

NATURAL RADIOCARBON MEASUREMENTS IN BRAZILIAN SOILS DEVELOPED ON BASIC ROCKS

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ABSTRACT. This paper presents ^{14}C , ^{13}C and chemical data of soil organic matter (SOM) in three soil profiles under native forests from Brazil: Londrina (southern), Piracicaba (southeastern) and Altamira (northern). The main objective is to use carbon isotopes in tropical and subtropical soils of Brazil to provide information about vegetation changes that occurred in relation to climate changes during the Holocene. ^{14}C data from SOM indicate that the organic matter in the soils studied is of at least Holocene age. ^{13}C data indicate that C_4 plants probably provided the dominant vegetation in Londrina and Piracicaba during the early and mid-Holocene and that C_3 plants provided the dominant vegetation in the Altamira region during the Holocene.

INTRODUCTION

Radiocarbon dating has been used in soil work since 1950. The main emphasis has been on chronological problems of soil genesis (Martel and Paul 1974), carbon dynamics and identifying parameters for the evaluation of biologically resistant forms of organic matter (O'Brien 1984). Because SOM decomposition and mineralization are relatively slow processes, only a few methods can provide useful data, *e.g.*, long-term experiments or, in some cases, natural ^{13}C measurements (Balesdent 1987).

We report here a list of ^{14}C , ^{13}C and chemical data of organic matter from soil profiles in three regions of Brazil. The aim of the project, developed in the Radiocarbon Laboratory of the CENA, was to associate ^{14}C dates with the ^{13}C signature of SOM to study the evolution of local vegetation. ^{14}C data allowed us to estimate SOM chronology and ^{13}C indicated the vegetation types C_3 and C_4 of the local paleoenvironment.

STUDY SITES

L. C. R. Pessenda, E. P. E. Valencia, P. B. Camargo and E. C. C. Telles collected 48 samples from soil profiles under natural forests. In July 1991, samples were collected from Londrina ($51^\circ 10' \text{W}$ $23^\circ 18' \text{S}$), state of Paraná, southern Brazil and Piracicaba ($22^\circ 43' \text{S}$ $47^\circ 38' \text{W}$), São Paulo, southeastern Brazil. The site of Altamira ($52^\circ 58' \text{W}$, $3^\circ 30' \text{S}$), Pará, northern Brazil, was sampled in February 1992. The natural forest at Londrina and Piracicaba is a Mesophytic semideciduous type and Altamira is part of the Amazon forest (Fig. 1).

The soils of Londrina and Altamira are clayey, with kaolinite predominating, and are classed as "Terra Roxa Estruturada", according to the Brazilian soil classification, "Alfisol" in Soil Taxonomy (USDA) and "Nitossol" in the FAO soil classification system. The clayey and kaolinitic soil at Piracicaba is called "Latossolo Vermelho Escuro" (Dark Red Latosol), according to Brazilian soil classification, "Oxisol" in Soil Taxonomy; "Ferralsol" in FAO classification.

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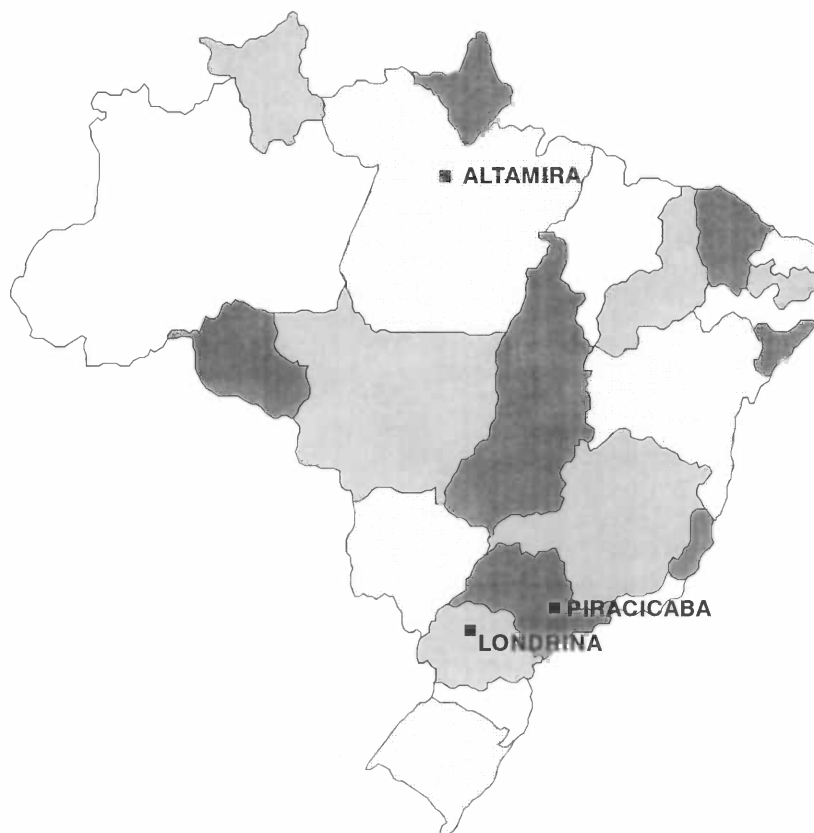


Fig. 1. Map of Brazil showing study sites

METHODS

At all sites, soils were sampled by collecting up to 5 kg in 10-cm increments from the surface to 180-cm depth. Samples for total SOM analyses (1 kg) were dried at 60°C to constant weight and root fragments were discarded by handpicking. Any remaining plant debris was removed by flotation in HCl 0.01 M and redried to constant weight. In order to minimize the effects of sample heterogeneity, all samples were ground, sieved (<200 μm) and homogenized for ^{13}C and ^{14}C measurements. The humin fraction was extracted from the 200 μm fraction (2.5 kg) according to conventional methods (Dabin 1971; Goh 1978; Anderson and Paul 1984): 1) acid digestion in hydrochloric acid 0.5 M at 70°C–80°C for 4 h and washing with distilled water until pH reaches 3–4; 2) reaction of solid residue with at least 30 liters (10 liters per extraction) of sodium pyrophosphate-sodium hydroxide 0.10 M for *ca.* 36 h (12 h per extraction) and washing with distilled water until the pH reaches 3–4; 3) hydrolysis of solid residue with 4 liters of 3 M HCl at 100°C for 12 h, washing until the pH reaches 3–4; and 4) the solid residue was dried at 40°C for 48 h and sieved (< 200 μm).

^{14}C dating, $\delta^{13}\text{C}$ and chemical analyses were performed between August 1991 and November 1992. ^{14}C analyses were carried out on total SOM and the humin fraction using benzene and liquid scintillation counting (Pessenda and Camargo 1991). Benzene samples were counted for at least 48 h in a low-level Packard 1550 liquid scintillation spectrometer. ^{14}C ages are expressed in conventional

years BP and percent modern carbon (pMC) relative to 95% of the activity of the NIST oxalic acid standard (HOxI) and normalized to a $\delta^{13}\text{C}$ of -25‰ PDB (Stuiver and Polach 1977). The analytical precision is ± 1.0 pMC.

The stable carbon isotopic ratios ($^{13}\text{C}/^{12}\text{C}$) of SOM were determined by isotope ratio mass spectrometry using CO_2 from samples combusted at 900°C in an atmosphere of pure oxygen. Results are expressed as $\delta^{13}\text{C}$ with respect to PDB standard in the conventional (‰) notation; the analytical precision is $\pm 0.2\text{‰}$. Carbon contents of soil samples were determined, using 1–5 g of the $<200\text{ }\mu\text{m}$ -sized fraction, using a C,H autoanalyzer. All samples were analyzed 2 or 3 times, with a coefficient of variation $<4\%$; values are expressed as weight percent of dry sample. Nitrogen contents were determined using 0.7 g of $<200\text{ }\mu\text{m}$ fraction using the Kjeldahl method; values are expressed as weight percent of dry sample. Soil density was calculated by collecting a mass of soil in a small cylinder of known volume. After drying to constant mass, the density was calculated. The soil pH was determined in water.

RESULTS AND DISCUSSION

Tables 1 through 3 show ^{14}C , $\delta^{13}\text{C}$, total organic carbon, total nitrogen, soil bulk density and soil pH values obtained for total SOM from Londrina, Piracicaba and Altamira, respectively. All the soil profiles show decreasing ^{14}C content with depth, except for the 140–150 cm sample interval of Altamira profile, which seems to record an age reversal. All surface samples have $^{14}\text{C} > 100$ pMC, showing the influence of thermonuclear ^{14}C in the recent organic matter. $\delta^{13}\text{C}$ values between the surface and the 40–50 cm interval are indicative of C_3 plants, and this reflects the current local vegetation (forest) in all three regions. These values remained almost constant for the Altamira profile from the soil surface to 180 cm depth; however, the Londrina and Piracicaba soils show a significant change from -21.6‰ to -15‰ in ^{13}C values.

TABLE 1. Londrina Soil Profile

Lab code (CENA-)	Sample horizon (cm)	^{14}C (pMC)	^{14}C (yr BP)	$\delta^{13}\text{C}$ (‰)	Total C (wt %)	Total N (wt %)	C/N	Soil bulk density (g/cc)	Soil pH
194	0 to 10	110 ± 1.2	--	-25.8	1.85	0.21	8.81	1.23*	5.4*
--	10 to 20	--	--	-25.1	1.43	0.16	8.94	--	--
--	20 to 30	--	--	-24.3	1.59	0.19	8.42	1.23*	5.3*
--	30 to 40	--	--	-24.2	1.29	0.15	8.60	--	--
193	40 to 50	90.3 ± 0.7	820 ± 60	-23.8	1.02	0.13	7.85	--	--
--	50 to 60	--	--	-23.2	1.00	0.11	9.09	--	--
--	60 to 70	--	--	-22.2	0.89	0.10	8.90	1.25*	5.5*
192	70 to 80	78.8 ± 1.1	1920 ± 60	-21.6	0.86	0.09	9.56	--	--
--	80 to 90	--	--	-21.0	0.85	0.09	9.44	--	--
196	90 to 100	74.3 ± 0.8	2390 ± 60	-21.3	0.99	0.10	10.00	--	--
--	100 to 110	--	--	-19.4	0.82	0.08	10.25	--	--
--	110 to 120	--	--	-18.5	0.71	0.07	10.00	--	--
195	120 to 130	50.8 ± 0.7	5450 ± 90	-16.8	0.71	0.06	11.83	--	--
--	130 to 140	--	--	-16.7	0.73	0.06	12.17	--	--
--	140 to 150	--	--	-15.5	0.78	0.06	13.00	1.43*	5.3*
--	150 to 160	--	--	-15.1	0.88	0.05	17.80	--	--
--	160 to 170	--	--	-14.9	0.87	0.05	17.40	--	--
218	170 to 180	31.3 ± 0.5	9340 ± 120	-15.0	0.93	0.05	18.60	--	--

*Values obtained from Ref. 8

TABLE 2. Piracicaba Soil Profile

Lab code (CENA-)	Sample horizon (cm)	^{14}C (pMC)	^{14}C (yr BP)	$\delta^{13}\text{C}$ (‰)	Total C (wt %)	Total N (wt %)	C/N	Soil bulk density (g/cc)	Soil pH
184	0 to 10	107.3 ± 0.8	--	-25.7	2.67	0.30	8.90	1.22*	5.8*
--	10 to 20	--	--	-25.7	1.59	0.16	9.94	1.35*	5.0*
--	20 to 30	--	--	-25.6	1.12	0.11	10.18	1.21*	5.0*
--	30 to 40	--	--	-23.8	0.96	0.09	10.67	1.16*	5.0*
191	40 to 50	85.8 ± 0.9	1230 ± 90	-22.7	0.79	0.07	11.29	1.29*	4.7*
--	50 to 60	--	--	-21.6	0.63	0.06	10.50	--	5.0*
--	60 to 70	--	--	-19.7	0.63	0.05	12.60	--	5.2*
223	70 to 80	71.8 ± 0.7	2680 ± 70	-19.0	0.64	0.05	12.80	--	5.2*
--	80 to 90	--	--	-18.7	0.63	0.05	12.60	--	--
222	90 to 100	68.8 ± 0.7	3030 ± 70	-17.2	0.56	0.04	14.00	--	--
--	100 to 110	--	--	-16.8	0.56	0.04	14.00	--	--
221	110 to 120	66.8 ± 0.7	3260 ± 70	-17.5	0.54	0.04	13.50	--	--
--	120 to 130	--	--	-16.8	0.47	0.04	11.75	--	--
--	130 to 140	--	--	-16.7	0.43	0.04	10.75	--	--
220	140 to 150	63.8 ± 0.6	3640 ± 70	-16.7	0.43	0.04	10.75	--	5.3*

*Values obtained from Ref. 9

TABLE 3. Altamira Soil Profile

Lab code (CENA-)	Sample horizon (cm)	^{14}C (pMC)	^{14}C (yr BP)	$\delta^{13}\text{C}$ (‰)	Total C (wt %)	Total N (wt %)	C/N	Soil bulk density (g/cc)	Soil pH
239	0 to 10	103.9 ± 0.8	--	-26.7	1.40	0.18	7.78	1.39*	5.5*
--	10 to 20	--	--	-25.6	0.78	0.12	6.50	--	--
--	20 to 30	--	--	-26.8	0.81	0.10	8.10	1.43*	5.1*
--	30 to 40	--	--	-25.7	0.68	0.09	7.55	--	--
237	40 to 50	84.1 ± 0.7	1440 ± 70	-25.7	0.57	0.08	7.12	--	--
--	50 to 60	--	--	-25.8	0.53	0.07	7.57	--	--
--	60 to 70	--	--	-25.6	0.41	0.07	5.86	--	--
236	70 to 80	70.8 ± 0.7	2790 ± 80	-25.4	0.39	0.06	6.50	--	--
--	80 to 90	--	--	-26.8	0.26	0.06	4.33	--	--
233	90 to 100	63.5 ± 0.7	3640 ± 90	-25.6	0.28	0.05	5.60	--	--
--	100 to 110	--	--	-25.7	0.23	0.05	4.60	--	--
232	110 to 120	55.0 ± 0.6	4800 ± 80	-25.0	0.25	0.04	6.25	--	--
--	120 to 130	--	--	-25.3	0.22	0.04	5.50	--	--
--	130 to 140	--	--	-25.5	0.25	0.04	6.25	--	--
231	140 to 150	57.9 ± 0.6	4390 ± 90	-26.5	0.31	0.04	7.75	1.41*	5.9*

*Values obtained from Ref. 8

Taking into account the increase of ^{14}C age with depth, the increase of $\delta^{13}\text{C}$ can be explained in two ways: 1) organic matter decomposition leads to the accumulation and transport of ^{13}C -enriched materials with depth in the profile; 2) during the pedological evolution of the soil profiles, the dominant vegetation changed from C_4 - to C_3 -dominant photosynthetic pathway. Similar ^{13}C records have also been documented in other studies in Brazil (Cerri 1986; Rocha 1990; Desjardins *et al.* 1991). Research is underway to test the postulated hypotheses, *e.g.*, phenol lignin analysis of selected soil samples to characterize past vegetation change in south and southeast regions of Brazil. Paleoenviromental changes during the last 30 ka yr BP have been documented in Central Brazil and the Amazon basin (Absy *et al.* 1991; Ledru 1993). Based on pollen analyses, these studies indicate periods of forest regression changing to savanna-type vegetation. Such evidence supports vegetation

changes as an explanation for the ^{13}C trend observed in the Piracicaba and Londrina soils. Work in progress in soils from Central Brazil will contribute to the understanding of the carbon isotopic record in Brazilian soils.

Table 4 shows ^{14}C dates, $\delta^{13}\text{C}$ and total carbon of the humin fraction from the same sites. In general, these data show less ^{14}C content for the humin fraction compared to bulk SOM. This difference is most pronounced in the Altamira soil. Similar patterns have been reported in other studies (Martel and Paul 1974; Campbell *et al.* 1967; Nowaczyk and Pazdur 1990). This reflects that SOM is composed of fractions of different age. Humic and fulvic acids that are removed during humin extraction are more mobile and can be sources of younger carbon transported downward from the shallow part of the soil. In the case of ^{13}C , we observed no significant differences between SOM and humin samples. The total carbon concentration of the humin fraction is significantly (up to five times) less than that of SOM. The results and ideas presented in the paper will be discussed in detail elsewhere, as a component of more comprehensive publications (Martinelli *et al.* 1996; Pessenda *et al.* in press).

TABLE 4. Humin Fraction of Soils of Londrina, Piracicaba and Altamira

Lab code (CENA-)	Site	Sample horizon (cm)	^{14}C (pMC) humin	^{14}C (pMC) total SOM	$\delta^{13}\text{C}$ (‰) humin	Total C (wt %) humin
241	Londrina	40 to 50	72.9 ± 0.7	90.3 ± 0.7	-22.9	0.22
230	Londrina	90 to 100	68.1 ± 0.6	74.3 ± 0.8	-21.3	0.24
240	Londrina	170 to 180	26.1 ± 0.4	31.3 ± 0.5	-14.5	0.25
243	Piracicaba	70 to 80	65.1 ± 0.9	71.8 ± 0.7	-19.3	0.13
242	Piracicaba	90 to 100	59.1 ± 0.8	68.8 ± 0.7	*	*
246	Piracicaba	110 to 120	57.8 ± 0.9	66.8 ± 0.7	-17.4	0.11
249	Altamira	50 to 60	56.6 ± 0.6	--	-26.4	0.12
250	Altamira	100 to 110	36.5 ± 0.5	--	-25.8	0.13
248	Altamira	130 to 140	29.5 ± 0.5	--	-26.2	0.10

*Insufficient material

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