.4	2.99	16.19	18	20	1	56.5
A2	4.2	0.7	0.5	0.2	0.01	1.3	12.1	1.41	14.81	10	49	1	58.2
A3	4.1	0.6	0.4	0.21	0.01	1.5	12.4	1.22	15.12	8	54	1	53.3
AB	4.1	0.6	0.7	0.20	0.01	1.4	11.2	1.51	14.11	11	48	1	27.6
B1	4.1	0.5	0.6	0.21	0.01	0.8	10.2	1.32	12.32	11	38	1	27.7
B2	4.1	0.4	0.4	0.2	0.01	0.9	8.1	1.01	10.01	10	47	1	25.0
Ab	3.9	0.4	0.6	0.18	0.01	1.5	9.7	1.19	12.39	10	57	2	33.1

S: sum of exchangeable bases; T: CEC at pH 7.0; V%: base saturation =  $(S/T) \times 100$ ; m: aluminum saturation =  $Al^{3+}/(S+Al^{3+})$  TOC: total organic carbon

Regarding cation exchange capacity (T), the values range from 7.59 to 24.96  $cmol_c\ kg^{-1}$ , while P contents vary between 0 and 9  $mg\ kg^{-1}$ , with the highest contents in surface, gradually reducing in subsurface, as observed in profiles P2, P4 and P5. The minimum and maximum contents of TOC were 9.7, 90.1 and 32.7  $g\ kg^{-1}$ , respectively, with highest content identified in the O horizon of profile P5. For the profiles, there were an irregular distribution of TOC contents in subsurface, confirming the indicatives of the allochthone origin of these profiles.

The high contents of TOC observed in the profiles, especially in the surface horizons, are related to the higher contents of aluminum also in surface, because the humic substances occur associated with cations such as  $Fe^{3+}$  and  $Al^{3+}$ , or even in combination with the mineral fraction of the soil, forming clay-metal-humus complexes that have greater stability (TAKAHASHI; DAHLGREN, 2016). According to Dortzbach *et al.* (2016a), who conducted studies in southern Brazil, in the regions of cold and humid climate, typical of high altitudes, the leaching of bases is favored, which contributed to the increase in  $Al^{3+}$  contents, making the soils chemically acidic. Additionally, such climatic conditions also condition lower speed of OM decomposition, resulting in high contents of TOC in the soil.

The silicon oxide contents ( $SiO_2$ ), determined by the sulfuric attack, range from 52 to 193  $g\ kg^{-1}$ , while for  $Al_2O_3$  the contents range from 84 to 233  $g\ kg^{-1}$  (Table 5). The contents of  $Al_2O_3$ , in the horizons, tend to be higher to the detriment of those of  $SiO_2$ , as in profile P3, in which the difference is greater than 100  $g\ kg^{-1}$ . Exceptions occurred for the profiles P1 and P2, in which the horizons have  $SiO_2$  contents higher than those of  $Al_2O_3$ . The  $Fe_2O_3$  content are little and irregular in depth, showing minimum and maximum contents of 15 and 88  $g\ kg^{-1}$ , respectively. Due to they lower than those of  $Al_2O_3$ , the values of the ratio between these two oxides are greater than 1.0. For  $TiO_2$  contents, the minimum

and maximum values are 1.7 and 11.4  $g\ kg^{-1}$ , respectively, with irregular distribution in subsurface probably due to the sedimentary nature of the material. Regarding the  $SiO_2/Al_2O_3$  ratio (ki weathering index), the values are considered little, ranging from 0.5 to 1.9, while for the  $SiO_2/(Al_2O_3+Fe_2O_3)$  ratio (kr index) the values are slightly lower than those of ki, ranging from 0.4 to 1.7.

### Pedogenesis

Based on morphological, chemical and physical properties of the studied soils, profile P1 was classified as *Argissolo Vermelho-Amarelo Distrófico nitossólico* according to the SiBCS (SANTOS *et al.*, 2018) and as Haplic Lixisol (Cutanic, Profundihumic) according to the WRB (IUSS WORKING GROUP WRB, 2015); P2 as *Cambissolo Húmico Distrófico típico* in the SiBCS, and as Dystric Cambisol (Loamic, Profundihumic) in the WRB; P3 as *Latossolo Vermelho-Amarelo Distrófico espresso húmico* in the SiBCS, and as Umbric Ferralsol (Clayic, Dystric); P4 as *Cambissolo Húmico Distrófico latossólico* in the SiBCS, and as Dystric Cambisol (Loamic, Profundihumic); and P5 as *Cambissolo Húmico Distrófico típico* in the SiBCS, and as Dystric Colluvic Cambisol (Clayic, Hyperhumic) in the WRB.

Rugged relief and the presence of steep slopes are factors that accelerate erosive processes (MODENESI-GAUTTIERI, 2000; OLIVEIRA *et al.*, 2014; PINTO *et al.*, 2015) and contribute to the transport and subsequent deposition of sediments that may function as parent material for soils and/or contribute to the deposition of material in pre-existing soils, and it is possible to verify buried soils in some points of the landscape. An example of this dynamics can be verified by analyzing the profile P5, in which a buried horizon (Ab) is observed below 100 cm deep. Although this high-mountain environment has occurrence of erosive

**Table 5** - Pedogenic oxides of soils in the Serra da Mantiqueira, Minas Gerais, Brazil

Horizon	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub>	ki	kr
	g kg <sup>-1</sup>						
Profile P1							
Ap	144	138	55	9.9	3.9	1.8	1.4
A1	132	132	49	10.2	4.2	1.7	1.4
A2	142	144	52	9.8	4.4	1.7	1.4
BA	159	159	59	9.9	4.2	1.7	1.4
Bt1	182	193	71	11.4	4.3	1.6	1.3
Bt2	193	203	75	10.5	4.3	1.6	1.3
Bt3	193	203	75	10.5	4.3	1.6	1.3
Profile P2							
A1	178	201	72	10.5	4.4	1.5	1.2
A2	113	99	23	3.3	6.8	1.9	1.7
A3	111	105	18	2.2	9.2	1.8	1.6
A4	85	84	19	2.9	6.9	1.7	1.5
Bi	110	106	24	4.5	6.9	1.8	1.5
C	114	106	15	1.7	11.1	1.8	1.7
Profile P3							
A1	140	179	88	6.5	3.2	1.3	1.0
A2	77	158	55	6.5	4.5	0.8	0.7
A3	75	204	64	7.4	5.0	0.6	0.5
A4	62	174	68	7.0	4.0	0.6	0.5
AB1	60	185	63	7.3	4.6	0.6	0.5
AB2	57	179	72	7.6	3.9	0.5	0.4
AB3	52	169	70	7.0	3.8	0.5	0.4
BA	54	161	65	7.4	3.9	0.6	0.5
Bi	54	161	65	7.4	3.9	0.6	0.5
Profile P4							
A1	76	214	76	8.0	4.4	0.6	0.5
A2	96	111	31	5.8	5.6	1.5	1.3
A3	86	101	29	5.4	5.5	1.5	1.2
AB	90	103	33	5.9	4.9	1.5	1.2
BA	90	120	37	6.2	5.1	1.3	1.1
B1	118	148	43	6.5	5.4	1.4	1.1
B2	130	160	47	6.8	5.3	1.4	1.2
BC	130	160	50	6.5	5.0	1.4	1.2
C1	133	160	43	6.3	5.8	1.4	1.2
C2	144	155	37	4.2	6.6	1.6	1.4
Profile P5							
O	118	199	53	10.9	5.9	1.0	0.9
A1	79	123	32	5.4	6.0	1.1	0.9
A2	99	192	53	6.6	5.7	0.9	0.7
A3	102	195	53	7.5	5.8	0.9	0.8
AB	112	205	56	7.1	5.8	0.9	0.8
B1	124	216	77	6.8	4.4	1.0	0.8
B2	124	233	55	6.9	6.7	0.9	0.8
Ab	106	196	37	6.1	8.3	0.9	0.8

ki:  $(\text{SiO}_2 / \text{Al}_2\text{O}_3) \times 1.7$ ; kr:  $(\text{SiO}_2 / 0.6) / ((\text{Al}_2\text{O}_3 / 1.02) + (\text{Fe}_2\text{O}_3 / 1.60))$

processes and sedimentation (FONTANA *et al.*, 2017; MODENESI-GAUTTIERI, 2000), some profiles are deep and well developed, reaching about 200 cm depth. According to Benites *et al.* (2003), herbaceous vegetation, characteristic of forests, begins to occupy the landscape as the soil becomes thicker (about 100 cm or deeper), reducing soil erosion and favoring its development. The establishment of this type of vegetation contributes to the supply of organic material (PINTO *et al.*, 2015) and also to the development of thicker soils.

In the profile P1 (*Argissolo/Lixisol*), located in the shoulder of the landscape, the small increment of clay in horizons Bt1 and Bt2, to the detriment of surface horizons A1 and A2, associated with the presence of blocky structural elements with shiny ped faces (clay films, Table 2), are indicative of the process of illuviation and eluviation (BUOL *et al.*, 2011; DORTZBACH *et al.*, 2016a). According to De Wispelaere *et al.* (2015) and Kögel-Knabner and Amelung (2021), the formation of aggregates in blocks with a at least moderate degree of development, associated with the presence of bright surfaces resulting from both the expansion and contraction of soil mass and clay eluviation and the presence of greater uniformity of the soil profile, may result from the pedoturbation process, characterizing a process called nitidization, which characterizes Nitisols. However, although the profile P1 showed the characteristics described by De Wispelaere *et al.* (2015) and Kögel-Knabner and Amelung (2021), not all the criteria to be classified as Nitisol were met, so P1 likely is in a condition of pedogenetic evolution (IUSS WORKING GROUP WRB, 2015).

Profile P3, a *Latossolo* (Ferralsol), located in the backslope of the landscape and at a higher elevation, is characterized by the low base saturation of the soils, which is related to losses of exchangeable bases by leaching, associated with the removal of silica, and to the high contents of quartz in the parent material, which is of acidic character (granites and gneisses) (BENITES *et al.*, 2003; BUOL *et al.*, 2011; SCHAETZL; ANDERSON, 2005). Additionally, these soils are also formed by pre-weathered sediments, which contributes to the low reserve of nutrients. The combination of these properties favors the development of the pedogenetic process of allitization. The values of  $k_i$  index observed in P3 were lower than 1.0, which demonstrates the predominance of Al oxides, due to the severe removal of Si, through the desilication process, favoring the formation of clayey-textured, gibbsitic soils (BUOL *et al.*, 2011; MARQUES *et al.*, 2011; MODENESI-GAUTTIERI, 2000; SCHAETZL; ANDERSON, 2005). Benites *et al.* (2003), evaluating *Latossolos* with *A húmico* horizons (Umbric Ferralsols) in the Serra da Mantiqueira, observed that the predominantly gibbsitic mineralogy

appears to be a relic of a deeper weathering mantle that covered these areas in the past.

For the other profiles (P2, P4 and P5), classified as *Cambissolos* (Cambisols), there is a small degree of pedogenetic development and expression of specific pedogenetic process (xanthization). However, the low values of the silt / clay ratio, associated with the low values of the  $k_i$  and  $k_r$  weathering indices, high acidity and low CEC, indicate a high degree of weathering of the sediments that form these soils. Despite these characteristics, which would indicate a high degree of pedogenesis, relief seems to be the main factor that promotes the low degree of pedogenetic development of these soils (FONTANA *et al.*, 2017). Although the humid climate condition favors the intensification of hydrolysis reactions and the desilication process (evidenced by the  $k_i$  and  $k_r$  indices), the rugged relief hinders the morphological development of these soils (especially P2, with less effective depth). According to Silva and Vidal-Torrado (1999), Modenesi-Gauttieri (2000) and Fontana *et al.* (2017), this pattern is typical of tropical cratonic regions, characterized by the absence of high-intensity sedimentation events and by the fact that the surface material has remained for a long time exposed to the action of weathering and subject to redistribution and reworking in the landscape.

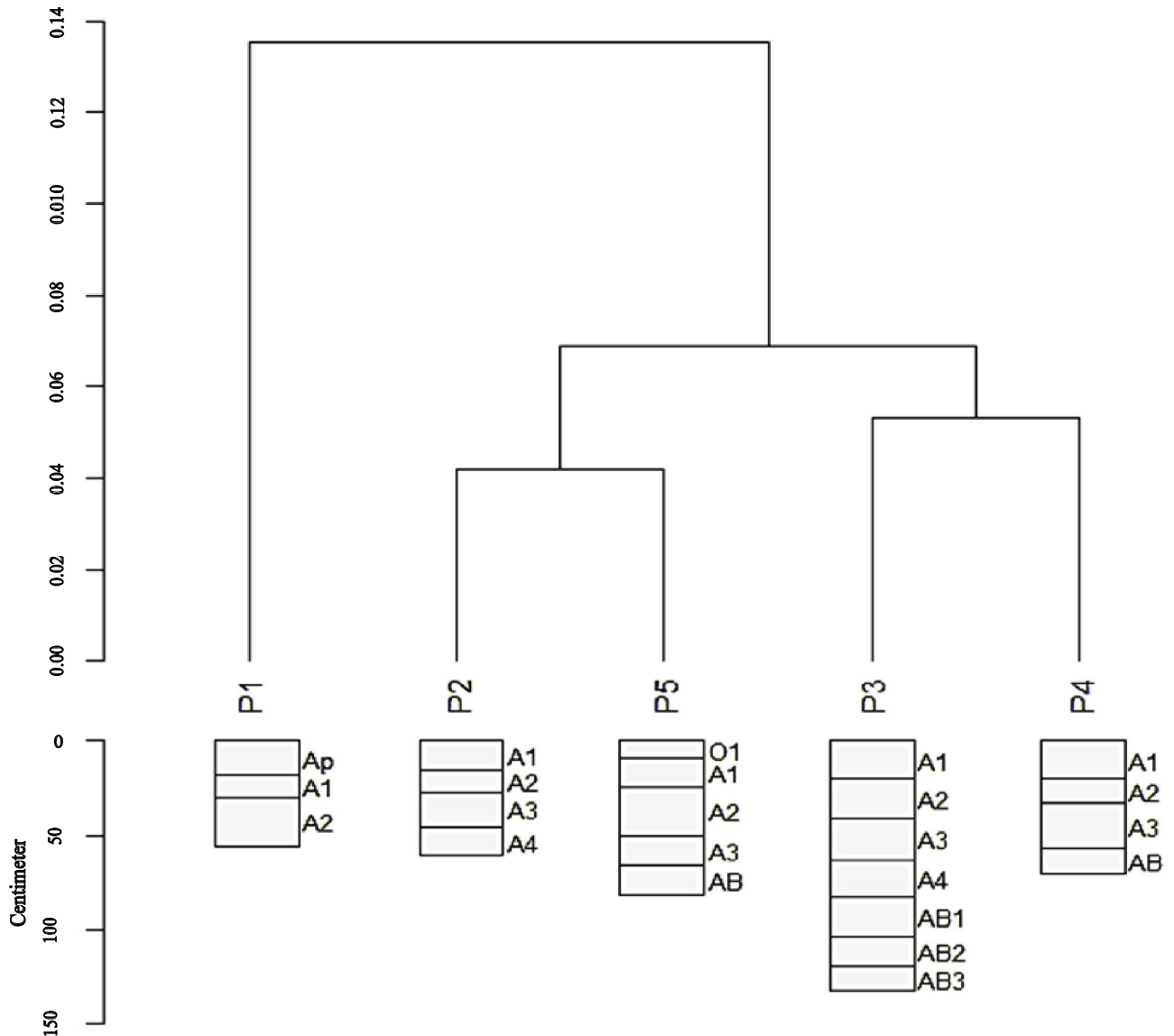
As for the colors verified in the soil profiles, according to Kämpf and Schwertmann (1983), Dixon, Weed and Parpitt (1990) and Silva and Vidal-Torrado (1999), they are possibly due to the greater participation of goethite to the detriment of hematite in the studied soils. According to the aforementioned authors, the coexistence of four factors controls the formation of goethite to the detriment of hematite, with emphasis on higher water activity in the soil, lower temperatures, high contents of organic matter and low Fe contents available in the soil. Resende, Curi and Santana (1988) defined, for this region, the soil water regime as *udic*, that is, typical of humid environments whose precipitation is well distributed throughout the year. This factor, associated with mild temperatures, high contents of TOC in surface and subsurface, usually above 14 g kg<sup>-1</sup>, and low contents of iron oxides (maximum of 88 g kg<sup>-1</sup>), favors the formation of goethite to the detriment of hematite, conferring a yellowish and brownish color to the soil (DIXON; WEED; PARPITT, 1990; KÄMPF; SCHWERTMANN, 1983; SCHAETZL; ANDERSON, 2005) as observed in the horizons with 7.5YR or 10YR hues of the profiles P2, P4 and P5. These morphological features characterize the xanthization process (goethization) (MARQUES *et al.*, 2011; SILVA; VIDAL-TORRADO, 1999). However, these profiles do not meet the value and chroma criteria for the xanthic qualifier (IUSS WORKING GROUP WRB, 2015), which should be an indication of a still incipient process.

The addition of organic material by vegetation and the transformation and translocation of these materials by the action of soil fauna or water flow, as well as the accumulation of OM in surface horizons, promote darkening and thickening of the A horizon, characterizing the melanization process (SCHAETZL; ANDERSON, 2005; SILVA; VIDAL-TORRADO, 1999). In studies with *Latosolos* with A *húmico* horizon (Umbric Ferralsols), Silva and Vidal-Torrado (1999) reported the occurrence of coal fragments in subsurface and stated that this may also have decisively influenced the process of melanization of the A horizon. Also, according to Modenesi-Gauttieri (2000) and Marques *et al.* (2011), some profiles may have

horizons with high OM contents only slightly affected by pedogenetic processes, because these horizons may have formed through the effect of the transport of sediments with high contents of OM, from the highest portions of the landscape. The greatest accumulation of OM, in surface, is observed in P5, giving rise to a not very thick O horizon. This accumulation may have been caused by the supply of organic material by the vegetation present and by the current mild climatic conditions.

According to the dissimilarity dendrogram between surface horizons (Figure 2), P1 (*Argissolo/Lixisol*) stands out for not showing similarity with the others, which

**Figure 2** - Dendrogram of hierarchical cluster analysis between profiles sampled in the Serra da Mantiqueira, Minas Gerais, Brazil. P1: Haplic Lixisol (Cutanic, Profundihumic); P2: Dystric Cambisol (Loamic, Profundihumic); P3: Umbric Ferralsol (Clayic, Dystric); P4: Dystric Cambisol (Loamic, Profundihumic); P5: Dystric Colluvic Cambisol (Clayic, Hyperhumic)



may be associated with the lower thickness of the A horizon, compared to the other profiles, in addition to differentiating itself with respect to chemical properties, showing lower pH and higher values of Al and m%. For profiles P2 and P5, both *Cambissolos* (Cambisols), there was greater similarity, despite being located at distinct elevations (862 and 1,326 m, respectively), but in the same position in the landscape (backslope; Table 1).

Despite the different TOC contents in these soils, other chemical properties such as pH and T value may have contributed to this grouping. In addition to profiles P2 and P5, similarity was also observed between P3 (*Latossolo/Ferralsol*) and P4 (*Cambissolo/Cambisol*), which, despite having received different classifications, are located at similar points in the landscape. For these profiles, there is a similar pattern regarding the distribution of high TOC contents in subsurface as well as pH values.

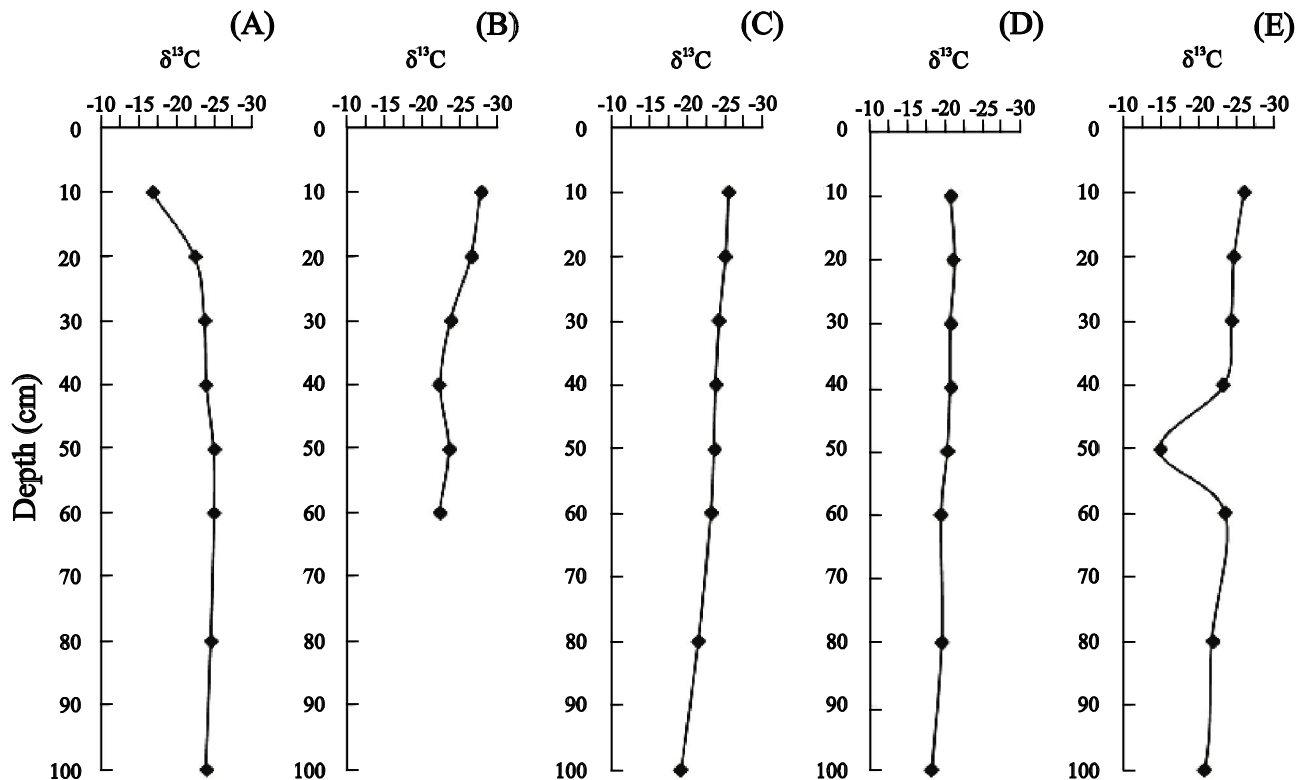
### $^{13}\text{C}$ (isotopic composition and distribution) and paleoenvironment

The mean values of  $\delta^{13}\text{C}$  and the respective values of the confidence interval at 95% probability for profiles P1, P2, P3, P4 and P5 are  $-23.0\% \pm 2.3$ ,  $-24.4\% \pm 2.4$ ,  $-23.3\% \pm 1.7$ ,  $-20.0\% \pm 0.8$  and  $-21.7\% \pm 2.7$ , respectively. In profile P1, the value of  $^{13}\text{C}$  is lower at the depth of 10 cm ( $-16.7\%$ ), with subsequent increase

at the depth of 20 cm ( $-22.4\%$ ), maintaining values close to  $-23\%$  up to 100 cm. In profiles P2, P3 and P4, the values of  $\delta^{13}\text{C}$  tend to decrease in subsurface and only profile P5 shows irregularity in the distribution of  $\delta^{13}\text{C}$ , with an abrupt decrease in the value at the depth of 50 cm ( $-14.7\%$ ) (Figure 3).

Through the analysis of  $\delta^{13}\text{C}$  of profiles P1 (Figure 3), there is a marked variation in the isotopic signature in surface (Ap horizon), an indication that there were anthropic interferences in these environments, in this case with gradual replacement of native forest vegetation by vegetation with  $\text{C}_4$  photosynthetic cycle, i.e. pasture, and whose effect can be observed up to the depth of 50 cm. In this profile, the values of  $\delta^{13}\text{C}$  in subsurface are close to  $-25\%$  at the depth of 60 cm (BA horizon), which denotes a past environment with predominance of  $\text{C}_3$  plants. In studies with altitude soils of the region of Santa Catarina, Brazil, Dortzbach *et al.* (2016b) also reported changes in the contents of  $\delta^{13}\text{C}$  in subsurface as a function of anthropic action. This current anthropic influence may also have resulted in the reduction of TOC contents and influenced the differentiation of P1 compared to the other profiles in the dissimilarity analysis (Figure 2). Although the profiles P1 and P2 are relatively close, in the environment in which the P2 profile is located, its lower thickness,

**Figure 3** - Distribution of  $\delta^{13}\text{C}$  isotopic in five profiles sampled in the Serra da Mantiqueira, Minas Gerais, Brazil. Profiles: P1 (a), P2 (b), P3 (c), P4 (d), and P5 (e)



associated with some climatic event that conditioned a lower water availability, may have favored the development of a mixed vegetation containing plants of C<sub>3</sub> and C<sub>4</sub> cycle, while in P1, the occurrence of a deep and well-developed soil associated with relatively higher altitude conditioned an environment that favored the maintenance of a mixed vegetation, but with predominance of tree vegetation.

In profiles P3 and P4, also close in the landscape, the signature of  $\delta^{13}\text{C}$  suggests a gradual change from vegetation of the mixed photosynthetic pathway of C<sub>4</sub> and C<sub>3</sub> to an environment where vegetation with C<sub>3</sub> photosynthetic pathway prevails. Since the profile P3 is located at a slightly highest elevation, tree vegetation was probably favored, justifying the slightly lower values of  $\delta^{13}\text{C}$ . Additionally, a pasture is established in P4, which explains the increase of  $\delta^{13}\text{C}$  contents in surface. In studies conducted with *Latossolos* with *A húmico* horizon (Umbric Ferralsols) of southern Minas Gerais, Modenesi-Gauttieri (2000) and Silva and Vidal-Torrado (1999) observed coal fragments in subsurface, which were related to fires that occurred at ages ranging from 6,850 to 9,250 years BP. This is evidence that, in the Serra da Mantiqueira region, a drier past climatic condition favored the occurrence of fires. Calegari *et al.* (2013), in a paleoenvironmental evaluation of an Oxisol (*Latossolo*) of southern Minas Gerais, Brazil, concluded that in this region, in a period dated between 12,000 and 6,000 years BP, approximately, the environment was an open savanna covered by grasses and with tree elements, a type of vegetation associated with a drier climate than the current one. Subsequently, the increase in humidity favored a more significant abundance of tree elements in the vegetation cover. This similarity between P3 and P4 identified by the isotopic signature was also compatible with the dendrogram of clusters using the chemical and physical properties of the profiles (Figure 2).

For profile P5, which is farther away than the others, there were  $\delta^{13}\text{C}$  values in subsurface similar to those verified for P3, except for the 50 cm layer, in which the high value of  $\delta^{13}\text{C}$  demonstrates a sudden change in vegetation and which may be evidence of a process of sedimentation and restart of vegetation establishment. Thus, the grouping with P2 is associated with factors other than paleoclimatic conditions, which were distinct from each other.

## CONCLUSION

The soils have a predominantly sedimentary origin, resulting from the erosive action favored by the relief. In profile P1, classified as *Argissolo* (Lixisol), the processes of eluviation and illuviation occur, while in profiles P2, P4 and P5, classified as *Cambissolos*

(Cambisols), the xanthization processes prevail in horizons still with a low degree of pedogenetic development. In profile P3, classified as *Latossolo* (Ferralsol), the allitization process is observed. All profiles showed the presence of the *A húmico* (umbric) horizon, demonstrating the action of the climate, favoring the accumulation of organic matter and the melanization process. The variation in the isotopic signature of  $\delta^{13}\text{C}$  indicates a dryer past condition, typical of savanna, with sparse tree vegetation, with gradual change to vegetation with predominant C<sub>3</sub> photosynthetic pathway. In P1 and P4, the highest values of  $\delta^{13}\text{C}$  in surface result from the replacement of forest vegetation with pasture.

## REFERENCES

- ALVARES, C. A. *et al.* Köppen's climate classification map for Brazil. *Meteorologische Zeitschrift*, v. 22, n. 6, p. 711-728, 2013.
- ÁVILA, L. F. *et al.* Partitioning of pluvial precipitation in a watershed occupied by Atlantic Forest in Mantiqueira range, MG State. *Ciência Florestal*, v. 24, n. 3, p. 583-595, 2014.
- BEEBE, K. R.; KOWALSKI, B. R. An introduction to multivariate calibration and analysis. *Analytical Chemistry*, v. 59, n. 17, p. 1007A-1017A, 1987.
- BENITES, V. D. M. *et al.* Solos e vegetação nos complexos rupestres de altitude da Mantiqueira e do Espinhaço. *Floresta e Ambiente*, v. 10, n. 1, p. 76-85, 2003.
- BOUTTON, T.W. *et al.*  $\delta^{13}\text{C}$  values of soil organic carbon and their use in documenting vegetation change in a subtropical savanna ecosystem. *Geoderma*, v. 82, p. 5-41, 1998.
- BUOL, S. W. *et al.* **Soil genesis and classification**. 6. ed. Chichester: John Wiley & Sons, 2011.
- CALEGARI, M. R. *et al.* Combining phytoliths and  $\delta^{13}\text{C}$  matter in Holocene palaeoenvironmental studies of tropical soils: an example of an Oxisol in Brazil. *Quaternary International*, v. 287, p. 47-55, 2013.
- COE, H. H. G.; CHUENG, K. F.; GOMES, J. G. Reconstituições da vegetação e inferências de paleoclimas através da utilização dos indicadores fitólitos e isótopos de carbono—exemplos de estudos no Brasil. *Revista Geonorte*, v. 3, n. 4, p. 248-261, 2012.
- DE WISPELAERE, L. *et al.* Revisiting nitic horizon properties of Nitisols in SW Ethiopia. *Geoderma*, v. 243/244, p. 69-79, 2015.
- DIXON, J. B.; WEED, S. B.; PARPITT, R. L. **Minerals in soil environments**. 2. ed. Madison: Soil Science Society of America Book Series, 1990.
- DORTZBACH, D. *et al.* Genesis and classification of soils from subtropical mountain regions of southern Brazil. *Revista Brasileira de Ciência do Solo*, v. 40, p. e0150503, 2016a.
- DORTZBACH, D. *et al.* Horizontes diagnósticos superficiais de Cambissolos e uso de  $\delta^{13}\text{C}$  como atributo complementar na

- classificação de solos. **Pesquisa Agropecuária Brasileira**, v. 51, n. 9, p. 1339-1348, 2016b.
- FONTANA, A. *et al.* Soils developed on geomorphic surfaces in the mountain region of the State of Rio de Janeiro. **Revista Brasileira de Ciência do Solo**, v. 41, p. 1-17, 2017.
- IUSS WORKING GROUP WRB. **World reference base for soil resources 2014**. International soil classification system for naming soils and creating legends for soil maps. Rome: FAO, 2015. (World Soil Resources Reports, 106).
- KÄMPF, N.; SCHWERTMANN, U. Goethite and hematite in a climosequence in southern Brazil and their application in classification of kaolinitic soils. **Geoderma**, p. 29, n. 1, p. 27-39, 1983.
- KÖGEL-KNABNER, I.; AMELUNG, W. Soil organic matter in major pedogenic soil groups. **Geoderma**, v. 384, p. 114785, 2021.
- MARQUES, F. A. *et al.* Relationship between soil oxidizable carbon and physical, chemical and mineralogical properties of umbric Ferralsols. **Revista Brasileira de Ciência do Solo**, v. 35, n. 1, p. 25-40, 2011.
- MEIRELES, L. D.; SHEPHERD, G. J.; KINOSHITA, L. S. Variações na composição florística e na estrutura fitossociológica de uma floresta ombrófila densa alto-montana na Serra da Mantiqueira, Monte Verde, MG. **Brazilian Journal of Botany**, v. 31, n. 4, p. 559-574, 2008.
- MELO, V. F. *et al.* Phosphorus adsorption of some Brazilian soils in relations to selected soil properties. **Open Journal of Soil Science**, v. 5, n. 5, p. 101-109, 2015.
- MENEZES, M. D. *et al.* Dinâmica hidrológica de duas nascentes, associada ao uso do solo, características pedológicas e atributos físico-hídricos na sub-bacia hidrográfica do Ribeirão Lavrinha-Serra da Mantiqueira (MG). **Scientia Forestalis**, v. 37, n. 82, p. 175-184, 2009.
- MODENESI-GAUTTIERI, M. C. Hillslope deposits and the quaternary evolution of the Altos Campos - Serra da Mantiqueira, from Campos do Jordão to the Itatiaia massif. **Revista Brasileira de Geociências**, v. 30, n. 3, p. 508-514, 2000.
- OLIVEIRA FILHO, A. T. *et al.* Tree population and community dynamics in the edge and interior sectors of a forest remnant in the Mantiqueira Range, SE Brazil, over a five-year interval (1999-2004). **Brazilian Journal of Botany**, v. 30, n. 1, p. 149-161, 2007.
- OLIVEIRA, V. A. D. *et al.* Soil erosion vulnerability in the Verde river basin, southern Minas Gerais. **Ciência e Agrotecnologia**, v. 38, n. 3, p. 262-269, 2014.
- PINTO, L. C. *et al.* Micromorphology and pedogenesis of mountainous Inceptisols in the Mantiqueira range (MG). **Ciência e Agrotecnologia**, v. 39, n. 5, p. 455-462, 2015.
- R CORE TEAM. **R: a language and environment for statistical computing**. Vienna, Austria: R Foundation for Statistical Computing, 2020.
- REBOITA, M. S. *et al.* Aspectos climáticos do estado de Minas Gerais (climate aspects in Minas Gerais State). **Revista Brasileira de Climatologia**, v. 17, p. 206-226, 2015.
- RESENDE, M.; CURI, N.; SANTANA, D. P. **Pedologia e fertilidade do solo: interações e aplicações**. Brasília: MEC/ESAL/POTAFOS, 1988.
- SANTOS, H. G. *et al.* **Sistema brasileiro de classificação de solos**. 5. ed. Brasília, DF: Embrapa, 2018. 356 p.
- SANTOS, R. D. *et al.* **Manual de descrição e coleta de solos no campo**. 7. ed. Viçosa, MG: Sociedade Brasileira de Ciência do Solo, 2015.
- SCHAETZL, R. J.; ANDERSON, S. **Soils: genesis and geomorphology**. 1. ed. Cambridge: Cambridge University Press, 2005. 833 p.
- SILVA, A. C.; VIDAL-TORRADO, P. Gênese dos Latossolos Húmicos e sua relação com a evolução da paisagem numa área cratônica do sul de Minas Gerais. **Revista Brasileira de Ciência do Solo**, v. 23, n. 2, p. 329-341, 1999.
- SOIL SURVEY STAFF. **Soil survey field and laboratory methods manual**. Soil Survey Investigations Report N° 51, Version 2.0. BURT, R.; SOIL SURVEY STAFF (ed.). U.S. Department of Agriculture, Natural Resources Conservation Service, 2014.
- TAKAHASHI, T.; DAHLGREN, R. A. Nature, properties and function of aluminum-humus complexes in volcanic soils. **Geoderma**, v. 263, p. 110-121, 2016.
- TEIXEIRA, P. C. *et al.* **Manual de métodos de análise de solo**. Brasília, DF: Embrapa, 2017.
- TROUW, R. A. J. *et al.* **Geologia da folha Itajubá SF. 23-YB-III**. Minas Gerais: Companhia de Pesquisa de Recursos Minerais CPRM/ Serviço Geológico do Brasil, 2007.
- YEOMANS, J. C.; BREMNER, J. M. A rapid and precise method for routine determination of organic carbon in soil. **Communications in Soil Science and Plant Analysis**, v. 19, p. 1467-1476, 1988.



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