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Methodological tests using Amazonian soil samples for ^{14}C-AMS dating

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Abstract

Although radiocarbon-accelerator mass spectrometry (^{14}C-AMS) is an important tool for the establishment of soil chronology, its application is challenging due to the complex nature of soil samples. In the present study, chemical extraction methodologies were tested to obtain the most representative age of Amazonian soil deposition by ^{14}C-AMS. We performed acid hydrolysis with different numbers of extractions, as well as treatments combining acid and bases and quartered and non-quartered samples. The ages of the soil organic matter (SOM) fractions were compared to the ages of naturally buried charcoal samples at similar depths. The results showed that the age of the non-hydrolyzable inert fraction of soil was closer to the age of charcoal and older than the ages of humin. It was also observed that the quartering process can influence the results, since the dating of the humin fraction showed variability in the results. Our results are important to provide information about the most suitable method for the ^{14}C-AMS dating of soil samples for paleoenvironment reconstruction studies.

Introduction

The radiocarbon (^{14}C) dating technique is widely used in paleoenvironmental reconstructions in association with other proxies such as bioindicators (e.g. diatoms, foraminifera, pollen) and stable isotope analyses (e.g. C, N and O) (Alexandrovskiy et al. 2020; Beckford et al. 2023; Gouveia et al. 2002; Jou et al. 2021; Pessenda et al. 1998; Trumbore 2009). However, radiocarbon chronology of the soil organic matter (SOM) is complicated due to the complexity of soil formation processes. This is aggravated by the variety of possible sources of contamination, e.g. bioturbation, root penetration, infiltration of organic and inorganic compounds dissolved in water, resulting in younger or older ages (Ahrens et al. 2015; Pessenda et al. 2001; Rumpel et al. 2012).

Soil type, vegetation composition, biological activity, land use, temperature and precipitation are some of the factors that influence soil carbon dynamics (e.g. storages and fluxes) (Becker-Heidmann et al. 1988). Likewise, the stabilisation of the SOM is related to formation processes and aspects such as

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climate, flora and fauna, parent material, topographic position and time (Jenny 1947). This means that different soil fractions, presenting distinct biogeochemical interactions and degrees of SOM fractionation (Schmidt et al. 2011), yield distinct radiocarbon ages (Campbell et al. 1987; Pessenda et al. 1996, 2001; Trumbore 2009). Indeed, soil is a complex open system that continuously receives organic carbon in different forms, resulting in a mixture of different organic components of the SOM. This implies that the SOM presents a wide range of radiocarbon signatures and, when radiocarbon dated, it yields an average apparent ^{14}C age for a given layer of the soil profile (Scharpenseel and Becker-Heidmann 1992; Trumbore and Zheng 1996; Wang et al. 1996). In fact, residence times in the SOM can vary from decades to thousands of years.

To overcome these issues and produce accurate soil chronologies, it is important to analyse soil composition and the range of ages that can be obtained by dating different soil fractions. Indeed, the SOM is formed by organic fractions of different ages, including humin, which is the most stable soil fraction and also the fraction whose age is considered to best represent soil age for paleoenvironmental reconstruction, mainly in tropical climate soils (Campbell et al. 1987; Becker-Heidmann et al. 1988). However, depending on the type of soil, biochemical interactions and SOM stabilisation mechanisms, other fractions of humic substances, such as humic acids, can also be suitable for dating (Trumbore and Zheng 1996).

All this complexity led to the development of several techniques of physical and chemical fractionation in order to isolate fractions of the SOM (Cheng and Kimble 2001). Common methods involve the chemical extraction of the soil humic substances (fulvic and humic acids, humin), with the advantage of being accessible and easy to handle (Oliveira et al. 2021; Olk et al. 2019). The choice of method will depend on the objective of each study and on the type of soil used. Therefore, there is no standard protocol for the radiocarbon dating of soil samples. In this paper, we have tested and adapted methodologies, employing acid and base washes, that are found in the literature for the radiocarbon dating of soil using the AMS technique.

Our objective was to obtain the most representative age of SOM deposition through tests of physical and chemical treatments from the Brazilian Amazon region without anthropogenic influence in a natural and preserved environment, and to compare the ages obtained from naturally buried charcoal with the soil collected from the same trench and similar depths. Since charcoal is considered a biologically inert material that tends to be physically stable (Gouveia et al. 2002; Pessenda et al. 1996, 2001, 2004), it is also very useful to establish the chronology in paleoenvironment reconstruction studies (McDonough et al. 2024; Rostami et al. 2024; Wang et al. 2024).

Materials and methods

Site description and soil sampling

The study area encompasses the states of Rondônia (RO) and Amazonas (AM), northern Brazil (Figure 1). This area is divided in two sectors: Tabajara (longitude between –62º08'50'' and –61º45'00'' and latitude between –8º45'00'' and –9º00'00'') and Estanho (longitude between –61º30'00'' and –61º05'20'' and latitude between –8º15'00'' and –8º40'50''). Part of these sectors is demarcated as indigenous land and part is a protected conservation unit called Campos Amazônicos (Amazonian fields) National Park, composed of the Amazon forest and the Brazilian cerrado (woody savannah) biomes. In both sectors, the altitude varies from 50 to 300 m a.s.l.

Three trenches of approximately 2 × 1 m were opened in two different sectors (Tabajara and Estanho) in the study region. In the Tabajara sector, the altitude is mostly between 50 and 150 m a.s.l. with a declivity of 0–7%. The Estanho sector presents altitudes that are mostly between 100 and 150 m a.s.l. in the woody savannah and 150–300 m a.s.l. in the forest. The Tabajara sector presents 2 trenches: T-FLO is located at 130 m a.s.l. under a vegetation of open ombrophilous forest containing trees of approximately 20–30 m, while the second trench (T-TRA) is located at 105 m a.s.l. between the open ombrophilous forest and the woody savannah vegetation. The Estanho sector presents only one trench

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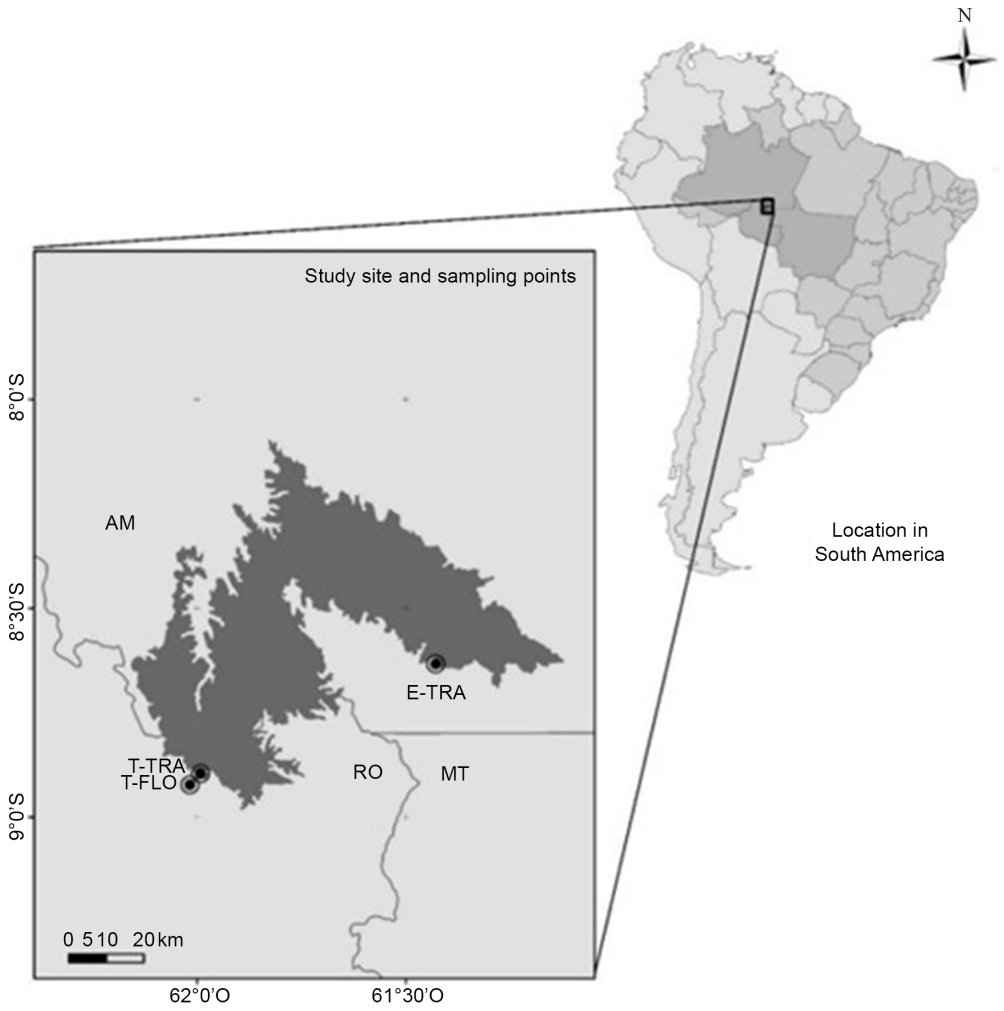


Figure 1. *Map of South America showing three trenches (E-TRA, T-TRA and T-FLO) in the study sites. The E-TRA trench is located in the Estanho sector with transitional vegetation, with tree plants in lower density when compared to the forest (woody savannah ecotone). The T-TRA trench is also located in a forest—woody savannah ecotone and the T-FLO trench is located in an area of forest vegetation, both belonging to the Tabajara sector.*

(E-TRA) at 150 m a.s.l., under a similar transitional vegetation found in the Tabajara sector, with a less dense forest than the Tabajara sector.

Sandy soil samples were collected at 10 cm intervals. Two charcoal and six soil samples from three different trenches (E-TRA, T-FLO, T-TRA), from 50 cm to 150 cm, were used for radiocarbon dating. The soil types were classified as Oxisol (E-TRA and T-FLO) and Entisol Quartzipsamment (T-TRA), according to the American soil classification (soil taxonomy—USDA) or Lixisols (E-TRA and T-FLO) and Arenosols (T-TRA), according to the World Reference Base/ FAO SOILS (WRB/FAO).

The climate of the study region is classified as humid tropical, with a mean annual precipitation varying from 2100 to 2600 mm and mean temperatures between 24 and 26ºC.

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Methodologies for ^{14}C dating

In the physical pretreatment stage, which preceded the chemical treatment, soil samples were sieved (212 micrometers) with the aim of removing contaminants such as plant and animal residues. A homogenization test stage was also carried out, using a quartering (Riffle Splitting) that repeatedly divides a soil sample into halves until the desired sample size is achieved (subsamples) (Gerlach et al. 2002). These subsamples were collected randomly and represented the total sample. The initial mass was 500 g until reaching a final mass of approximately 5 g to be used in the chemical treatment. The Riffle Splitting was cleaned with MilliQ water and dried between samples. This test was carried out with the aim of observing whether the quartering of the samples can help with their homogenization. In this work, results from the same samples both quartered and non-quartered will be presented for comparison. Therefore, approximately 500 g of soil were quartered before being sieved with the help of an automatic shaker.

For the chemical pretreatment, methodologies suggested by Trumbore and Zheng (1996), Paul et al. (2001), Pessenda et al. (2001, 1996), and Jou et al. (2021) were used with small modifications/adaptations regarding molarity, sample quantities and reaction time and temperature. The most important changes were in the chemical test with ABA (acid, base, acid) treatment, where we tested bases only with NaOH and NaOH+$Na_4P_2O_7$ and the limit of acid treatments to obtain the carbon from the residue that was not hydrolyzed. Four different chemical treatments were used for soil samples and one for charcoal (Oliveira et al. 2021). Figure 2 illustrates the chemical treatments used.

After the physical treatment, all samples underwent chemical treatment. However, only the samples that were submitted to the TC and ABA* chemical treatments were quartered, while the samples from the NHC and ABA chemical treatments were not quartered. The acid hydrolysis treatment (NHC) was compared with the test with quartered and non-quartered samples. During the chemical pretreatment rinses with MilliQ water were performed at least three times between treatments with different reagents to neutralise the pH of the solution. In all treatments, samples were washed several times with MilliQ water until the pH became neutral and the residue was left to dry in an oven at 80ºC. During the treatment, a centrifuge (3000 rpm/3 min) was used for the separation of the supernatant and the residue. Approximately 5 g of sample underwent chemical pretreatment for each of the tests mentioned:

Total organic carbon (TOC): The aim of this treatment was to obtain the total organic carbon, because the inorganic carbonate was removed. This chemical treatment is a weak hydrolysis. Samples were quartered and the chemical pretreatment involved a single extraction with 30 mL of 0.1M HCl at room temperature. After washing with distilled water to neutralise the pH, the residue was dried at 80ºC for approximately 24 hr.

Non-hydrolysable carbon (NHC): This pretreatment aimed for the isolation of the non-hydrolysable carbon (NHC) from the soil, which is considered a stable fraction. For the chemical pretreatment, extractions with HCl (1.0M; 30 mL) at 90ºC were performed. Each extraction lasted for 2 hr, until the supernatant was clear. During the treatment, a centrifuge (3000 rpm for 3 min) was used for the separation of the supernatant and the residue. In a second test, we varied the number of extractions (1, 5 and 10 times) in quartered and non-quartered samples until the supernatant was clear.

Acid-base-acid (ABA) with NaOH: This treatment aimed for the isolation of the humin fraction, which is considered the most stable and the most representative of the SOM age. HCl 0.5M was used for a period of 4 hr, repeating the procedure until the supernatant colour became transparent. After sample washings, 30 mL of NaOH 0.1 M was used for a maximum period of 30 min and repeated until the supernatant was clear (maximum of 5 washes), aiming to remove the humic acids. The last acid hydrolysis was undertaken for a period of 2 hr, using approximately 30 mL of HCl 6M at 90ºC, and repeated until the supernatant was clear.

Acid-base-acid (ABA*) with NaOH + $Na_4P_2O_7$: In order to remove fulvic acids, we used 30 mL of HCl 0.5M at 80ºC for 4 hr, until the supernatant was clear. Next, 30 mL of a mixture of $Na_4P_2O_7$ and NaOH 0.1M (pH=13) was used for 12 hr for the solubilization of humic acids for a maximum of

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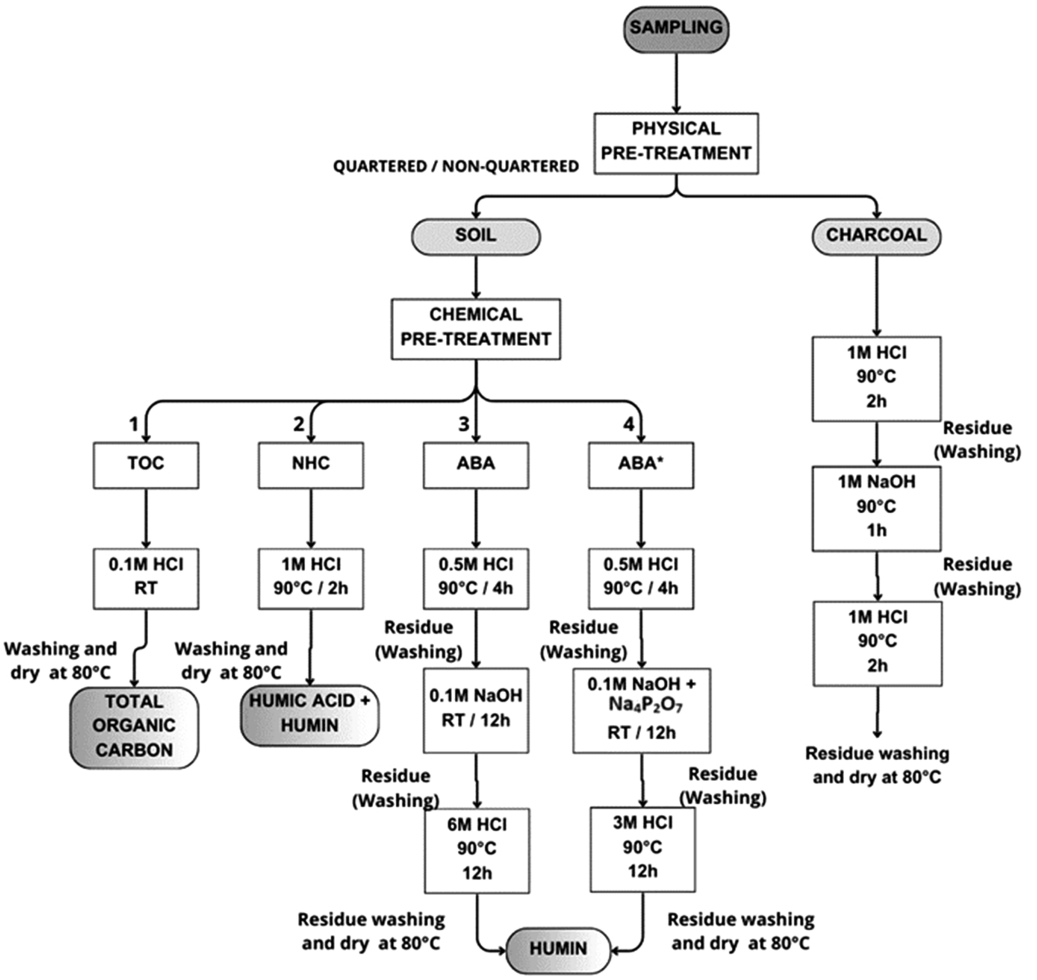


Figure 2. *Methodology used for measurement by ^{14}C (TC: total carbon, NHC: non-hydrolysable carbon, ABA: acid-base-acid, RT: room temperature).*

3 times, until the supernatant was clear. The last acid hydrolysis was then performed for a period of 2 hr using HCl 3M at 90ºC, aiming for the removal of organic residues and the contamination by atmospheric CO_2.

Acid-base-acid (ABA) for charcoal: The soil from charcoal samples was removed. Approximately 30 mg of sample was used for the chemical pretreatment with HCl 1M at 90ºC for 2 hr, until the supernatant was clear. After that, the samples were mixed with NaOH 1M at 90ºC for 1 hr, repeating the procedure until the supernatant colour became clear. The last treatment was with HCl 1M at 90ºC for 2 hr until the supernatant was clear.

After chemical treatment, the samples go through the combustion processes in order to convert into carbon dioxide and then conversion into graphite by zinc reduction process (Macario et al. 2015). The samples were prepared in the radiocarbon laboratory of the Fluminense Federal University (LAC-UFF) and most of them were measured in the radiocarbon laboratory of the Australia National University (ANU).

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Results and discussion

The ^{14}C-AMS results for the samples submitted to different treatments are presented in Table 1. When compared to the other protocols, the NHC method gave older dates in different soil layers, meaning that it was the most effective method for the extraction of the fulvic and humic acid fractions.

The IAEA-C9 reference samples have an average pMC value (^{14}C activity) between 0.12 and 0.21 (International Atomic Energy Agency) (Hogg et al. 1995; Scott 2003). However, isotopic fractionation may occur during sample preparation and measurement and the AMS background may vary depending on the laboratory, which may influence the final result. In the reference samples (IAEA-C9), the measurements that differed from the others were those with ABA* chemical treatment.

The soils of the profiles T-FLO, T-TRA and E-TRA present a sandy texture dominated by particles of the sand fraction and with low content of total organic carbon along the profile (see supplementary material). The sand is associated with the free or labile organic matter and the humic and fulvic acids are the fractions considered as the ones presenting low molecular weight and higher solubility and mobility in the soil (Stevenson 1994). The silt and clay fractions, on the other hand, are associated with the majority of organic carbon in soils, in the non-labile fraction, being a more stable and transformed material in which the older carbon is associated with the clayey mineral surfaces (Telles et al. 2003).

As expected, despite the TOC extraction with 0.1M HCl that probably helped in the removal of fulvic acids, the total carbon samples yielded the most recent dates in comparison with the other protocols used. The sample from the E-TRA trench, 150 cm depth, was the only exception to this with the protocol ABA* presenting a more recent age result of 1405 ± 25 BP, but this sample was quartered.

In most of the layers, protocols ABA and ABA* presented intermediate results between NHC (older results) and TC (more recent results). For the samples from the E-TRA and T-TRA trenches with 150 cm depth, the ABA and NHC protocols yielded similar results. For samples from the T-FLO trench, at depths of 50 cm and 150 cm, the protocol ABA* yielded results like those given by the NHC protocol. For sample T-FLO (50 cm), the 3 protocols gave results that agreed with each other. The charcoal fragments presented radiocarbon ages of 2880 ± 50 BP and 5220 ± 60 BP for E-TRA (60 cm) and E-TRA (170 cm), respectively, like the ones obtained with the NHC protocol for soil samples E-TRA (50 cm) and E-TRA (150 cm).

In general, older fractions of the SOM can be found in association with the soil minerals and in thinner fractions of soil such as clay. The only components not associated with minerals that can be persistent in soils are the black carbon (BC) and the fossil carbon. According to Jaffé et al. (2013), the BC deposited in soil can be found in dissolved form (DBC) and be exported to humid zones, rivers and ultimately to the ocean. It was previously believed that charcoal was a resistant material that, after being incorporated into the soil, stayed there in a stable form (Jaffé et al. 2013). Studies have shown that BC can persist in the soil from a few years up to millennia, depending on environmental factors such as soil properties, fauna, temperature and the source of the BC (Czimczik and Masiello 2007; Nguyen et al. 2010; Singh et al. 2012). The radiocarbon dating of charcoal fragments is important due to the charcoal structural stability, which means that it tends to be resistant to carbon exchanges with the environment and thus presents reliable radiocarbon dates. Therefore, we have analysed charcoal as a chronological reference for the different soil fractions.

Studies comparing the humin fraction, bulk soil and charcoal fragments at the same depths in profiles of Oxisols indicated that the ages of the humin fraction and charcoal tend to be similar (Pessenda et al. 1996, 2001). According to the results of the first trench (Table 1), the radiocarbon age of the SOM with NHC extraction was the closest to the age of charcoal fragments in the depths of 1.5 and 1.7 m, the difference between the ages of soil and charcoal was only 6%. When the depth increases, the radiocarbon age of the SOM tends to increase, indicating a higher protection and recalcitrance of the SOM (Rethemeyer et al. 2005; Rumpel and Kögel-Knabner 2002). At the surface layers of the soil, there is a higher influence of recent materials that decrease the age of the SOM.

In the ABA* chemical treatment, the base with the mixture NaOH+$Na_4P_2O_7$ is used to potentialize the removal of the humic acids. However, by comparing this method with the ABA treatment that uses

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Table 1. *Radiocarbon results for the samples analysed with different treatments*

Sector	Vegetation	Trench	Material	Depth (cm)	Physical treatment	ID-LACUFF	Chemical treatment	Age ^{14}C BP*	F ^{14}C
Estanho	Transition	E-TRA (1°)	Charcoal	50-60	–	160118	ABA (Charcoal)	2880 ± 50	0.698 ± 0.004
			Charcoal	160-170	–	160119		5220 ± 60	0.522 ± 0.004
			Oxisol	50-60	Quartered	190708	ABA*	925 ± 25	0.891 ± 0.003
					Not quartered	170137	ABA	610 ± 30	0.927 ± 0.003
					Not quartered	160120	NHC	1750 ± 50	0.803 ± 0.005
					Quartered	190722	TC	380 ± 30	0.953 ± 0.003
				150-160	Quartered	190709	ABA*	1405 ± 25	0.839 ± 0.002
					Not quartered	170138	ABA	4570 ± 30	0.566 ± 0.002
					Not quartered	160121	NHC	5550 ± 70	0.501 ± 0.004
					Quartered	190723	TC	3330 ± 25	0.661 ± 0.002
Tabajara	Forest	T-FLO (2°)	Oxisol	50-60	Quartered	190710	ABA*	2385 ± 25	0.743 ± 0.002
					Not quartered	170139	ABA	1490 ± 20	0.831 ± 0.003
					Not quartered	160122	NHC	3120 ± 50	0.677 ± 0.005
					Quartered	190724	TC	1115 ± 20	0.871 ± 0.002
				150-160	Quartered	190711	ABA*	7090 ± 45	0.414 ± 0.002
					Not quartered	170140	ABA	5780 ± 40	0.487 ± 0.002
					Not quartered	160123	NHC	8430 ± 80	0.350 ± 0.004
					Quartered	190725	TC	5515 ± 25	0.503 ± 0.002
Tabajara	Transition	T-TRA (3°)	Arenosols	50-60	Quartered	190712	ABA*	>MODERN	1.002 ± 0.002
					Not quartered	170141	ABA	50 ± 25	0.994 ± 0.003
					Not quartered	160124	NHC	>MODERN	1.018 ± 0.005
					Quartered	190726	TC	>MODERN	1.025 ± 0.004
				150-160	Quartered	190713	ABA*	4400 ± 30	0.578 ± 0.002
					Not quartered	170142	ABA	8410 ± 40	0.351 ± 0.002
					Not quartered	160125	NHC	8520 ± 100	0.346 ± 0.004
					Quartered	190727	TC	3470 ± 30	0.649 ± 0.002
–	–	–	ref:IAEA-C9	–	–	190485	ABA*	34690 ± 330	0.013 ± 0.005
					–	190481	ABA	42060 ± 670	0.005 ± 0.0004
					–	190483	NHC	42210 ± 500	0.005 ± 0.0003
					–	190482	TC	41360 ± 520	0.006 ± 0.0004

* All ages (age ^{14}C BP) were rounded according to Stuiver and Polach (1977).

only NaOH, it is not possible to observe any pattern of ageing. According to Olk et al. (2019), the extraction of the humic acids from the soil with $Na_4P_2O_7$ and NaOH are similar in all aspects. The International Humic Substances Society (IHSS) claims that humic acids can be removed with NaOH (IHSS 2018). There is also the possibility that the difference in the results between the ABA* and ABA chemical treatments are due to the fact that in the treatment with NaOH+$Na_4P_2O_7$ the samples were quartered, while the samples that followed the ABA treatment with NaOH were not.

It was expected that the ages of the soil sample obtained from the TOC treatment would be younger than the ages obtained by other methods. However, the use of the acid treatment with 0.1M HCl (weaker hydrolysis) helped with the removal of fulvic acids, since the total carbon age represents the average age of the total SOM, justifying the proximity of the dates. It is important to consider that the samples used to measure the total organic carbon age were also quartered.

There are some protocols that combine density-chemical fractionation and a density-size (Marzaioli et al. 2010) fractionation or only chemical treatment (ABA) to study models of soil carbon turnover to determine the distribution of carbon into fast (annual turnover), slow (decadal to centennial turnover) and passive (millennial and longer turnover) pools. To do this, it is interesting to separate the different fractions of SOM.

Acid hydrolysis treatment (NHC) results

The NHC method compared to other treatments proved to be efficient and with results close to charcoal ages at the same depth. Aiming to analyse the possibility of establishing a maximum number of extractions with acid hydrolysis and check whether the quartering of samples affect the results, we performed tests with 1, 5 and 10 acid extractions (Table 2). A comparison between the ages of the charcoal fragments and those of samples extracted until the supernatant was clear (limit) can be seen in Figure 3. For this purpose, soil samples from the Estanho sector (E-TRA) at depths of 50 and 150 cm were used (Table 2).

The R1, R2 and R3 are replicates (three) to increase the statistics in Table 2.

The results for non-quartered samples at 50 cm depth indicate that 5–10 extractions yielded similar radiocarbon ages for the SOM when compared to a single extraction. By comparing the individual values obtained in each of the extractions with the charcoal fragment result 2880 ± 50 BP (Table 1) in the same depth, it is possible to observe an agreement, especially in the samples that underwent 5 extractions. Regarding the NHC result of 1750 ± 50 BP (Table 1), which is the number of extractions until the supernatant is transparent with a total of 11 extractions, it is possible to observe a younger age in comparison with 5 and 10 extractions (Figure 3). This is possibly because the more acid extractions are carried out, the more sample loss and consequently isotopic fractionation can occur, which can compromise the result. In samples of 150 cm depth, the results were similar, indicating that extractions with 5 to 10 repetitions were more effective, as they are closer to the charcoal age of 5220 ± 60 BP (Table 1) at the same depth, like what happened with the NHC age of 5550 ± 70 BP (Table 1) after 12 extractions until the supernatant became clear.

Figure 3 shows the ages of the quartered and non-quartered samples that underwent the NHC treatment, with the corresponding number of acid treatments. The result obtained for charcoal at the same depth is also shown for comparison.

Quartered samples yielded younger ages than non-quartered samples. This was more subtle for the sample of 150 cm than for the sample of 50 cm depth. Soil is an open heterogeneous system with different pools presenting distinct ages. Close to the surface, soil is more active and the dynamics of the SOM is greater. This means that surface layers of the soil present more active pools and a higher variety of younger SOM ages. There is also the possibility of modern contamination during the quartering of the samples, which would be responsible for the young ages. Alternatively, by simply homogenising the samples, a mixture of younger soil fractions occurred. Reference samples did not show this discrepancy

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Table 2. *Radiocarbon ages of soil samples subjected to different numbers of extractions with HCl 1M at 90ºC*

Sector	Vegetation	Trench	Material	Depth (cm)	Physical treatment	LACUFF	N° extractions	Replicas	Age ^{14}C BP*	F ^{14}C
Estanho	Trasition	E-TRA (1°)	Oxisol	50-60	Not quartered	180080	1X HCl	R1	1070 ± 30	0.875 ± 0.003
						180103		R2	1180 ± 50	0.862 ± 0.006
						180081	5X HCl	R1	2830 ± 30	0.703 ± 0.003
						180104		R2	3010 ± 60	0.688 ± 0.005
						180082	10x HCl	R1	2260 ± 30	0.755 ± 0.003
						180105		R2	2210 ± 60	0.759 ± 0.005
						180106		R3	2650 ± 60	0.719 ± 0.006
				150-160		180093	1X HCl	R1	4790 ± 50	0.551 ± 0.003
						180094		R2	4370 ± 50	0.581 ± 0.004
						180095	5x HCl	R1	5520 ± 60	0.503 ± 0.004
						180096		R2	5450 ± 50	0.507 ± 0.003
						180097	10x HCl	R1	5830 ± 50	0.484 ± 0.003
						180083		R2	6430 ± 40	0.449 ± 0.002
				50-60	Quartered	190715	1X - HCl	R1	655 ± 25	0.922 ± 0.003
						190716	5X- HCl	R2	1025 ± 20	0.881 ± 0.002
						190717	10X- HCl	R3	350 ± 20	0.957 ± 0.002
				150-160		190718	1X - HCl	R1	3595 ± 35	0.639 ± 0.003
						190719	5X- HCl	R2	4275 ± 25	0.587 ± 0.002
						190721	10X- HCl	R3	4695 ± 35	0.557 ± 0.002
–	–	–	Mineral coal	–	Not quartered	220008	ABA	–	37040 ± 300	0.009 ± 0.004
					Quartered	220009	ABA	–	40330 ± 310	0.006 ± 0.003

*All ages (age ^{14}C BP) were rounded according to Stuiver and Polach (1977).

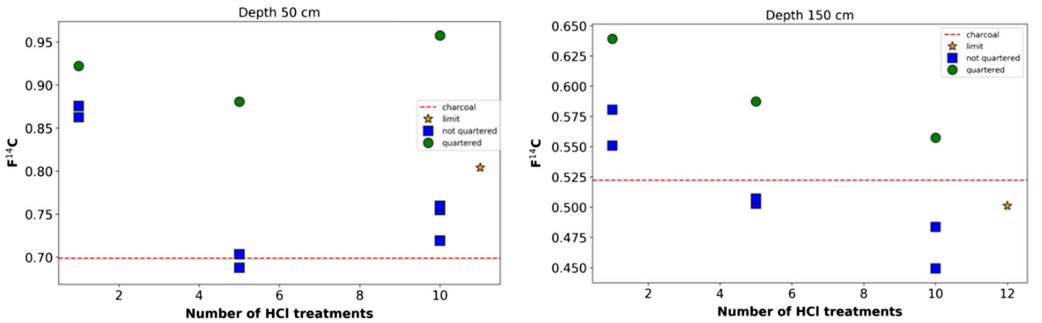


Figure 3. *Comparison between the $F^{14}C$ of quartered and non-quartered samples that underwent the NHC treatment. (Only the Estanho sector with transitional vegetation and type Oxisoil was used in this graph the E-TRA profile. The error is included in the size of the symbol).*

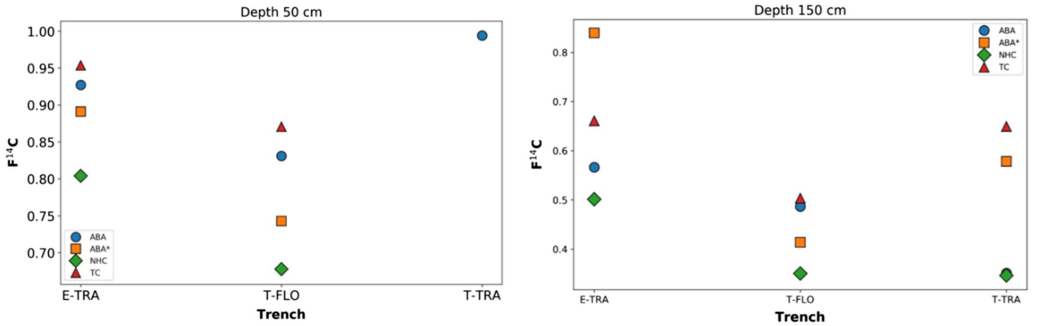


Figure 4. *All $F^{14}C$ of samples obtained by different chemical tests. The three trenches of a two different sectors (Tabajara and Estanho) in the study region were used. In the Tabajara sector the first trench T-TRA with transitional vegetation and Entisol and the second trench T-FLO with vegetation forest and Oxisol. The Estanho sector with trench E-TRA with transitional vegetation and Oxisol. (The error is included in the size of the symbol).*

and younger ages, corroborating the hypothesis that there was no contamination during the process of chemical treatment (Table 2).

Figure 4 shows a comparison of the ages of all samples with 50 cm and 150 cm depth obtained using all the different physical and chemical treatments. It is observed that the age yielded by the NHC treatment for non-quartered samples is the one that is closest to the charcoal result.

Usually, in studies of environmental reconstruction in tropical soils, the chemical pretreatments employed are a combination of acid and base (Pessenda et al. 2001; Trumbore and Zheng 1996) for the isolation of the humin fraction, considered the most stable fraction of the soil. For soils of temperate climates, in studies of the average residence time of carbon in the soil, the treatment using only acid hydrolysis for radiocarbon dating is more common.

Conclusions

The main conclusion of this study is that in tropical soils (Oxisols and Entisols) presenting a sandy texture, low TOC, and higher concentration of fulvic acids in relation to humic acids, the use of a chemical treatment with acid hydrolysis for the isolation of the NHC stable fraction of the soil may be the best option for the radiocarbon dating of soil samples. From the experiments performed in this study,

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it was observed that limiting the number of acid extractions is recommended, with best results after 5 acid extractions. This avoids excessive losses of carbon during the extraction processes, especially in soils with low TOC, reducing the time required for treatment and therefore the contamination risks.

Another important finding is that quartering the samples provided younger radiocarbon ages of the soil. The principle of quartering soil samples is for their homogenization, which, when carried out, can add more recent fractions that were not present in the part of the sample before quartering. For ^{14}C dating with the AMS technique, an average of 2–3 g of soil is usually sufficient for chemical treatment. However, depending on the TOC content of the sample, higher or lower amounts may be required. In any case, these sample amounts are too small to be representative of the whole, considering that soil is an open and heterogenous system.

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