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Carbon isotopic fractionation in subtropical Brazilian grassland soils. Comparison with tropical forest soils

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Abstract

The natural relationship $^{13}C/^{12}C$ determined in three soil profiles under grass vegetation indicated a depletion in organic ^{13}C at depth: the $\delta^{13}C$ was between −18‰ and −15‰ in the A horizons and ranged from −18 to −22‰ at depth. Previous work showed that in forest soils, where $\delta^{13}C$ was near −28‰ in the upper horizon, there was, on the contrary, a relative enrichment of the lower strata. This meant that $\delta^{13}C$, initially different in the various topsoils, became more equal at depth. Comparison between dark, deep horizons (sombric horizons), which are certainly of illuvial origine, would confirm this: $\delta^{13}C$ of grassland and a forest sombric horizon were almost equal at around −22‰. These results might mean that, in natural ecosystems, the isotopic carbon composition of the soil underlying humus would be independent of the vegetation type. This would have practical implications for the use of ^{13}C as a tracer for soil organic matter studies.

Introduction

According to their metabolism, plants may be divided into three types: C–3, C–4 and CAM, which have different $^{13}C/^{12}C$ ratios (Tenhunen *et al.*, 1983). Each type has characteristic natural $\delta^{13}C$ values. Thus, in C–3 plants $\delta^{13}C$ ranges from −25 to −30‰; in C–4 plants it varies from −8 to −18‰; and in CAM (Crassulacean acid metabolism) plants, it is around −17‰.

The $\delta^{13}C$ values of soil surface organic matter would be, roughly, identical to the vegetation from which it had originated. Consequently in the Brazilian tropical forest where most of the trees are C–3 plants, the $\delta^{13}C$ of soil organic matter could be easily differentiated from that of grassland soil organic matter which originated from tropical gramineae, all of them being C–4 plants.

This was actually verified. There are several results concerning the isotopic composition of the organic matter of Brazilian forest soils. These show that, in the forest soils of the northwest coast—Bahia (Flexor, 1974; Flexor and Volkoff, 1977; Volkoff *et al.*, 1978), in Amazonian forest soils near Manaus (Volkoff *et al.*, 1982) as well as in forest soils of the southeast forest—São Paulo (Modenesi *et al.*, 1982),the $\delta^{13}C$ of the surface layer ranges from −25 to −30‰. Soils under natural grass vegetation have been analyzed in only one site in São Paulo state; the $\delta^{13}C$ found in the surface layer of this soil was approximately −14.5‰.

This fact was utilized in order to evaluate the dynamics of the carbon incorporation when a C–4 plant (a sugar cane) was cultivated over forest cleared soil (Cerri *et al.*, 1985). In this case, when organic materials of different origins were mixed, the $\delta^{13}C$ was a very good tracer for soil organic matter evolution studies.

The $\delta^{13}C$ measurements on natural forest soils have also indicated that the $\delta^{13}C$ varied with depth in the same soil. In a forest latosol in the south of Bahia, the $\delta^{13}C$ varied from −29 to −28‰ at the

surface to −27 to −25‰ at 50 cm depth; in Amazon latosols the $\delta^{13}C$ varied from −28 to −27‰ at the surface to −25‰ at depth. This has been interpreted as a consequence of carbon-isotopic discrimination during the humification process and humus biodegradation in the soil.

A marked difference with depth was also noted in a grassland soil (Modenesi *et al.*, 1982). Isotopic analyses showed that the $\delta^{13}C$ reached −22‰ at depth, while in the surface it was −14 to −15‰. But in this case, the analyzed layer was an underlying sombric horizon, which could be interpreted either as a humic illuvial horizon or as a covered-up A paleo-horizon. Only two samples have been analyzed, one of the surface soil and another one from the sombric horizon. Data were, therefore, insufficient to indicate whether this difference between the surface and the soil at depth, was due to a natural, continuous variation of the carbon isotopic composition within the profile, as observed in forest soils, or whether the difference in $\delta^{13}C$ was connected with two distinct types of organic matter. One, on the top of the soil, might have been originated by C–4 plants of the existing grassland. The other, the organic matter of the sombric horizon, is perhaps inherited from a paleo C–4/C–3 vegetation, now buried.

Thus there is a lack of information about the vertical variation of organic carbon isotopic composition in soils under natural grassland. We do not know if, as under forest, these soils present isotopic discrimination with depth.

If humus formation and biodegradation, or humus-leaching phenomenon, caused an isotopic discrimination, a corrective factor must always be introduced when ^{13}C is to be used as a natural tracer of organic matter evolution, for example, after preplanting clearing and cultivation (natural grasslands cultivated or reforested by C–3 plants, forest soils cultivated under C–4 plants) or after paleoclimatic changes.

On the other hand, this natural isotopic discrimination must allow the use of ^{13}C as a natural tracer for studies of the dynamics of organic matter in soils in equilibrium with natural vegetation, of grass as well as forest.

To clarify the situation regarding the $\delta^{13}C$ variation in grassland soils, a more detailed study, with typical Brazilian grassland soils, was carried out. It was complemented by a comparative study of grassland and forest soils with sombric horizons. Soils with such horizons are commonly found in the Southeast part of Brazil, either under grass or under forest natural vegetation, and the isotopic relationship between their sombric horizon and upper horizon are unknown.

Materials and methods

Materials

Two typical South Brazilian soils under grass vegetation were analyzed: a Brunizem of Rio Grande do Sul, profile MRS2 (Volkoff *et al.*, 1984). Two soils with sombric horizons, were also selected: one under grass vegetation, a Cambisol, profile MMG1 in the South of the state of Minas Gerais (Volkoff *et al.*, 1984), the other under forest, a Latosol in the Paraná state, profile GPR1 (Volkoff and Cerri, 1978). All these soils were free from carbonates. The main characteristics of the four soils are summarized in Table 1.

Methods

The $\delta^{13}C$ was measured as CO_2 obtained by the complete combustion of the organic matter of a soil sample ground to pass a 2-mm seive. A sample of 5–30 mg, enough to obtain about 0.1 millimol CO_2, was placed in a pyrex tube with 1.0 g CuO. The tube was evacuated down to 10^{-3} torr, sealed and heated in a furnace for 16 h. After cooling, the CO_2 was purified using dry ice and liquid nitrogen baths.

The CO_2 was then measured in a mass spectrometer model MM 602E, VG Micromass, and $\delta^{13}C$ values were determined in relation to the standard (PDB standard).

$$\delta^{13}C = \left(\frac{^{13}C/^{12}C \text{ sample}}{^{13}C/^{12}C \text{ standard}} + 1\right) \times 1000$$

Maximum absolute deviation was 0.1%.

Results

Grassland soils (MRS2 and MSC1)

In the Brunizem profile (MRS2) a gradual change of $\delta^{13}C$ was noted (Fig. 1) from the surface

Table 1. Analytical data for soil profiles (Volkoff and Cerri 1978; Volkoff *et al.*, 1979; Volkoff *et al.*, 1984)

Horizons	c + fst[a]	pH		OM	C/N	S	T	Al	S/T
	%	H_2O	KCl	%		meq/100 g			
Profile MRS 2 (Grassland)									
A	34	5.5	4.1	6	17	7.6	13.4	0.6	57
A3	38	5.6	4.0	3	19	6.7	14.0	1.0	48
B	47	6.0	3.8	2	17	6.8	15.0	2.4	45
Profile MSC 1 (Grassland)									
A11	56	4.7	3.9	57	18	4.2	43.0	4.0	10
A12	63	4.8	4.1	50	19	1.0	31.3	3.3	3
B	48	5.2	4.4	9	19	0.2	12.0	0.6	2
Profile MMG 1 (Grassland)									
A11	46	4.8	4.0	10	16	0.7	12.6	2.8	5
A3	56	5.0	4.4	4	23	0.2	8.0	2.1	2
B1	49	5.1	4.5	4	28	0.1	8.8	1.9	1
B2	49	5.1	4.5	2	24	0.1	5.4	1.4	2
Profile GPR 1 (Forest)									
A11	42	4.3	3.7	7	12	2.6	16.0	4.1	16
A12	42	4.0	3.6	6	11	2.1	13.0	4.9	13
B1	48	4.4	3.8	2	9	2.3	11.9	4.1	19
B2	53	4.4	3.9	1	9	2.2	7.9	3.8	28

[a] c, clay; fst, fine silt; OM, Organic matter; S, sum of exchangeable Ca^{2+}, Mg^{2+}, Na^+ and K^+; T, CTC calculated with $CaCl_2$ at pH7; Al, exchangeable Al^{3+}.

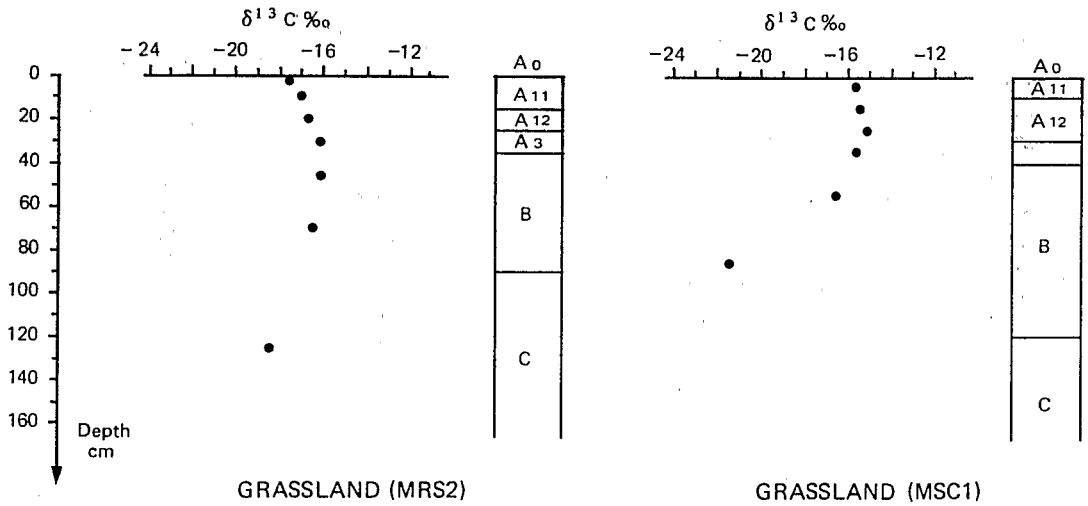

Fig. 1. The $\delta^{13}C$ variation with increasing depth in two grassland soils

(−18‰) to the A3 horizon and the upper part of the B horizon (−16‰) and the C horizon where $\delta^{13}C$ reached −18.5‰. From the surface downwards depth the soil organic matter was first richer in ^{13}C, and then it gradually decreased. A similar change in the arbon isotopic composition was observed in the humic Cambisol of Santa Catarina (MSC1). However, in this soil, the depletion in the deeper horizon (horizon C) was greater: $\delta^{13}C$ ranging from −15 to −16‰ in the upper part of the soil profile, reached −21.5‰ in the C horizon.

Soils with a sombric horizon

Soil under grassland vegetation (MMG1). In the first 40 cm the $\delta^{13}C$ changed from −17‰ at the surface to −15‰ in the A3 horizon (Fig. 2). The

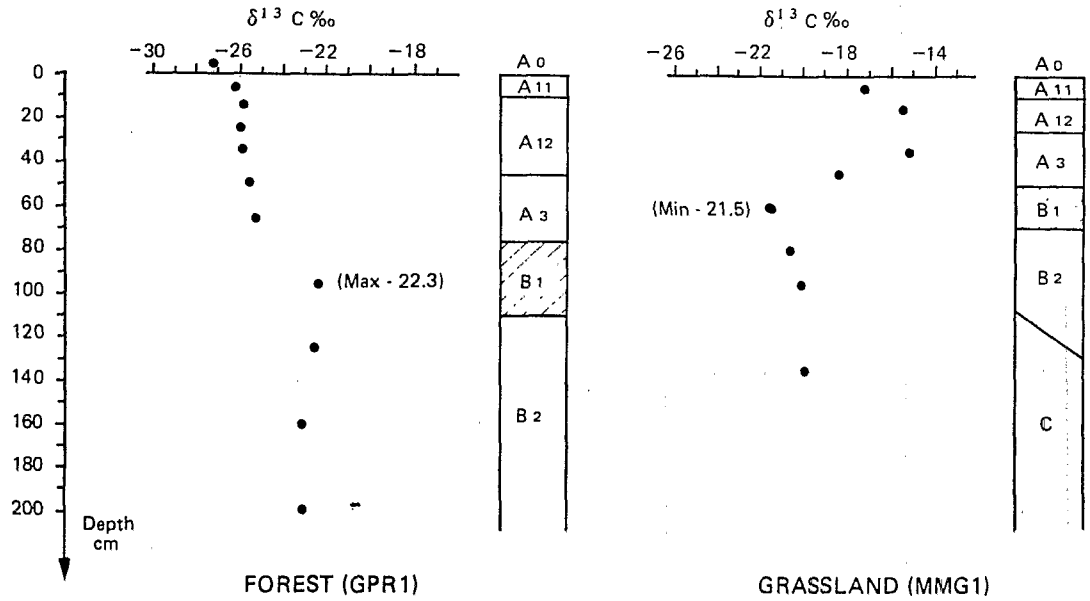

Fig. 2. The $\delta^{13}C$ variation with increasing depth in a grassland and a forest soil with sombric horizon (B1 is the sombric horizon)

values were in accordance with those found previously in the two grassland soils analyzed. The $\delta^{13}C$ value decreased rapidly. In the sombric horizon (between 50 and 70 cm) $\delta^{13}C$ was -21.5‰, therefore quite close to that published in the literature (Modenesi *et al.*, 1982). In horizons B2 and C, $\delta^{13}C$ was constant at -19‰.

Forest soil (GPR1). In the litter layer of this soil, the $\delta^{13}C$ was -27.5‰, and in the upper 50 cm, it was near -25‰. Such values were in accordance with those found in the forest soils of São Paulo state (Modenesi *et al.*, 1982). In the A3 horizon (Fig. 2) the $\delta^{13}C$ increased. At about 1 m, in the B1 horizon, which is here a sombric horizon, the $\delta^{13}C$ reached -22.3‰. At depth, in B2, the $\delta^{13}C$ decreased very little and became constant at -23‰. In B1 of this forest soil, the $\delta^{13}C$ was therefore very close to the $\delta^{13}C$ of the dark horizon of the grassland soil.

Conclusions

The results presented in this paper confirmed the difference between the carbon isotopic composition of grassland and forest soil organic matter. Under grassland, the $\delta^{13}C$ of the upper soil layers ranged from -15 to -18‰, and under forest, it ranged from -26 to -28‰.

In both grassland and forest soils, the ratio $^{13}C/^{12}C$ of the total humus of the soil increased from the A11 to the A12 horizon. The increase continued at depth in the forest soil, but on the contrary, in the grassland soil the ^{13}C concentration decreased at depth.

Under grassland $\delta^{13}C$ changed to values ranging from -18 to -22‰. In the forest soils, $\delta^{13}C$ of the deep horizons varied between -23 and -25‰: -25‰ was obtained in the deep layer of the Amazon and south Bahia forest soils (Flexor and Volkoff, 1977; Volkoff *et al.*, 1982) and a value near -23‰ was obtained in this study for a southeast forest soil. The appreciable reduction of the difference in the deep horizons was noteworthy.

It seemed therefore, that the $\delta^{13}C$, although different at the soil surface under grassland and under forest, converged to the same value with increasing depth.

The $\delta^{13}C$ variations in the profile may be related to the humus composition changes. With increasing depth, there were always more free fulvic acids in the humus. The comparison of the two grassland soils without sombric horizons showed that the humus of the acid soil (MRS2) had few free fulvic acid compounds (Volkoff *et al.*, 1979) while the

humus of the strongly acid soil (MSC1) was rich in free fulvic acids (Volkoff *et al.*, 1982). The latter profile was the most depleted in ^{13}C at depth and it was confirmed that, in acid grassland soils, the ^{13}C depletion might be correlated with the free fulvic acid content of the soil humus.

Reverse correlations were observed in forest latosols. In these soils the humus became gradually richer in free fulvic acids with depth and at the same time there was an increase in the total $^{13}C/^{12}C$ ratio.

It could signify that $\delta^{13}C$ values converged when the humus became rich in free fulvic acids at depth and also that the isotopic composition of this underlying humus was independent of the surface vegetation.

This will be emphasized in soils with sombric horizons. In these soils the sombric horizon was not a peculiar horizon with regard to the humus characteristics (biochemical or isotopic composition). Its humus was always rich in free fulvic acids, poor in humin (in both soils analyzed, humin represented less than 30% of total C of the layer), which was not specific for this horizon; such characteristics were close to those of the horizons which were found immediately above and below it. All these observations lead to belief that the carbon of this horizon was not a carbon inherited from a buried paleohorizon A. A small accumulation of illuvial carbon might explain its origin.

In the grassland soil this sombric horizon corresponded to a maximum ^{13}C depletion. In the forest soil it corresponded to maximum enrichment. In both sombric horizons, the $\delta^{13}C$ reached almost the same value ($-21.5‰$ under grass, and $-22.3‰$ under forest).

From such evidence it could be assumed that the organic compounds which move at depth have an isotopic composition irrespective of the plant cover. These compounds could have originated from hypothetical plant species of intermediate isotopic composition, which would give particularly few polymerized humic fractions easily translocated at depth. More probably it would have occurred during the decomposition of the plant material, of C–3 plants in the grassland soil, of C–4 plants in the forest soil. Humification processes might have produced humic substances which affected an isotopic composition close to that of the original plants, and humic substances with a poor or less constant composition independant of the plant cover.

These results confirmed the value of the isotopic methods and suggest a path for new research on the dynamics of soil organic matter based on isotopic biochemistry.

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