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Study Of Elemental Mass Size Distributions In Amazonia During The LBA/CLAIRE/SMOCC-2002 Campaign

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ABSTRACT

During the LBA/CLAIRE/SMOCC experiment in September-November 2002, aerosol samples were collected with a 12-stage small deposit area low pressure impactor (SDI) and a 10-stage MOUDI cascade impactor in the state of Rondônia, Brazil. The MOUDI samples were analysed for the particulate mass (PM) by weighing and the SDI samples were analysed for 28 elements by PIXE. Most of the PM occurred in the submicrometer size fraction during the burning period (11 September to 8 October). The mass median aerodynamic diameter (MMAD) for the PM was somewhat larger during the night than during the day. A night-day difference in MMAD was also seen for elements such as S and K, but not for the crustal elements Al, Si, Ti, Mn, and Fe or for the biogenic element P. During the burning period, PM, S, and K tended to have two major modes in the submicrometer size range and one minor mode in the coarse size range. The two submicrometer modes were centered at around 0.3 and 0.7 μm and correspond to the condensation and droplet modes. The droplet mode was particularly pronounced during the night, most likely because of its more efficient production at the higher relative humidity during the night.

Keywords: atmospheric aerosols, multielement analysis, size distribution, biomass burning, Brazil.

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1. INTRODUCTION

The LBA/CLAIRE/SMOCC experiment in Amazonia, September-November 2002, aimed at investigating the interactions between smoke from biomass burning, cloud microphysics, precipitation, and climate. The campaign spanned from the peak of the burning season, with high smoke concentrations, to fairly clean conditions in the early rainy season. The tropospheric aerosol research team from Ghent University (UGent) participated in the ground-based component of the experiment and utilised various collection devices to obtain aerosol samples for laboratory analysis. Here, selected results from the cascade impactor samplings are presented.

2. EXPERIMENTAL

The UGent samplers were set up at a pasture site (Fazenda Nossa Senhora Aparecida; 10°45'50" S, 62°21'36" W, 284 m above sea level) in the state of Rondônia, Brazil. Two cascade impactors were deployed at the site and operated in parallel from 9 September until 14 November. One impactor was a 10-stage rotating version of the microorifice uniform deposit impactor (MOUDI) [1], which operates at a flow rate of 30 L per min. The calibrated cut-points (d_{50} -values) for the inlet and 10 stages of this device are 18, 9.9, 6.2, 3.1, 1.8, 1.0, 0.603, 0.301, 0.164, 0.094, and 0.053 μm aerodynamic diameter (AD). As collection surfaces in the MOUDI we used 37-mm diameter aluminium foils (4 mg/cm²) for the impaction stages and a Whatman QM-A quartz fibre filter as back-up filter. The foils and filters had been pre-heated at 550°C to remove organic contaminants. The other cascade impactor was a 12-stage small deposit area low pressure impactor (SDI) [2], operating at a flow rate of 11 L per min. The SDI is a multi-jet device with jets clustered closely together, so that the diameter of the aerosol deposition area remains smaller than 8 mm. This is a very advantageous feature when PIXE is used for the analysis. The experimental cut-points (d_{50} -values) for the 12 stages of the SDI are 8.50, 4.08, 2.68, 1.66, 1.06, 0.796,

0.591, 0.343, 0.231, 0.153, 0.086, and 0.045 μm AD. Upstream of the device was an inlet with cut-point of 15 μm AD. Thin Kimfol polycarbonate films (1.5 μm thick) were used as collection surfaces in the SDI. Separate day and night samples were mostly collected with the two cascade impactors, and the collection time per sample varied from 12 hours in September to up to 48 hours in November.

The MOUDI samples were analysed for the particulate mass (PM) by weighing each impaction foil and back-up filter before and after sampling with a microbalance (with 1 μg sensitivity). The weighings were done at 20°C and 50% relative humidity and the foils and filters were pre-equilibrated at these conditions for at least 24 hours before the actual weighings. The SDI collection surfaces were analysed for up to 28 elements (i.e., Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ba, and Pb) by particle-induced X-ray emission spectrometry (PIXE) using a 2.4 MeV proton beam. Details on the PIXE procedures are given in Ref. [2] and in the references cited therein.

3. RESULTS AND DISCUSSION

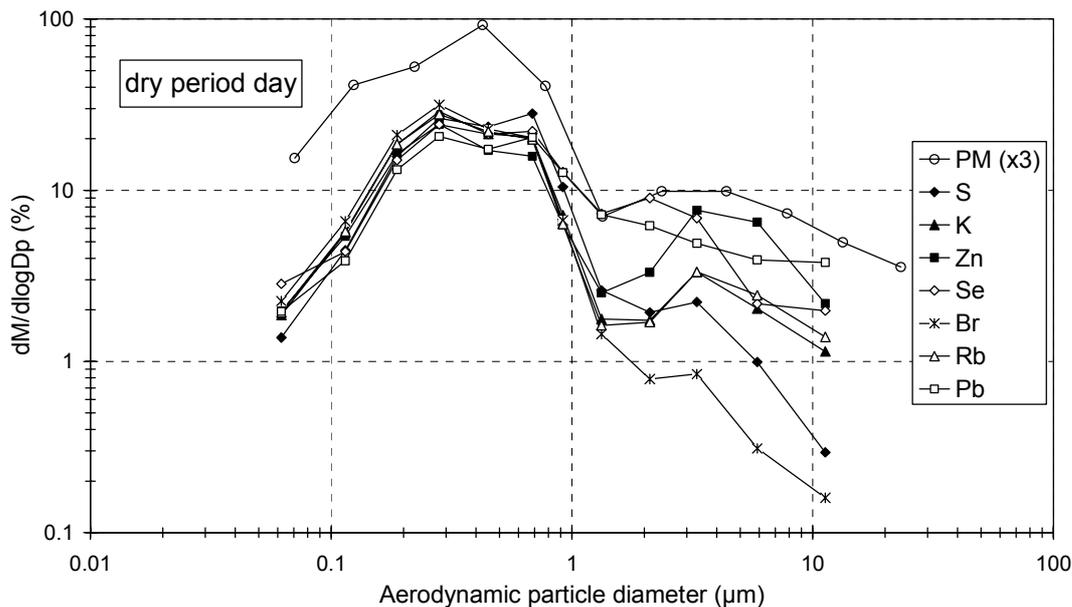


FIGURE 1. Average mass size distributions in the dry period daytime sample set.

Average mass size distributions were calculated for the PM and the various elements for the dry (11 September to 8 October), transition (8 to 30 October), and wet period (30 October to 14 November) of the campaign, and for the dry period also separately for the day and night samples. On the basis of the individual size distributions, average mass median aerodynamic diameters (MMADs) were also derived for each of the five sample sets. Details on the calculation of MMADs from cascade impactor data can be found in Ref. [3]. Figure 1 shows the average distributions (with D_p indicating the aerodynamic particle diameter) for the PM and 7 elements in the dry period daytime sample set. PM and the 7 elements tend to have two major modes in the submicrometer size range and they have one minor mode in the coarse size range. The two submicrometer modes are clearly seen in the SDI data, but not so much in the MOUDI (i.e., PM) data. This is a consequence of the larger number of submicrometer impaction stages in the SDI than in the MOUDI (the SDI has 7 impaction stages with cut-point below 1 μm , the MOUDI only 5) and it indicates that the larger number of stages is needed for unraveling the size distribution in detail. The two submicrometer modes are centered at around 0.3 and 0.7 μm and correspond to the condensation and droplet modes, as defined and seen in other studies [4]. Most of the mass of the PM and of the 7 elements is in the submicrometer size range and their MMADs are around 0.4 μm (Table 1). The fine modes point to high-temperature sources and/or gas-to-particle conversion processes. During the dry period, biomass burning was undoubtedly the major source for the PM, K, Zn, and Rb. The crustal elements (Al, Si, Ti, Mn, and Fe) and the biogenic element P exhibited a unimodal coarse size distribution in the dry period daytime samples and their MMADs are around 4 μm (Table 1). Table 1 shows that the MMADs of the PM, S, and the pyrogenic (biomass burning) elements are somewhat larger during the night than during

the day. From the detailed SDI size distributions, it could be seen that the two submicrometer modes were located at around 0.3 and 0.7 μm during both day and night, but that the droplet mode (at 0.7 μm) had become more pronounced during the night. The droplet mode for sulphate is believed to be due to its formation in the liquid aerosol phase [5] and this process is expected to be more efficient at the higher relative humidity that is observed during the night. Furthermore, hygroscopic aerosol components may experience hygroscopic growth, thereby transferring some material from the condensation to the droplet mode. For the crustal elements and the biogenic element P, no night-day difference in MMAD is observed (Table 1). This indicates that the crustal or biogenic aerosol components are non-hygroscopic.

During the transition and especially the wet period, the MMADs of the PM and the pyrogenic elements (K, Zn, Rb) shifted to larger values than during the dry period. This was a result of the fact that the supermicrometer mode became gradually more pronounced than the submicrometer mode(s). It also indicates that the contribution from crustal and biogenic/biological particles (which are mainly contained in supermicrometer sizes) became increasingly more important than that from pyrogenic particles (which are essentially confined to the submicrometer sizes). During the dry period, the coarse PM mode was, on average, about 5 times less intense than the submicrometer PM mode; in the intermediate period, it was about 2 times less intense, but during the wet period, the coarse PM mode had, on average, become 2 times more intense than the fine PM mode.

Table 1. Average mass median aerodynamic diameters (in μm) and associated standard deviations for the PM and selected elements in the dry period daytime samples (N=24), dry period night-time samples (N=24), transition period samples (N=20), and wet period samples (N=7) from SMOCC-2002.

Variable	Dry period daytime	Dry period night	Transition period	Wet period
PM	0.38 \pm 0.03	0.55 \pm 0.18	0.74 \pm 0.40	2.72 \pm 1.13
Al	3.68 \pm 0.38	3.62 \pm 0.43	4.07 \pm 0.61	4.01 \pm 0.80
Si	3.90 \pm 0.43	3.78 \pm 0.42	4.10 \pm 0.51	4.38 \pm 0.64
P	3.78 \pm 0.24	4.14 \pm 0.38	4.36 \pm 0.33	4.34 \pm 0.46
S	0.40 \pm 0.05	0.57 \pm 0.09	0.50 \pm 0.06	0.53 \pm 0.13
K	0.36 \pm 0.04	0.46 \pm 0.08	0.51 \pm 0.14	2.45 \pm 1.39
Ca	4.26 \pm 0.64	4.36 \pm 0.72	4.32 \pm 0.58	3.67 \pm 0.96
Ti	3.90 \pm 0.50	3.92 \pm 0.35	4.41 \pm 0.53	4.43 \pm 0.46
V	3.59 \pm 0.56	3.54 \pm 1.15	3.89 \pm 1.15	3.33 \pm 1.60
Mn	4.19 \pm 0.50	4.27 \pm 0.51	4.71 \pm 0.76	4.82 \pm 0.40
Fe	3.91 \pm 0.51	3.90 \pm 0.33	4.37 \pm 0.49	4.63 \pm 0.33
Zn	0.44 \pm 0.10	0.55 \pm 0.18	0.73 \pm 0.34	2.44 \pm 1.83
Se	0.48 \pm 0.09	0.56 \pm 0.09	0.51 \pm 0.08	0.45 \pm 0.07
Br	0.32 \pm 0.04	0.41 \pm 0.05	0.37 \pm 0.04	0.42 \pm 0.09
Rb	0.36 \pm 0.04	0.45 \pm 0.07	0.44 \pm 0.08	1.63 \pm 1.36
Pb	0.54 \pm 0.11	0.58 \pm 0.14	0.65 \pm 0.13	0.59 \pm 0.08

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