

Properties of aerosols from sugar-cane burning emissions in Southeastern Brazil

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Abstract

The influences of biomass burning emissions in the composition of aerosol have been studied during 1 year around the city of Piracicaba (Southeastern Brazil). Inhalable particles, separated in PM_{2.5} and coarse particulate mode (CPM, with size in the range ($2.5 < d_p < 10 \mu\text{m}$)), were sampled from April 1997 to March 1998 and analyzed for BC, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr, Pb. The average concentrations of PM_{2.5}, CPM, BC and chemical elements were statistically higher in the dry season than in the wet season. The results of absolute principal component analysis showed four and three different sources for PM_{2.5} and CPM, respectively. Sugar-cane burning is the main source of PM_{2.5} representing 60% of PM_{2.5}, soil dust accounted for 14%, and industries and oil combustion contributed with 12% each one. Resuspended soil is the main source of CPM followed by industrial emissions and sugar-cane burning. The sampling and analytical procedures applied in this study showed that sugar-cane burning and agricultural practices are the main sources of inhalable particles, possibly altering the aerosol composition around the city of Piracicaba.

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1. Introduction

In the Northern Hemisphere the main source of aerosols is linked to fossil fuel burning, whose emissions have been well documented, while in tropical areas biomass burning may be one of the most important global source of atmospheric particles (Crutzen and Andreae, 1990; Oglesby et al., 1999). Aerosol particles from biomass burning are important in the radiative balance of the atmosphere, through a complex micro-

physical process, possibly affecting the ground-based radiation budget (Oglesby et al., 1999; Ramanathan et al., 2001). The carbonaceous aerosols (black carbon and organic aerosol) are identified as playing a major role in the absorption of solar radiation. These aerosols, together with the resulting reflection of solar radiation to space, lead to large changes (global mean radiative aerosol forcing range from -0.5 to $+0.2 \text{ W m}^{-2}$) in the solar radiation absorbed on the surface (Ramanathan et al., 2001; Streets et al., 2001). Additionally, the particles emitted by biomass burning can affect the concentration of cloud condensation nuclei, probably changing the hydrological cycles and cloud albedo (Roberts et al., 2001; Rosenfeld, 1999).

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Due to the large fire catastrophes of anthropogenic origin in recent years and the intensive scientific efforts over the last decade, the general public as well as the scientific community are now aware that emissions from biomass burning represent a large perturbation to global atmospheric chemistry, particularly in the tropics. Biomass burning includes the burning of forests, savannas, and agricultural lands. Brazil plays an important role in biomass burning emissions, with the detection by AVHRR of about 235,000 fire spots in 2004 (www.cptec.inpe.br/queimadas). Most of these fires occurred in the southern part of the Amazon basin during the dry season (from August to November). Emissions from these fires have significant impacts on the concentration of trace gases and aerosols over a large area ([Artaxo et al., 2002](#); [Yamasoe et al., 2000](#)). From Southeastern through Northeastern Brazil sugar-cane burnings are also key contributors in terms of emissions, as already highlighted a decade ago by [Crutzen and Andreae \(1990\)](#). Brazil owns 25% of the global sugar-cane areas, and is the major sugar-cane producer in the world. Currently, it has 4,500,000 ha of sugar-cane crops and more than 1,100,000 rural workers are involved in the sugar-cane industry ([Zamperlini et al., 2000](#)). The area cultivated with sugar-cane in the state of São Paulo in Southeastern Brazil, reaches approximately 24,000 km². In order to facilitate harvesting, which also occurs in others places such as Hawaii and Africa, the sugar-cane is burned and most fires occur every year during the dry season (from May to November). About 20 t of sugar-cane dry matter per hectare is burned, contributing to a global emission with approximately 0.48 Tg of carbon per year. As a result, aerosol and trace gases emitted from sugar-cane fires have significant effects on the composition and acidity of rainwater over large areas of Southern Brazil ([Lara et al., 2001](#)). Despite its importance, little information is available about the effects of sugar-cane burnings on aerosol particles ([Azevedo et al., 2002](#); [Martinelli et al., 2002](#)).

The focus of this paper was the investigation of the chemical and physical characteristics of sugar-cane burning aerosol emissions, looking especially at the elemental composition, and source apportionment of fine and coarse mode aerosols. The use of real-time aerosol monitors (TEOM and Aethalometer) allowed obtaining of diurnal patterns, while stacked filter units (SFU) separated fine and coarse mode aerosol.

2. Methodology

The city of Piracicaba is located in the western part of the Piracicaba River basin. It has approximately 320,000 inhabitants and a population density of 242

inhabitants km⁻² ([Fig. 1](#)). In an area encompassed by a circumference centered by the city and with a radius of 20 km (area of approximately 1200 km²), the land use is dominated by sugar-cane plantations (80%), followed by pastures (11%), urban areas (6%) and forests (3%) ([Lara et al., 2001](#); [Krushe et al., 2002](#)). Additionally, more than 1000 small industries were found ([Lara et al., 2001](#)).

Aerosol sampling was performed day and night from April 1997 through March 1998 using the SFU ([Hopke et al., 1997](#)). The inhalable particles (PM₁₀) have been sampled in the SFU on 47 mm diameter nuclepore polycarbonate filters in two separated size fractions: fine particulate mode, PM_{2.5} ($d_p < 2.5 \mu\text{m}$) and coarse mode, CPM ($2.5 < d_p < 10 \mu\text{m}$). Each sample was taken over a period of 48 h. The sampling site was located in the meteorological station of the “Escola Superior de Agricultura Luiz de Queiroz—ESALQ”. This site lies about 4 km from the Piracicaba downtown and less than 1 km from the nearest sugar-cane plantation. The SFU inlets were located 3 m above the ground to minimize direct influences of local resuspended soil dust. The dominant wind direction was from the sugar-cane plantations to the sampling station.

In order to identify the daily variability of the sugar-cane emissions in the concentration of PM₁₀ and BC, from 3rd October until 13th November, we employed a real time aerosol mass monitor—the Tapered Element Oscillating Microbalance (TEOM), series 1400a operated with a time resolution of 10 min, and a heating of the inlet at 50 °C. The organic carbon (OC) concentration was measured with 10 min time resolution, in the PM_{2.5} fraction by a direct automatic thermal-CO₂ technique, performed by the Ambient Carbon Particulate Monitor, series 5400. During the analysis the collected sample is heated first to 3401 °C and then to 7501 °C determining the concentrations of organic and total carbon, respectively. Black carbon (BC) was also determined during this period using an Aethalometer with the same time resolution. During this time the samples were classified in two different conditions: days with and without sugar-cane burning impacts. Parameters such as precipitation, weekends, and holidays were used in separating these periods. Gravimetric mass and BC were measured in the nuclepore filters. BC was measured by a reflectance technique according to the method developed by [Reid et al. \(1998\)](#). Elemental composition was measured by particle-induced X-ray emission (PIXE), a multi-elemental technique that allows the identification of about 21 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr, and Pb). PIXE detection limits are about 1 ng m⁻³ for elements with $Z > 20$, and about 10 ng m⁻³ for elements from Na to K. More details about PIXE technique and aerosol sampling can

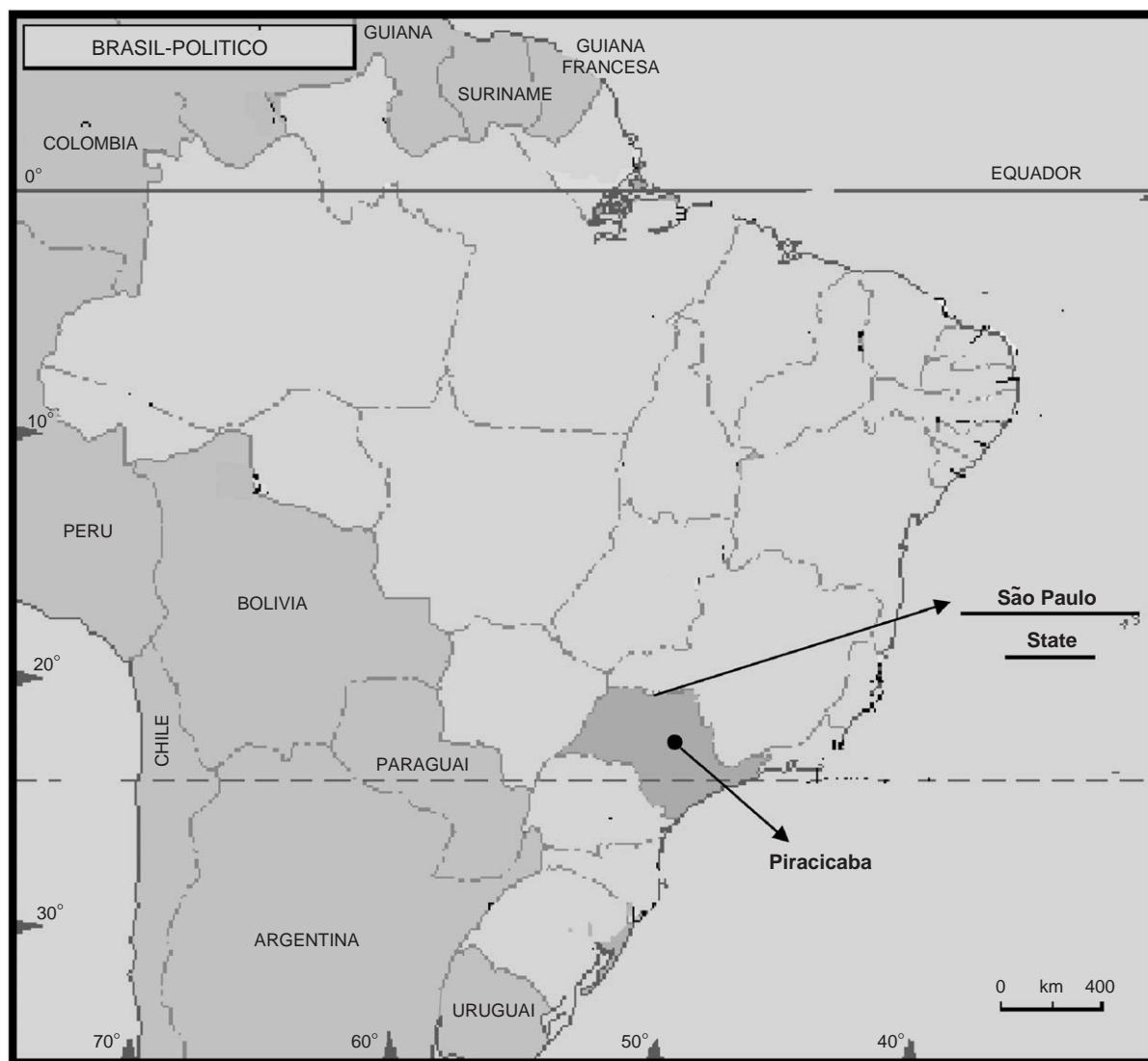


Fig. 1. Map of Brazil with divisions of the states showing the sampling site (Piracicaba in the State of São Paulo). Names of states are underlined.

be obtained from Artaxo et al. (1999) and Yamasoe et al. (2000).

Multivariate analyses have been successful when applied to studies of environmental problems (Hopke, 1991). In order to help the identification of possible aerosol sources and quantify the source apportionment we performed principal component analysis (PCA) and absolute principal component analysis (APCA) (Thurston and Spengler, 1985; Swietlicki et al., 1996). ANOVA tests (Tukey honest significant test) were used to evaluate the seasonal differences in the concentrations of the elements.

3. Results

Sugar-cane is burned and harvested from May to November. This period is coincident with the dry season in Southern Brazil. From December to April the wet pattern prevails and there are fewer burning activities in the area of Piracicaba and in all State of São Paulo (Fig. 2). According to Fig. 2, the peak of the burning season (August) is just after the minimum of precipitation. Based on this fact and for statistical purposes we grouped samples according to the occurrence of fire events: dry season (May–November), coincident with

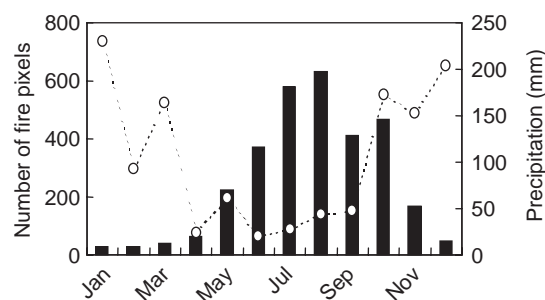


Fig. 2. Number of fires pixels (black column) in São Paulo State (www.cptec.inpe.br/queimadas) during 1997–1998 and mean monthly precipitation (dashed line) in Piracicaba City (www.esalq.br).

the sugar-cane burning season and wet season (December–April), coincident with non-burning season.

Fig. 3 shows the aerosol mass and BC concentrations for the whole sampling period. The PM_{10} concentration had a large seasonal variability. Higher concentrations were found during the dry season and smaller concentrations during the wet season. The highest concentration ($238 \mu\text{g m}^{-3}$) was found in early September and the smallest concentrations ($9.3 \mu\text{g m}^{-3}$) in middle October, just after the first rains (Fig. 3a). BC concentration also had the same pattern of seasonal variability of the inhalable particulate (Fig. 3b). The highest concentration ($10.7 \mu\text{g m}^{-3}$) was observed in middle August and the lowest one in the end of December ($0.8 \mu\text{g m}^{-3}$). By grouping particles and chemical elements in the wet and dry seasons, several important differences emerge between these two groups. The average concentrations of $PM_{2.5}$, CPM, BC and chemical elements were statistically higher ($P < 0.01$) during the dry season than in the wet season (Table 1). For instance, the PM_{10} wet season average concentration was equal to $34.1 \mu\text{g m}^{-3}$, and increased to $90.7 \mu\text{g m}^{-3}$ during the dry season. Coarse particulate mode represented the largest fraction of PM_{10} , consisting of 75.0% and 66.1% of the PM_{10} mass during dry and wet seasons, respectively.

Since the sugar-cane biomass burning happens mostly around 5:00–6:00 p.m., we investigated the diurnal pattern of BC and PM_{10} . Hourly PM_{10} and BC concentrations and BC/OC ratio are shown in Fig. 4. Further, we grouped the concentrations according to burning and non-burning days collected from 3rd October until 13th November. There was a peak in the PM_{10} concentration between 7:00 and 10:00 a.m. This occurred in both situations (Fig. 4a). A second peak in the PM_{10} concentration occurred between 6:00 and 11:00 p.m., but only during burning days (Fig. 4a). A similar peak occurred for BC in the same time of the day and also only during burning days (Fig. 4b). In the rest of the daytime, the BC concentration was quite constant

and with no significant difference between burning and non-burning days (Fig. 4b). The diurnal cycle of OC measured by the 5400 Ambient Carbon Particulate Monitor presents a similar pattern as the BC concentration. The OC aerosol can be originated from direct emissions of particles, such as biomass burning (Azevedo et al., 2002), and also from atmospheric secondary formation from gaseous precursors. The ratio of BC/OC varies significantly along the day (Fig. 4c). The maximum value of the ratio BC/OC occurred, again only during burning days, between 6:00 and 11:00 p.m., coincident with the time of the sugar-cane fires. During the day and before the burning time, it is possible to observe a sharp decrease in the ratio (BC/OC $< 40\%$), indicating two processes: a reduction in the direct emission of BC by the sugar-cane fires, and the secondary production of OC particulate in the atmosphere. Chow et al. (1996) have pointed out that the limit of 50% of (BC/OC) indicates the presence of secondary organic aerosols in the urban atmosphere. The non-burning days did not show a strong gradient in the ratio, presenting a BC/OC ratio $< 25\%$. This fact points to the possibility of changes in the production of OC related to sugar-cane burning emissions.

In order to study the aerosol sources in the region of Piracicaba, PCA was performed including the chemical composition of fine and coarse mode particulates. The communality for each variable, which represents the fraction of each variable that is explained by the retained factors, was typically higher than 82% (fine mode) and 93% (coarse mode). This indicated that the factors could explain most of the data variability. For the fine mode, four factors have been retained. They explained 92% of the variance of the data set (Table 2). The first one is loaded with $PM_{2.5}$, BC, K, S, and Br representing biomass burning ($PM_{2.5}$, BC, K) and it explained 27.6% of the variance of the data. The second factor is associated with Al, Si, Ca, Fe, and Ti, characteristics elements of resuspended soil; it explained 24.5% of the variance. The third factor (22.3% of the variance) is associated with heavy metals due to the significant loads for Zn, Pb, Cu, and Mn. The association of these elements with Fe can be related to industrial process involving ferrous smelter emissions. The last factor has significant loads for V and Ni, representing aerosols from residual oil combustion and explained 17.6% of the variance of the data. In order to quantify the relative importance of each identified source in the fine fraction, the APCA has been used to derive the source apportionment in the fine mode aerosol. Standard procedures for the APCA calculations were applied (Thurston and Spengler, 1985). Table 3 shows the absolute elemental source profile for $PM_{2.5}$. Elements like S, Cl, and K and $PM_{2.5}$ were 2–10 times higher in the biomass burning source profile. The source

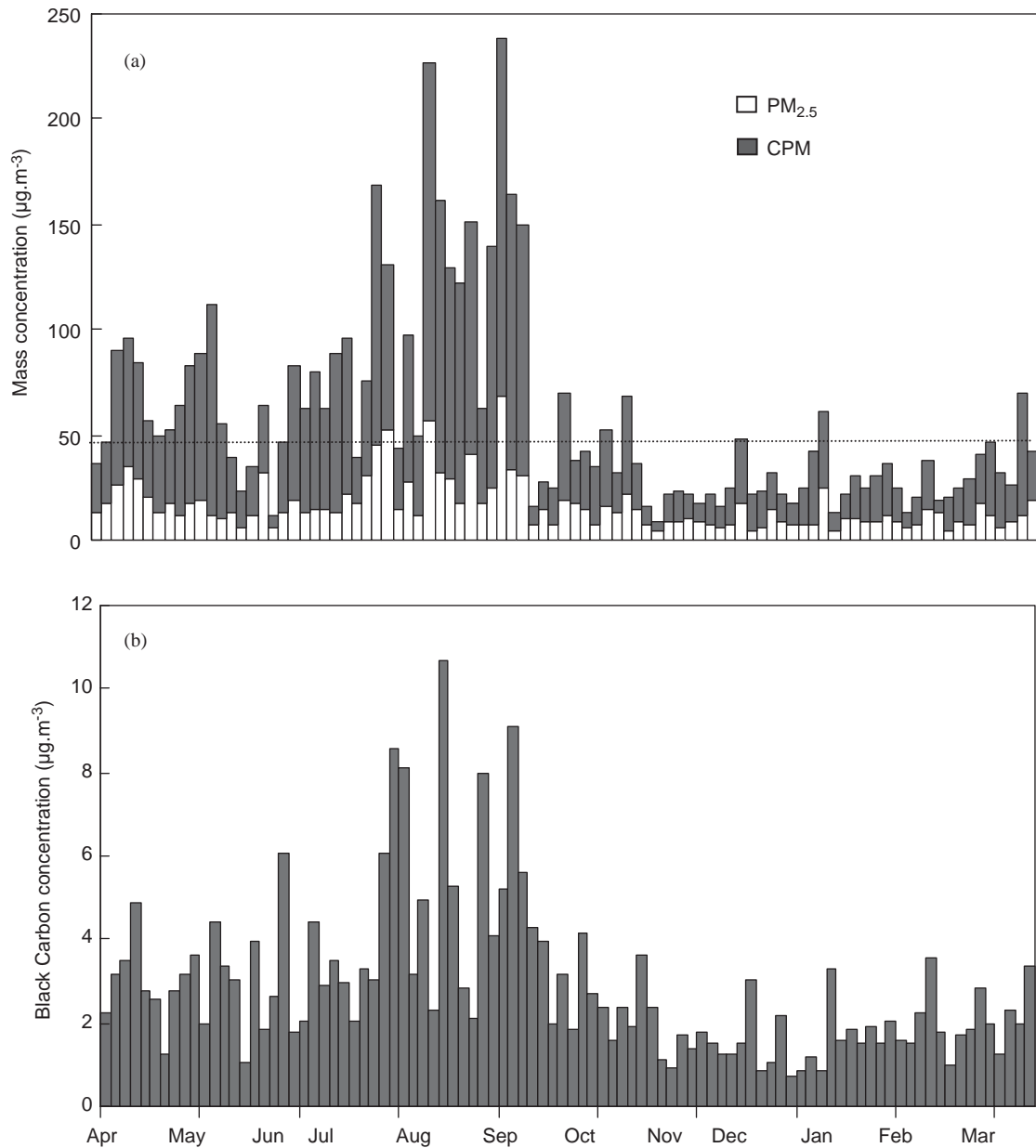


Fig. 3. Temporal variability of (a) fine and coarse mode mass concentrations. The sum of the two fractions results in the PM_{10} concentrations (inhalable particles), and (b) black carbon mass concentration. Aerosol sampling was performed from April 1997 through March 1998.

apportionment of $\text{PM}_{2.5}$ obtained using APCA is shown in Fig. 5a. Sugar-cane burning is the major source of $\text{PM}_{2.5}$, contributing with 60% of the fine mode aerosol mass. The second major source is resuspended soil dust representing 14% of the $\text{PM}_{2.5}$. Heavy metals and oil combustion contribute each one with 12% of the total fine particulate. The model could apportion 98% of the fine mode mass concentration.

For the coarse mode, the PCA factor loading matrix after Varimax rotation showed three components (Table 4). Communalities were always higher than 93% and three factors explained 96% of the variance of the coarse mode data. The first factor is clearly associated with soil dust, since it is loaded with CPM, Al, Si, Ti, Ca, and Fe and could explain 62.1% of the variance of the data. The second factor explained 20.8% of the

Table 1

Concentration averages and standard deviation of the elements (expressed in ng m^{-3}), BC, $\text{PM}_{2.5}$ and CPM (expressed in $\mu\text{g m}^{-3}$), during the dry and wet season and annual period, correspondent to the sampling period from April 1997 through March 1998

	Fine particulate mode, $\text{PM}_{2.5}$, ($d_p < 2.5 \mu\text{m}$)						Coarse particulate mode, CPM, ($2.5 < d_p < 10 \mu\text{m}$)						
	Dry season		Wet season		Annual		Dry season		Wet season		Annual		
	Mean	σ	Mean	σ	Mean	σ	Mean	σ	Mean	σ	Mean	σ	
$\text{PM}_{2.5}^a$	22.7	14.5	11.6	5.9	16.1	11.6	CPM ^a	68.1	43.2	22.6	14.4	41.1	37.1
BC ^a	4.2	2.2	2.1	0.9	2.9	1.9	—						
Al	342.7	315.6	166.1	145.3	237.9	244.7	Al	3097	2354	880.2	801.2	1782	1948
Si	556.2	447.1	306.1	197.7	407.8	343.8	Si	5486	3806	1522	1314	3134	3263
P	5.9	3.1	5.1	3.9	5.4	4.8	P	73.7	38.8	52.5	26.8	61.1	33.7
S	1898	1271	1087	689	1417	1042	S	1046	737.9	364.3	263.1	641.4	610.0
Cl	18.1	20.3	5.6	5.9	12.0	9.23	Cl	140.4	118.7	33.7	58.1	84.8	106.1
K	601.7	389.0	196.6	145.7	361.4	336.3	K	806.6	508.5	228.7	134.7	463.6	442.2
Ca	109.6	107.5	51.5	37.3	75.1	71.1	Ca	1241	799.1	309.7	283.1	688.7	717.3
Ti	44.8	37.8	23.9	19.3	32.4	29.9	Ti	485.0	370.6	136.3	146.8	278.1	311.9
V	86.6	84.2	33.1	30.8	54.8	64.0	V	99.9	97.2	18.2	22.3	57.9	80.4
Cr	3.8	4.3	2.3	2.2	2.9	3.3	Cr	3.5	2.7	—	—	3.5	2.7
Mn	15.4	12.0	10.1	6.2	12.3	9.3	Mn	61.0	37.4	19.0	17.8	36.1	34.3
Fe	447.6	314.1	260.6	150.5	336.7	247.7	Fe	3646	2733	1119	1071	2147	2285
Ni	17.1	15.4	7.3	6.1	11.3	9.4	Ni	20.3	10.1	4.3	4.8	12.1	9.4
Cu	5.6	4.7	3.6	1.9	4.4	3.5	Cu	8.9	7.1	2.4	2.1	5.2	3.6
Zn	105.8	172.8	76.7	59.6	88.5	119.3	Zn	77.0	58.7	45.1	36.2	58.1	53.8
Br	7.4	5.0	3.1	1.9	4.9	4.1	Br	3.5	2.3	2.8	1.8	3.1	2.2
Pb	23.9	27.7	18.1	10.7	20.5	19.6	Pb	15.1	10.9	9.9	7.9	12.0	9.9

^aExpressed in $\mu\text{g m}^{-3}$, σ = standard deviation.

variance. It represents heavy metals emissions with high factor loadings for Pb and Zn. The third factor (13.6% of the variance) is loaded with K and S and it is related to biomass burning emissions. Fig. 5b shows the source profile apportionment of CPM. The contribution of resuspended soil dust to CPM represents 51%, biomass burning 25%, and industrial emissions 20%. The APCA model could explain 96% of the coarse mode mass.

4. Discussion

The PM_{10} concentration during the dry season in the Piracicaba region is similar to the values observed in Rondônia, Amazon Basin, where extensive deforestation and associated fires have occurred in the last years (Artaxo et al., 2000, 2002) and higher than that observed in São Paulo metropolitan area (Castanho and Artaxo, 2001). However, during the wet season the PM_{10} values are higher than Rondônia and similar to those found in São Paulo metropolitan area. The annual average PM_{10} (Table 1) around Piracicaba is slightly higher than the Brazilian air pollution standard limit for PM_{10} of $50 \mu\text{g m}^{-3}$. Coarse particulate mode dominates the PM_{10} concentration which is possibly associated with biomass burning and the large area of bare soils around

Piracicaba. The biomass burning during the harvest period emits coarse particulate originated from the burning itself to the atmosphere and allows the soil dust resuspension. The soil cultivation for sugar-cane or other crops causes a strong soil resuspension during all year due to the large area of bare soils exposed (Cerri et al., 2001). This increases the magnitude of the coarse mode aerosols compared to the fine mode.

In large urban areas, such as São Paulo and Santiago, Chile, the main sources of aerosol particles are emissions linked to fossil fuel combustion (Artaxo et al., 1999; Castanho and Artaxo, 2001), while in the area around Piracicaba biomass burning is the strongest source. It is not surprising that agricultural related factors can influence the composition of aerosols in the State of São Paulo so much. Ten percent of the total area of this State is used for sugar-cane plantations and biomass burning is one of the major contributors to the aerosol in South America. There are several evidences showing that sugar-cane burning has a large impact on the atmospheric composition of the region of Piracicaba. Lara et al. (2001) have reported acid rain in four different sites at the Piracicaba River Basin. Although there is an industrial area in this region, the main source of acid rain is associated with sugar-cane burning (Lara et al., 2001).

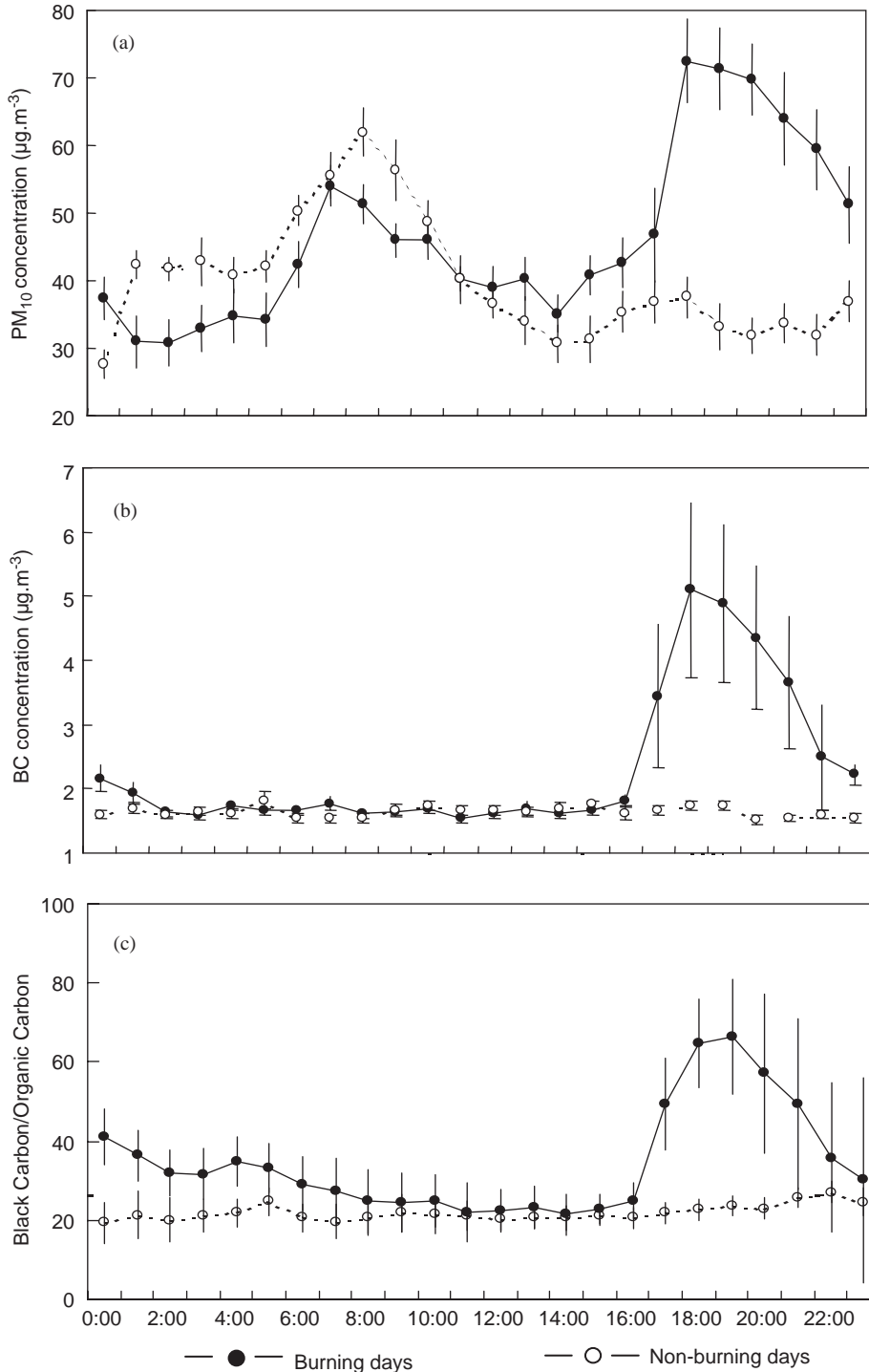


Fig. 4. Diurnal cycle during the burning and non-burning days for (a) mass concentration of PM₁₀, (b) mass concentration of BC, and (c) black carbon/organic carbon ratio.

Factor analysis has showed the large influence of sugar-cane burning emissions in the composition of fine particulate mode. Four factors explain most of the

composition of fine mode aerosol. The most important source is sugar-cane burning, which represents 60% of the total fine mode mass. Additional statistical analysis

Table 2

Varimax rotated factor loadings for the PM_{2.5}, BC and elemental concentrations of the fine particulate mode sampled from April 1997 through March 1998 at the city of Piracicaba

Elemental	Factor 1	Factor 2	Factor 3	Factor 4	Communalities
	Biomass burning	Soil	Heavy metals	Oil combustion	
PM _{2.5}	0.79	0.44	0.20	0.33	0.96
BC	0.88	0.29	0.20	0.27	0.96
Al	0.47	0.83	—	0.20	0.96
Si	0.50	0.82	0.20	—	0.96
S	0.64	0.36	0.20	0.58	0.88
K	0.79	0.45	—	0.20	0.89
Ca	0.44	0.60	—	0.48	0.82
Ti	0.43	0.84	—	0.30	0.98
V	0.21	0.23	0.20	0.92	0.98
Mn	0.20	0.37	0.76	0.27	0.82
Fe	0.33	0.67	0.56	0.27	0.94
Ni	0.23	0.22	0.24	0.92	0.99
Cu	0.35	—	0.86	—	0.88
Zn	—	—	0.94	—	0.90
Br	0.86	0.40	0.20	—	0.95
Pb	—	—	0.91	0.20	0.89
var. (%)	27.6	24.5	22.3	17.6	

Only factor loadings larger than 0.2 are shown.

Table 3

Absolute aerosol source apportionment for the PM_{2.5}, BC (expressed in $\mu\text{g m}^{-3}$) and elemental concentrations (expressed in ng m^{-3}) of the PM_{2.5}

Elemental	Factor 1	Factor 2	Factor 3	Factor 4	Concentration model/measured
	Biomass burning	Soil	Heavy metals	Oil combustion	
PM _{2.5}	9.8	2.2	1.9	1.9	0.98
BC	1.9	0.3	0.4	0.3	0.96
Al	117	84.9	—	22.6	0.94
Si	195	120	40.4	—	0.87
P	1.4	1.4	1.7	0.3	0.88
S	761.4	167.5	115.1	312.6	0.96
Cl	6.8	2.2	—	3.4	1.03
K	260.4	60.2	—	28.8	0.97
Ca	36.3	19.8	—	18.7	0.99
Ti	14.1	10.6	—	4.6	0.90
V	12.1	5.9	9.7	28.6	1.03
Cr	0.8	0.3	1.1	0.3	0.85
Mn	2.3	1.5	6.8	1.3	0.97
Fe	92.0	70.5	133	34.3	0.98
Ni	2.6	1.1	2.5	5.3	1.01
Cu	1.3	—	2.8	—	0.93
Zn	—	—	97.5	—	1.10
Br	3.5	0.7	0.6	—	0.99
Pb	—	—	17.6	2.1	0.96

with elements that were not included in the factor model emphasizes this point. The Spearman correlation ($P < 0.01$) of the factor scores 1 identified in the fine

mode (sugar-cane burning) with Cl ($r = 0.72$), Mg ($r = 0.59$), and P ($r = 0.54$) are statistically significant ($P < 0.01$), supporting the identification of this source by

the factor model. These elements were identified in biomass burning emission studies (Levine et al., 1995; Echalar et al., 1995; Yamasoe et al., 2000). In terms of soil dust mass apportionment in the fine mode, the high value obtained in this study (14%) can be explained by the fact that the sugar-cane burning process generates significant convection and raises soil dust by the convective plume, mixing up biomass burning aerosols with fine soil dust. Besides, the resuspended soil is also associated with bare soils around Piracicaba region. Additionally, emissions from sugar-cane burning are

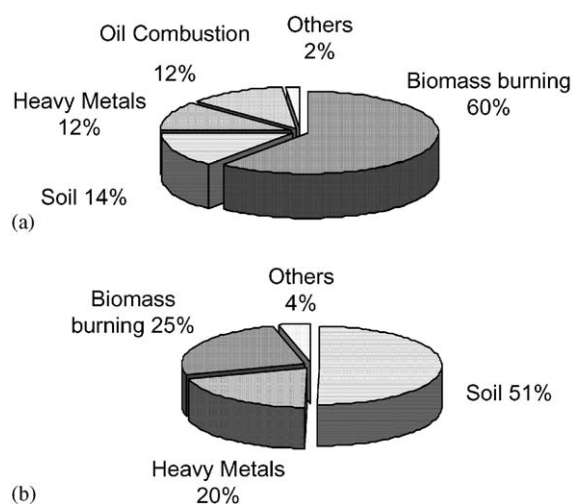


Fig. 5. Source apportionment of (a) fine mode particulate, and (b) coarse mode particulate. The quantification of the contribution of the sources has been done using absolute principal component analysis (APCA) for each factor identified in the principal component analysis.

responsible for 64% of the fine mode BC concentration in Piracicaba, a comparable value (55%) found for Piracicaba region using isotopic techniques in aerosol (Martinelli et al., 2002). A similar value was obtained in other biomass burning studies (Ferek et al., 1998; Yamasoe et al., 2000; Chankina et al., 2001). The ratio of BC to $PM_{2.5}$ is about 19% higher than the values observed in forest fires ranging from 13% to 18% (Echalar et al., 1995; Yamasoe et al., 2000). This is because the fires in the sugar-cane plantations occur mainly in the flaming phase, responsible for higher ratio of BC emissions, in a contrary way of the forest fires which occur mainly in smoldering phase (Yamasoe et al., 2000).

As expected, resuspended soil is the main source of CPM. It represents 51% of the total coarse mode mass. The identification of the third factor as sugar-cane burning is due to the strong presence of S and K in this factor (Yamasoe et al., 2000). In addition, the significant correlation of the factor 1 (biomass burning) identified in the fine particulate mode with this factor 3 in the coarse mode is also an evidence of the biomass burning origin in this third coarse mode factor (Table 5).

The significant correlations between soil dust in the coarse mode and sugar-cane burning in the fine mode (Table 5) emphasizes the relation between the sugar-cane burning emissions with soil dust resuspension. The significant correlation between the fine and coarse soil dust factors indicates the adequacy of the identification of the sources, as well as it occurs to fine and coarse heavy metals emission factors.

The averages of PM_{10} concentration over 1 h obtained from TEOM equipment are significantly higher during the period when the sugar-cane is burnt. The biomass burning usually starts around 5:00–6:00 p.m. The

Table 4
Varimax rotated factor loadings for the CPM and elemental concentrations of the coarse particulate mode sampled from April 1997 through March 1998 at the city of Piracicaba

Elemental	Factor 1	Factor 2	Factor 3	Communalities
	Soil	Heavy Metals	Biomass burning	
CPM	0.89	0.24	0.38	0.99
Al	0.94	—	0.25	0.99
Si	0.91	0.23	0.34	0.98
S	0.66	—	0.71	0.99
K	0.76	0.22	0.57	0.99
Ca	0.83	0.29	0.41	0.97
Ti	0.94	0.22	0.22	0.94
Mn	0.84	0.43	0.26	0.96
Fe	0.94	0.26	—	0.94
Zn	0.36	0.89	—	0.93
Pb	—	0.95	—	0.96
Var (%)	62.1	20.8	13.6	

Only factor loadings larger than 0.2 are shown.

Table 5
Spearman's correlation of factor scores identified by PCA between fine and coarse mode particulate^a

Coarse particulate mode factors	Fine particulate mode factors			
	Biomass burning	Soil dust	Heavy metals	Oil combustion
Soil dust	0.54	0.37	—	—
Heavy metals	—	—	0.38	—
Biomass burning	0.39	—	—	—

^aOnly statistically significant ($P < 0.01$) correlations are shown.

morning peak in PM_{10} concentrations at 7:00–10:00 a.m. in the days with and without biomass burning (Fig. 4a) is characteristic of the forming and growing of the diurnal boundary layer, when wind speeds start resuspended soils nearby the sampling site. It is interesting to note the significant difference between the burning and non-burning periods around 6:00 and 10:00 p.m. This is the time when sugar-cane is burned, emitting inhalable particles and increasing significantly the PM_{10} concentrations to the atmosphere. The same trend was observed for BC concentrations (Fig. 4b), suggesting that the sugar-cane burning is the main responsible for the increasing of the BC concentrations along the diurnal cycles, as well as for the PM_{10} concentration. These changes in the aerosol properties such as concentration values and chemical composition is even more important if we call attention to the fact that the large population who has faced these biomass burning episodes during the last four decades. Aerosols, particularly those less than $2.5\mu m$ in diameter ($PM_{2.5}$), appear to have the greatest potential for damaging health because they can penetrate deep into the lungs and reach the lower respiratory system (Hamilton and Mansfield, 1991; EPA, 1996).

5. Conclusions

High levels of pollutants have been measured during the sugar-cane burning season in the city of Piracicaba. A complex system of air pollution sources modulates the concentration of pollutants in the air around Piracicaba. As there is intense biomass burning in other regions in Brazil possible influences of medium and long-range transport of upwind fires emissions also could contribute to the air pollution in this area. During the entire year, the influence of the sugar-cane burning can be seen in the composition of fine and coarse particulate modes and in the variations of BC concentration. With this study it was possible to identify the influence of sugar-

cane burning in the composition of aerosol in an urban center, and until now this was completely unknown. The results of APCA have showed that there is a large contribution of sugar-cane fires to the structure of the aerosol, 60% of the fine mode mass, 64% of the BC mass and 25% of the coarse mode mass can be attributed to emissions from sugar-cane burning. The aerosols and BC released from biomass burning can act as CCN. It affects cloud albedo by altering the hygroscopic properties of CCN and the solar heating caused by BC can supposedly reduce cloudiness. Through this process, the cloud microphysical and radiative process in tropical rain and cloud systems can hypothetically be affected with potential climatic and hydrological consequences.

Sugar-cane burning altering the structure of air composition has already taken place over the city of Piracicaba. What happens around the city of Piracicaba could also be experimented by other regions in Southeast Brazil. In the state of São Paulo the main land use is pasture and sugar-cane crops. They cover an area around 50 and 10%, respectively, of the total area of the state. In both cases biomass burning is a common feature. Although these aerosols from biomass burning have an atmospheric residence time of a few days to several weeks, they can be widespread over long distances (hundred to thousands of kilometers). They also could be interfering in the quality of the air, regional climate changes, and in hydrological cycles.

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References

- Artaxo, P., Oyola, P., Martinez, R., 1999. Aerosol composition and source apportionment in Santiago de Chile. *Nuclear Instruments and Methods in Physics Research B* 150, 409–416.
- Artaxo, P., Martins, J.W., Yamasoe, M.A., Procópio, A.S., Pauliquevis, T.M., Andrea, M.O., Guyon, P., Gatti, L.V., Leal, A.M.C., 2002. Physical and chemical properties of aerosols in the wet and dry seasons in Rondônia, Amazonia. *Journal of Geophysical Research* 107 (D20), 8081.
- Azevedo, D.A., Santos, C.Y.M., Aquino Neto, F.R., 2002. Identification and seasonal variation of atmospheric organic

- pollutants in Campos dos Goytacazes, Brazil. *Atmospheric Environment* 36, 2383–2395.
- Castanho, A.D., Artaxo, P., 2001. Wintertime and summertime São Paulo aerosol source apportionment study. *Atmospheric Environment* 35, 4889–4902.
- Cerri, C.E.P., Ballester, M.V.R., Martinelli, L.A., 2001. GIS Erosion Risk Assessment of the Piracicaba River Basin, Southeastern Brazil. *Mapping Sciences & Remote Sensing* 38, 157–171.
- Chankina, O.V., Churkina, T.V., Ivanov, A.V., Ivanov, V.A., Ivanova, G.A., Koutsenogii, K.P., Kovalskaya, G.A., 2001. Multielemental composition of the aerosols of the forest fires of boreal forests upon burning of forest combustibles. *Nuclear Instruments and Methods in Physics Research A* 470, 447–447.
- Chow, J.C., Watson, J.G., Lu, Z., 1996. Descriptive analysis of PM_{2.5} and PM₁₀ at regionally representative locations during SJVAQS/AUSPEX. *Atmospheric Environment* 30 (12), 2079–2112.
- Crutzen, P.J., Andreae, M.O., 1990. Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. *Science* 250, 1669–1678.
- Echalar, F., Gaudichet, A., Cachier, H., Artaxo, P., 1995. Aerosols emissions by tropical forest and savanna biomass burning: characteristics trace elements and fluxes. *Geophysical Research Letters* 22, 3039–3042.
- EPA (Environmental Protection Agency), 1996. National Air Quality and Emissions Trends Reports, 1995. Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- Ferek, R.J., Reid, J.S., Hobbs, P.V., 1998. Emissions factors of hydrocarbons, halocarbons, trace gases and particles from biomass burning in Brazil. *Journal of Geophysical Research Letters* 103 (D24), 32107–32118.
- Hamilton, R.S., Mansfield, T.A., 1991. Airborne particulate elemental carbon: its sources, transport and contribution to dark smoke and soiling. *Atmospheric Environment* 225, 715–723.
- Hopke, P.K., 1991. Receptor Modeling for Air Quality Management. Elsevier, Amsterdam.
- Hopke, P.K., Xie, Y., Raunema, T., Biegalski, S., Landsberger, S., Maenhaut, W., Artaxo, P., Cohen, D., 1997. Characterization of the gent stacked filter unit PM₁₀ sampler. *Aerosol Science and Technology* 27, 726–735.
- Krushe, A.V., Camargo, P.B., Cerri, C.E., Ballester, M.V., Lara, L.B.L.S., Victoria, R., Martinelli, L.A., 2003. Acid rain and nitrogen deposition in a sub-tropical watershed (Piracicaba): Ecosystem consequences. *Environmental Pollution* 121 (3), 389–399.
- Lara, L.B.L.S., Artaxo, P., Martinelli, L.A., Victoria, R.L., Camargo, P.B., Krusche, A., Ayers, G.P., Ferraz, E.S.B., Ballester, M.V., 2001. Chemical composition of rainwater and anthropogenic influences in the Piracicaba river basin, Southeast Brazil. *Atmospheric Environment* 35, 4937–4945.
- Levine, J.S., Cofer, W.R., Cahoon, D.R., Winstead, E.L., 1995. Biomass burning: a driver for global change. *Environmental Science and Technology* 29, 120–125.
- Martinelli, L.A., Camargo, P.B., Lara, L.B.L.S., Victoria, R.L., Artaxo, P., 2002. Stable carbon and nitrogen isotope composition of bulk aerosol particles in a C4 plant landscape of Southeast Brazil. *Atmospheric Environment* 36, 2427–2432.
- Oglesby, R.J., Marshall, S., Taylor, J.A., 1999. The climate effects of biomass burning: investigations with a global climate model. *Environmental Modelling and Software* 14, 253–259.
- Ramanathan, V., Crutzen, P.J., Kiel, J.T., Rosenfeld, D., 2001. Aerosols, climate, and the hydrological cycle. *Science* 294, 2119–2124.
- Reid, J.S., Hobbs, P.V., Lioussé, C., Martins, J.V., Weiss, R.E., Eck, T.F., 1998. Comparisons of techniques for measuring shortwave absorption and black carbon content of aerosols from biomass burning in Brazil. *Journal of Geophysical Research-Atmospheres* 103 (D24), 32031–32040.
- Roberts, G.C., Andrea, M.O., Zhou, J., Artaxo, P., 2001. Cloud Condensation nuclei in the Amazon Basin: “Marine” conditions over a continent? *Geophysical Research Letters* 0, 1–4.
- Rosenfeld, D., 1999. TRMM observed first direct evidence of smoke from forest fires inhibiting rainfall. *Geophysical Research Letters* 26, 3105–3108.
- Streets, D.G., Gupta, S., Waldhoff, S.T., Wang, M.Q., Bond, T.C., Yiyun, B., 2001. Black carbon emissions in China. *Atmospheric Environment* 35, 4281–4296.
- Swietlicki, E., Puri, S., Hanson, H.C., 1996. Urban air pollution source apportionment using a combination of aerosol and gas monitoring techniques. *Atmospheric Environment* 30, 2795–2809.
- Thurston, G.D., Spengler, J.D., 1985. A quantitative assessment of source contribution to inhalable particulate matter pollution in metropolitan Boston. *Atmospheric Environment* 19, 9–25.
- Yamasoe, M.A., Artaxo, P., Miguel, A.H., Allen, A.G., 2000. Chemical composition of aerosols particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements. *Atmospheric Environment* 34, 1641–1653.
- Zamperlini, G.C.M., Santiago-Silva, M., Vilegas, W., 2000. Solid-phase extraction of sugar cane soot extract for analysis by gas chromatography with flame ionization and mass spectrometric detection. *Journal of Chromatography A* 889 (1–2), 281–286.