Two-year study of atmospheric aerosols in Alta Floresta, Brazil: Multielemental composition and source apportionment

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Abstract

Atmospheric aerosol samples were collected nearly continuously from August 1996 until September 1998 at Alta Floresta in a primary forest region of the Amazon basin, Brazil. The sampling device consisted of a stacked filter unit (SFU), which separates the aerosol into a coarse (2–10 μm equivalent aerodynamic diameter (EAD)) and a fine (<2 μm EAD) size fraction. The coarse and fine filters of all SFU samples (205 in total) were analysed for the particulate mass (PM), black carbon (BC), and up to 47 elements (from Na upward). The multielemental analyses were done by a combination of PIXE and instrumental neutron activation analysis. Absolute principal component analysis was used for source (source type) identification and apportionment. Five components were identified in the fine size fraction, i.e. mineral dust, a biomass burning (pyrogenic) component (with PM, BC, S, K, Zn, Br, Rb and I, having loadings in the range 0.7–0.9), a Na/Ca component, a biogenic component (with P), and an almost pure Pb component. On average 67% of the fine PM was attributed to the pyrogenic component, 14% to the mineral dust, 7% each to the biogenic and Na/Ca components, and 4% to the Pb component. The relative contribution from the pyrogenic aerosol varied substantially with season, however. It was generally between 60% and 100% during the dry season. During the wet season, on the other hand, it often became insignificant. During that season, most of the fine aerosol was attributed to the biogenic component. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Amazon basin contains the largest extent of tropical forest on Earth, over 5 million km². However, over the past 25 years rapid development has led to the deforestation of over 500,000 km² in Brazil alone [1]. This led to changes in the atmospheric composition caused by deforestation

and biomass burning, and these changes have local, regional and even global effects on air chemistry and climate. Because of the importance of the problem, several intensive field campaigns have been undertaken in the past two decades, and these have been extended with long-term measurements since the early 1990s. Since a few years, intensive research is being carried out within the framework of the Large Scale Biosphere-Atmosphere Experiment in Amazonia (LBA) [1]. With regard to long-term measurements on the atmospheric aerosol concentration and its composition, Artaxo et al. [2] and Echalar et al. [3] presented and discussed data sets for up to three sites, where the elemental concentrations were obtained by PIXE. Two of the sites were Cuiabá (16°S, 56°W), south of the Amazon rain forest in a cerrado (Savanna) region, and Alta Floresta (9°52′S, 56°05′W), in a primary forest region which is heavily stressed by land clearings and gold mining. At both sites, long-term collections were also performed for subsequent multielemental analysis by a combination of PIXE and instrumental neutron activation analysis (INAA). The addition of INAA allowed us to obtain more accurate data for the light elements (Na, Al), and also provided data for various additional interesting elements, including the metals and metalloids As, Se, In, Sb and the halogen I. The results from this work at Cuiabá were described earlier [4,5]. Here, we present and briefly discuss the results from similar work at the Alta Floresta site.

2. Experimental

Atmospheric aerosol samples for combined PIXE and INAA were collected nearly continuously at Alta Floresta from 22 August 1996 until 10 September 1998, with an interruption from 25 October 1996 to 6 February 1997. The sampling device consisted of a stacked filter unit (SFU), which separates the aerosol into a coarse (2–10 μm equivalent aerodynamic diameter (EAD)) and a fine (<2 μm EAD) size fraction. The filter materials used were 8 μm pore size (Apiezon-coated) and 0.4 μm pore size Nuclepore polycarbonate filters for the coarse and fine size fractions, re-

spectively. The collection time per sample varied from 12 h to one week, but was typically around one day. The coarse and fine filters of all SFU samples (205 in total) and a number of field blanks were analysed for the particulate mass (PM), black carbon (BC), and up to 47 elements (from Na upward). PM was obtained by weighing each filter before and after sampling with a microbalance at 20 °C and 50% relative humidity. BC was determined with a light reflectance technique, using a similar approach as employed by Andreae [6] and Andreae et al. [7]. The multielemental analyses by INAA and PIXE were done as described in [4,8] and the references cited therein. Absolute principal component analysis (APCA) with VARI-MAX rotation [9] was used to identify the major aerosol components (source types) in each of the two size fractions and to apportion the PM and the various aerosol constituents to these components.

3. Results and discussion

3.1. Average concentrations and fine-to-coarse concentration ratios

PM, BC and virtually all elements exhibited much higher atmospheric concentrations during the dry (biomass burning) season (June–October) than during the rest of the year (wet season). During the dry season, the levels of fine and coarse PM were in the range of 20–200 and 15–80 μg/m³, respectively. The time trends for PM10 (sum of fine and coarse) and fine PM are shown in Fig. 1. Average concentrations were calculated for the separate dry and wet seasons in each of the two size fractions, and are presented in Table 1 for the PM, BC and 38 elements. In the study by Echalar et al. [3], whereby PIXE was used for the elemental analysis, similar averages are presented for the PM, BC and 26 elements at Alta Floresta, and this for the period from August 1992 to March 1995. Overall, our averages for the 1996–1998 period are comparable to those obtained in that earlier study. For example, Echalar et al. [3] obtained average fine PM levels of 47 ± 41 and 5.5 ± 3.5 μg/m³ for
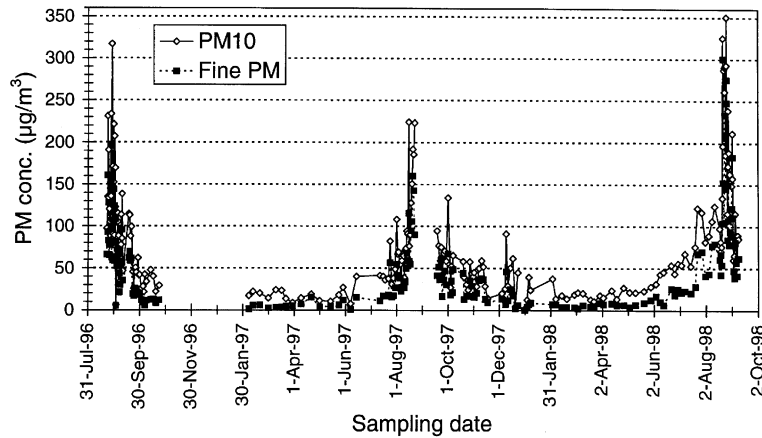
Fig. 1. Time trends of the PM10 (sum of fine and coarse) and fine PM concentrations at Alta Floresta.

the dry and wet seasons, respectively, whereas our values are 63 ± 55 and 9.9 ± 9.9 μg/m³; the average coarse PM levels in the earlier study were 34 ± 21 and 16.4 ± 9.4 μg/m³ for the dry and wet seasons, respectively, and our corresponding values are 37 ± 25 and 15.1 ± 9.9 μg/m³.

PM, BC, S, K, Zn, As, Br, Sb and I were mostly associated with the fine size fraction. This is seen in Fig. 2, which shows the median fine to coarse concentration ratios for our entire data set. The crustal elements Al, Si, Ca, Sc, Ti and Fe, the elements V and Mn (which are essentially also crustal elements, as appeared from their crustal enrichment factors), and the biogenic element P all have median fine/coarse ratios of 0.2–0.3 only.

3.2. Receptor modelling by absolute principal component analysis

The data set for the fine size fraction was subjected to APCA receptor modelling. Twenty-two variables (i.e. PM, BC, Na, Al, Si, P, S, K, Ca, Sc, Ti, V, Mn, Fe, Zn, Br, Rb, Sb, I, La, Sm and Pb) were included in this analysis. Five components were identified, i.e. mineral dust (with loadings of about 0.9 for the crustal elements Al, Si, Sc, Ti, Fe, La, Sm, and also for V and Mn), a biomass burning (pyrogenic) component (with PM, BC, S, K, Zn, Br, Rb and I having loadings in the range 0.7–0.9), a Na/Ca component, a biogenic component (with P), and an almost pure Pb component.
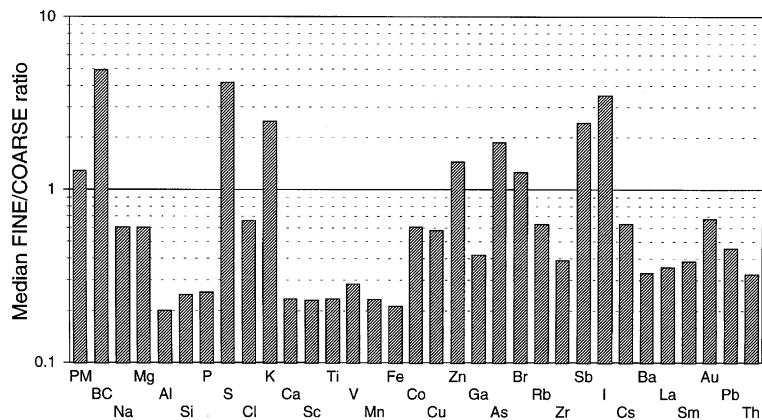

Fig. 2. Median fine-to-coarse concentration ratios at Alta Floresta.

Table 1
Average concentrations and associated standard deviations for the PM, BC and 38 elements in the fine and coarse size fractions for the dry and wet seasons (PM and BC are in μg/m^3, the elements in ng/m^3)

	Fine size fraction				Coarse size fraction			
	Dry season		Wet season		Dry season		Wet season	
	Mean ± SD	N[a]	Mean ± SD	N[a]	Mean ± SD	N[a]	Mean ± SD	N[a]
PM	63 ± 55	152	9.9 ± 9.9	51	37 ± 25	152	15.1 ± 9.9	51
BC	7.7 ± 6.3	152	1.55 ± 1.56	52	1.46 ± 1.28	152	0.38 ± 0.27	52
Na	96 ± 69	152	51 ± 62	52	153 ± 105	149	82 ± 104	51
Mg	198 ± 141	23	36 ± 32	13	250 ± 120	20	69 ± 50	20
Al	640 ± 700	149	96 ± 80	52	3100 ± 2500	151	450 ± 460	52
Si	540 ± 540	144	146 ± 136	51	2200 ± 1800	151	390 ± 360	52
P	24 ± 17	84	13.9 ± 14.5	47	80 ± 65	102	87 ± 74	48
S	890 ± 500	151	270 ± 280	50	169 ± 146	94	86 ± 52	43
Cl	112 ± 95	81	37 ± 81	9	108 ± 72	149	65 ± 47	51
K	1280 ± 960	152	220 ± 240	52	410 ± 330	151	240 ± 160	52
Ca	53 ± 60	114	24 ± 33	45	210 ± 160	150	53 ± 35	52
Sc	0.066 ± 0.063	140	0.0114 ± 0.0084	48	0.28 ± 0.21	150	0.044 ± 0.043	52
Ti	28 ± 27	133	4.8 ± 3.7	49	114 ± 91	149	17.6 ± 18.3	52
V	0.76 ± 0.62	145	0.160 ± 0.111	51	2.8 ± 2.0	147	0.47 ± 0.43	51
Cr	15.4 ± 17.3	11	1.5	1	18.1 ± 19.0	4		
Mn	2.7 ± 1.8	146	0.70 ± 0.44	51	13.5 ± 11.1	150	2.4 ± 1.6	52
Fe	270 ± 270	149	46 ± 38	52	1220 ± 930	152	200 ± 190	52
Co	0.101 ± 0.077	80	0.025 ± 0.021	30	0.160 ± 0.104	100	0.041 ± 0.028	30
Cu	1.33 ± 1.11	56	0.40 ± 0.38	19	2.1 ± 1.3	91	0.59 ± 0.21	30
Zn	8.6 ± 6.0	144	2.3 ± 2.2	50	5.3 ± 3.5	126	2.2 ± 1.3	47
Ga	0.49 ± 0.32	35	0.099 ± 0.014	3	0.89 ± 0.57	96	0.22 ± 0.13	16
As	0.7 ± 2.1	75	0.081 ± 0.071	20	0.34 ± 0.60	55	0.075 ± 0.040	9
Se	0.33 ± 0.17	28	0.194 ± 0.096	9	0.58 ± 0.46	4	0.138 ± 0.065	4
Br	17.7 ± 16.2	145	4.0 ± 4.8	44	11.2 ± 13.2	79	2.4 ± 1.5	32
Rb	8.1 ± 8.9	86	1.34 ± 0.73	16	4.8 ± 3.3	24	2.5 ± 3.2	16
Sr	2.3	1	0.31 ± 0.02	2	4.0 ± 3.1	59	0.83 ± 0.38	25
Zr	2.3 ± 1.3	17	0.44 ± 0.10	3	6.0 ± 4.4	71	1.66 ± 0.81	15
In	0.0161 ± 0.0111	14	0.0051 ± 0.0030	3	0.0139 ± 0.0069	15	0.0089 ± 0.0137	18
Sb	0.28 ± 0.26	117	0.16 ± 0.23	51	0.16 ± 0.27	55	0.041 ± 0.045	29
I	3.0 ± 1.7	147	0.71 ± 0.63	48	1.1 ± 2.9	101	0.21 ± 0.11	37
Cs	0.077 ± 0.070	20	0.029 ± 0.033	8	0.117 ± 0.084	58	0.021 ± 0.006	13
Ba	15.1 ± 4.6	3	2.5	1	13.9 ± 10.4	30	4.9 ± 1.7	7
La	0.30 ± 0.24	83	0.060 ± 0.045	32	0.72 ± 0.50	140	0.130 ± 0.107	45
Ce	1.14 ± 0.78	8	0.25	1	3.1 ± 1.6	34	0.83 ± 0.28	6
Sm	0.030 ± 0.022	74	0.0065 ± 0.0041	27	0.066 ± 0.045	138	0.0130 ± 0.0107	42
Eu	0.029 ± 0.020	32	0.0080 ± 0.0039	2	0.073 ± 0.107	49	0.0112 ± 0.0046	16

		N		N		N		N
W	0.34 ± 0.19	4	0.073	1	0.23 ± 0.21	24	0.077 ± 0.069	12
Au	0.018 ± 0.050	41	0.00189 ± 0.00080	8	0.5 ± 1.8	13	0.0033 ± 0.0053	6
Pb	4.1 ± 7.9	61	0.78 ± 0.49	32	5.5 ± 6.1	8	2.1 ± 2.4	17
Th	0.178 ± 0.120	62	0.031 ± 0.015	15	0.46 ± 0.27	131	0.088 ± 0.068	35

[a] N is the number of samples in which the element was observed above its detection limit.

The average fine PM concentration was slightly overpredicted (i.e. by about 10%) by our 5-component APCA. Of the average predicted fine PM, 67% was attributed to the pyrogenic component, 14% to the mineral dust, 7% each to the biogenic and Na/Ca components, and 4% to the Pb component. The relative contribution from the pyrogenic aerosol varied substantially with season, however. It was generally between 60% and 100% during the dry season, with largest percentages when the fine PM level was most elevated. During the wet season, on the other hand, it often became insignificant. The percentage apportionments of the average predicted fine PM concentrations of the two separate seasons (dry and wet) to each of the five components are presented in Table 2.

Our 5-component APCA solution can be compared to the APCA solutions that were obtained by Echalar et al. [3] for the same Alta Floresta site. In their APCA, 13 variables (i.e. PM, BC, Al, Si, P, S, K, Ca, Ti, Mn, Fe, Zn and Pb) were included. Echalar et al. [3] did not obtain a Na/Ca component, but they also observed a Pb component, and they attributed it to gold mining activities in the region. During the dry season, 75% of the fine PM was on average apportioned to biomass burning, 14% to soil dust, and 11% was unexplained; in the wet season 65% was attributed to biogenic emissions, 7% to soil dust, and 28% to gold mining. When comparing these data with those in Table 2, we can conclude that there is good agreement for the dry season, but somewhat less for the wet season. For the latter season, we attributed 40% to biogenic aerosol, 16% to biomass burning, 14% to soil dust and 9.4% to the Pb (gold mining) component. It should be indicated here that discriminating between pyrogenic and biogenic emissions

Table 2
Percentage apportionment of the average predicted fine PM concentrations of the two separate seasons (dry and wet) to each of the five components, as derived from APCA

Component	Dry season	Wet season
Soil dust	14	14
Biomass burning	70	16
Na/Ca	6.2	20
Biogenic emissions	5.4	40
Pb	3.9	9.4

is not easy, especially in the wet season. Echalar et al. [3] did not identify a pyrogenic component in that season, so that their 65% for the biogenic emissions should most likely be compared to the sum of our pyrogenic and biogenic components (which add up to 56%). As to the difference for the gold mining attribution, it is quite possible that the impact from the gold mining activities on the Alta Floresta fine aerosol was actually lower in the 1996–1998 period than in the 1992–1995 period. It is noteworthy in this context that Echalar et al. [3] found that the attribution to gold mining was smaller in the 1994–1995 wet season than in the earlier wet seasons.

Acknowledgements

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