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Short communication

Stable carbon and nitrogen isotopic composition of bulk aerosol particles in a C4 plant landscape of southeast Brazil

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Abstract

The carbon and nitrogen isotopic compositions of aerosol particles collected in the Piracicaba region, where C4 plants like sugarcane and pasture dominate the land cover, were measured. For comparison, aerosol particles were also analyzed from the Santarém region, Amazon basin, where the main land cover is primary forest. The average $\delta^{13}C$ value of samples collected in Piracicaba was equal to $-20.9 \pm 0.8‰$. The average $\delta^{13}C$ of samples collected in Santarém was almost 5‰ smaller than in Piracicaba ($-25.8 \pm 0.5‰$). This difference between the two sites was attributed to the presence of C4 material in Piracicaba aerosol particles. On the other hand, there was no statistical difference between the average $\delta^{15}N$ values observed in Piracicaba ($10.6 \pm 2.8‰$) and Santarém ($11.5 \pm 2.1‰$). The $\delta^{13}C$ and $\delta^{15}N$ values of aerosol particles collected in Santarém were higher than vegetation tissues and soil organic matter, which are the potential sources of organic matter to aerosol particles.

Keywords: Carbon stable isotope; Nitrogen stable isotope; Aerosol particles; Atmosphere; C4 plants; Amazonia; Brazil

1. Introduction

Biomass burning is an important source of aerosol particles and trace gases to the atmosphere, especially in areas with intensive land use changes or agricultural practices (Levine et al., 1995). Several studies have attempted to characterize the chemical and physical composition of aerosol particles originated by vegetation fires (e.g. Simoneit et al., 1990; Abas et al., 1995; Yamasoe et al., 2000). Conversely, few studies have attempted to determine the stable isotopic composition of these particles (Chesselet et al., 1981; Cachier et al., 1985; Simoneit, 1997; Ballentine et al., 1998; Norman et al., 1999). Stable isotopes of carbon have being used as a tracer of organic matter origin in several other studies in terrestrial and aquatic environments. They are especially useful in situations where there are sources with distinct isotopic compositions.

In the Piracicaba River basin more than 80% of the land is covered with C4 plants (pasture or sugarcane) and the remaining area with C3 plants (Martinelli et al., 1999). Sugarcane is burned from May to October, launching annually more than 50,000 tons of carbon to the atmosphere and changing the chemical composition of rain water (Lara et al., in press). A high concentration of PM_{10} (particles $<10\,\mu m$) was observed in the Piracicaba region during the biomass-burning season, with an average of $88\,\mu g\,m^{-3}$. For the non-burning period, the average PM_{10} concentration was $50\,\mu g\,m^{-3}$ (Lara et al., in press). Our objective in this study is to investigate the origin of the organic matter in aerosol particles in the Piracicaba River basin, using its carbon and nitrogen stable isotopic composition as a tracer. For comparison, the isotopic composition was also determined in aerosol particles collected in the Amazon basin.

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2. Methods

From August 1999 to September 2000, aerosol sampling was performed in the São Paulo State, Brazil, near the city of Piracicaba (22°42′30″S; 47°38′00″W), and from May to August 2000 at the Floresta Nacional do Tapajós (2°51′25″S; 54°57′32″W), which is a national forest reserve located south of the city of Santarém in the northeast region of the Amazon basin (Fig. 1). Fine mode ($dp < 2\,\mu m$) aerosol particles were collected using a Stacked Filter Unit (SFU) placed in both sites at 5 m above the ground. Aerosol mass concentration and isotopic ratio in this mode were measured. Each sample was taken over a period long enough to accumulate aerosol mass for isotopic analysis that varied from 24 to 72 h. The land use is totally distinct between these two sites. Considering an area encompassed by a circumference centered by the Piracicaba sampling point and with a radius of 20 km (area of approximately 1200 km^2), almost 80% of this area is covered with sugarcane plantations and 10% with pasture (Lara et al., in press). Therefore, approximately 90% of this area is covered with C4 plants. Conversely, although there are pasture fields in the Santarém region, primary tropical rain forest is the most important land cover in that region.

Carbon and nitrogen isotopic compositions were determined by combusting quartz filters with aerosol samples using a Carlo Erba elemental analyzer coupled with a Finnigan Delta-E mass spectrometer fitted with double inlet and double collector systems. Results are expressed in $\delta^{13}C$ (‰) and $\delta^{15}N$ (‰) relative to PDB and atmospheric air isotopic standards, respectively, defined as

$$\delta = \left(\frac{R_{sample}}{R_{std}} - 1\right) \times 1000, \quad (1)$$

where R_{sample} and R_{std} are the $^{13}C:^{12}C$ or $^{15}N:^{14}N$ of the sample and standard, respectively. Samples were analyzed at least in duplicate with a maximal difference of 0.3‰ and 0.8‰ in carbon and nitrogen, respectively, between replicates. Statistical differences between populations were tested by two samples *t*-test assuming unequal variation.

Fig. 1. Map of Brazil showing the two sampling sites and land-use in an area encompassed by a circumference centered by each sampling point and with a radius of 20 km (area of approximately 1200 km^2).

3. Results and discussion

The average $\delta^{13}C$ value of fine mode aerosol particles collected in Piracicaba was equal to -20.9 ± 0.8‰, ranging from -20.0‰ to -22.8‰ (Table 1). The $\delta^{13}C$ values measured in Santarém were significantly smaller ($P < 0.01$) than Piracicaba. The average value was equal to -25.8 ± 0.5‰, the most depleted value was equal to -26.9‰ and the most enriched was equal to -24.9‰ (Table 2). The average $\delta^{15}N$ value in Piracicaba was equal to 10.6 ± 2.8‰, which was not statistically different than the average value found in the Amazon region (11.5 ± 2.1‰). The variability of the $\delta^{15}N$ values in both places was higher than the variability observed for $\delta^{13}C$ values.

In order to relate, through stable isotopic composition, aerosol particles with their sources it is first necessary to investigate if significant isotopic fractionation occurs during the combustion process (Currie et al., 1999). If it does, this fractionation has to be taken into account when particles and sources are compared. This possibility is quite likely, since particles produced during combustion are complex mixtures, including volatile compounds condensed onto existing aerosols and thermally altered plant debris (Turekian et al., 1998). In laboratory conditions, Turekian et al. (1998) found that the $\delta^{13}C$ values of particles produced during combustion of C3 plants (*Eucalyptus* sp. and *Colospherum mopane*) were approximately 0.5‰ heavier than the unburned plant. On the other hand, the $\delta^{13}C$ of particles produced during combustion of C4 plants (*Cenchris cilliarus, Antephora pubesence,* and *Saccharum officinarum*, sugarcane) were approximately 3.5‰ lighter than the source. Another combustion experiment made in laboratory conditions (Currie et al., 1999), found that the $\delta^{13}C$ values of particles was on average 0.5‰ lighter than the C3 unburned plants (pine and oak). These are relatively minor changes compared with the large isotopic difference ($\sim$15–18‰) that exist between C3

Table 1
$\delta^{13}C$ and $\delta^{15}N$ values of aerosol particles collected in Piracicaba

Sampling date	$\delta^{13}C$ ‰ (*)	$\delta^{15}N$ ‰ (*)
31/08–04/09	−22.0	13.8
04/09–08/09	−21.2	10.6
08/09–16/09	−21.0	8.3
16/09–19/09	−20.7	11.0
19/08–25/09	−20.2	9.3
25/09–04/10	−20.2	8.7
04/10–13/10	−20.4	9.1
13/10–20/10	−21.2	11.2
20/10–09/11	−20.9	9.0
09/11–24/11	−22.3	12.6
24/11–10/12	−22.8	
10/12–04/01	−21.2	10.2
07/01–14/02	−20.2	7.9
14/02–10/03	−20.6	7.0
29/03–28/04	−21.5	9.6
28/04–10/05	−21.7	9.1
16/05–23/05	−20.1	9.8
23/05–29/05	−20.4	9.6
29/05–10/06	−20.5	9.7
10/06–17/06	−21.1	9.1
17/06–27/06	−20.2	9.3
27/06–04/07	−20.0	9.3
04/07–07/07	−21.1	18.7
17/07–02/08	−21.8	14.9
02/08–16/08	−20.2	10.2
17/08–15/09	−20.3	17.2

Table 2
$\delta^{13}C$ and $\delta^{15}N$ values of aerosol particles collected in the Amazon Basin (Santarém primary forest)

Sampling date	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰
16/05–19/05	−26.85	10.49
10/07–12/07	−26.72	10.41
19/05–22/05	−26.61	10.42
17/07–19/07	−26.43	11.24
16/05–22/05	−26.28	9.93
07/08–09/08	−26.20	9.84
26/06–28/06	−26.13	9.87
28/07–31/07	−26.09	10.92
04/08–07/08	−26.08	10.67
07/07–10/07	−26.02	11.09
22/05–29/05	−26.00	15.45
12/07–14/07	−25.95	10.33
14/07–17/07	−25.87	11.18
11/08–14/08	−25.81	10.27
19/07–24/07	−25.79	11.66
03/07–07/07	−25.73	11.52
14/08–18/08	−25.65	10.94
28/06–03/07	−25.59	11.10
24/07–28/07	−25.57	11.16
21/06–26/06	−25.55	12.32
09/08–11/08	−25.54	9.72
31/07–04/08	−25.49	10.34
29/05–02/06	−25.48	14.54
18/08–21/08	−25.42	10.06
12/06–16/06	−25.41	15.62
02/06–07/06	−25.29	17.36
16/06–21/06	−25.29	12.64
25/08–28/08	−25.22	8.37
07/06–12/06	−25.16	14.78
21/08–25/08	−24.89	9.79

and C4 (sugarcane) plants. The isotopic fractionation during combustion for nitrogen was higher than for carbon. Particles produced during combustion were approximately 6.6‰ heavier than the unburned plants and no difference was found between C3 and C4 for plants (Turekian et al., 1998).

The $\delta^{13}C$ values of sugarcane leaves collected in the Piracicaba region by Cerri et al. (1985) and Bernardes (2000) was equal to −13.2‰ and −13.5‰, respectively. The $\delta^{13}C$ of the soil in sugarcane and pasture areas appears to be a function of the time that the culture had been established (Cerri et al., 1985; Vitorello et al., 1989; Bernoux et al., 1998). For instance, the $\delta^{13}C$ of soil organic matter, after 12 years of sugarcane cultivation changed from −25.1‰ to −23.0‰, and after 50 years decreased to −20.2‰ (Vitorello et al., 1989). Therefore, based on the fact that the ^{13}C isotopic fractionation between aerosol and its fuel is small (Turekian et al., 1998; Currie et al., 1999), and also taking into account the 6.6‰ ^{15}N isotopic fractionation found for C4 plants, it is likely that aerosol particles in Piracicaba are composed by a mixture of C3 and C4 sources (Fig. 2a). Supporting this hypothesis, there is the fact that biomass burning and soil dust are the main sources of organic material to aerosol particles in Piracicaba (Lara et al., in press). In addition, Cachier et al. (1985) found similar isotopic values during the burning season in a savanna region of Africa.

Based on the facts that sugarcane is burned during the dry season, from March to October, and that Cachier et al. (1985) found heavier $\delta^{13}C$ values during the dry season in Africa, it was first hypothesized that the contribution of C4 material to the atmosphere would dominate during the dry season, and C3 sources would be minimum. In fact, the average $\delta^{13}C$ values became 0.5‰ heavier during the dry season at the Piracicaba sampling site (Fig. 3). However, the dry season average (-20.7 ± 0.7‰) was not statistically different from the rainy season average (-21.2 ± 0.9‰). Therefore, it appears that C4 material is an important source of organic matter to aerosol particles all year round. The same trend was observed for $\delta^{15}N$, smaller values were observed during the rainy season (9.6 ± 1.8‰) than during the dry season (11.1 ± 3.1‰), but again these averages were not statistically distinct.

The relative contribution of C4 plants (%C4) to aerosol particles can be estimated by the following

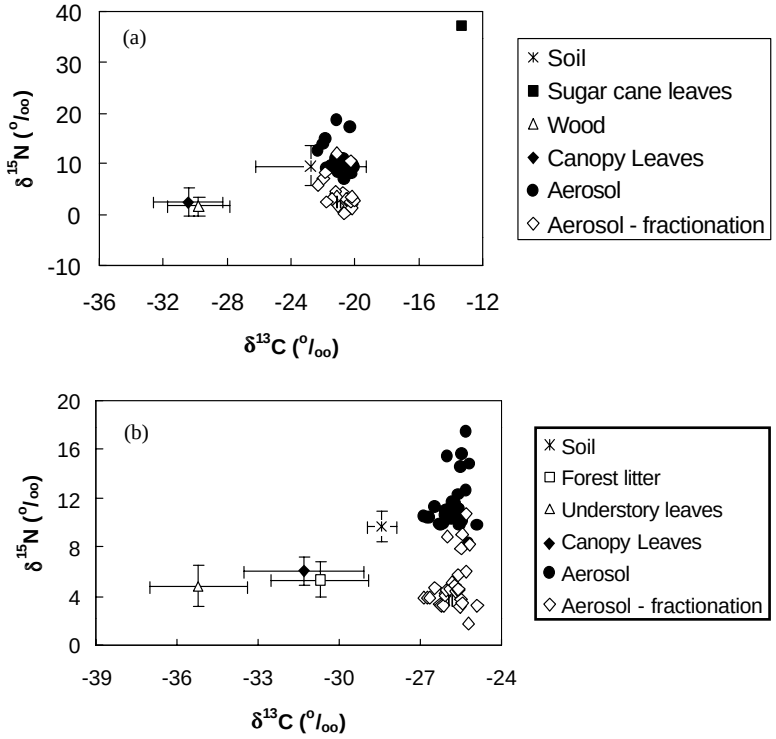

Fig. 2. Plot of $\delta^{13}C$ vs $\delta^{15}N$ including vegetation tissues, soil organic matter and aerosol particles. (a) Piracicaba and (b) Santarém. Isotope composition of vegetation tissues and soil organic matter in Piracicaba are from Bernardes (2000). Isotope compositions of vegetation tissues are from (Ometto, J.P., unpublished data) and soil organic matter from (Teles, E., unpublished data). The legend "Aerosol—fractionation" denotes that from each $\delta^{15}N$ value was subtracted 6.6‰, relative to the ^{15}N isotopic fractionation found by Turekian et al. (1998).

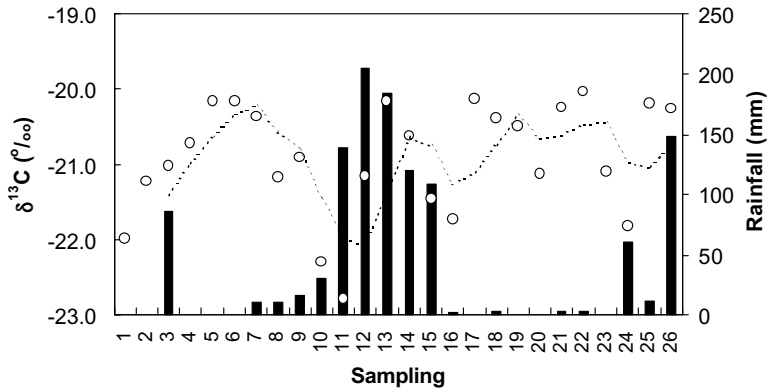

Fig. 3. Temporal variation of $\delta^{13}C$ values of aerosol particles and rainfall in the Piracicaba sampling site. Circles are $\delta^{13}C$ values, the dashed line is a 2 points moving average and bars represent rainfall.

equation:

$$\%C4 = \frac{\delta^{13}C_{\text{aerosol}} - \delta^{13}C_{C3}}{\delta^{13}C_{C4} - \delta^{13}C_{C3}}, \quad (2)$$

where $\delta^{13}C_{\text{aerosol}}$ is the isotopic composition of aerosol particles, $\delta^{13}C_{C3}$ is the isotopic composition of the source of C3 origin, assumed to be the average $\delta^{13}C$ value found for leaves of C3 vegetation in Piracicaba

(−30.5‰, Bernardes, 2000); and $\delta^{13}C_{C4}$ is the isotopic composition of the source of C4 origin (−13.5‰) (Fig. 2a). Using the average $\delta^{13}C$ value of particulate aerosol in Eq. (2), the estimated contribution of C4 material to aerosol particles would be of approximately 55%, being the minimum and the maximum contribution 45% and 62%, respectively.

While in Piracicaba biomass burning from sugarcane and soil dust appear to be the main sources of organic matter to aerosol particles, the natural primary forest emissions appears to be the main sources in Santarém during the wet season (Artaxo et al., 1998). The $\delta^{13}C$ and $\delta^{15}N$ values measured for aerosol particles in Santarém were always statistically higher ($P<0.01$) than the ones for vegetation samples or soil organic matter (Fig. 2b). For instance, the average $\delta^{13}C$ of Santarém aerosol it was approximately 6.0‰ higher than the average $\delta^{13}C$ values of several tree leaves collected in Santarém. Even applying the fractionation of 6.6‰, the $\delta^{15}N$ values of Santarém aerosol are still statistically different than the foliar $\delta^{15}N$ values found in that region. Based on this difference it is reasonable to hypothesize that foliar tissues are not the main source of organic matter to aerosol particles in the Amazon region. Indeed, according to Artaxo et al. (1998) aerosol in the Amazon region is a complex mixture that includes many different types of particles like: pollen, spores, bacteria, algae, protozoa, fungi, fragments of leaves, excrement and fragments of insects. Therefore, it is likely that the contribution in different proportion of all these materials resulted in $\delta^{13}C$ and $\delta^{15}N$ values smaller than vegetal tissues and soil organic matter.

In conclusion, the C4 organic material that was introduced in the Piracicaba basin by replacement of primary forests by sugarcane and pasture was already present in soils (Vitorello et al., 1989) and in rivers (Martinelli et al., 1999). In this study we showed that C4 material is also present in the local atmosphere. In the Amazon Basin site (Santarém) the $\delta^{13}C$ and $\delta^{15}N$ values of aerosol particles were higher than vegetation tissues and soil organic matter, suggesting that aerosol sources other than plant fragments are contributing to aerosol particles in that region. In particular, gas-to particle conversion of VOCs such as terpenes has to be studied in detail.

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