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Long term measurements of the elemental composition and optical properties of aerosols in Amazonia

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Abstract. Aerosols are being collected and analyzed for trace elements in two sites in Amazonia since January 2008. On eof the site, Manaus is located in a very pristine area in Central Amazonia. The site is nt affected directly by any urban plume for thousands of kilometers. A second site is located in Porto Velho, in a region with heavy land use change and deforestation. Optical properties (light scattering ad absorption) are also being measured in order to study the climatic impact of aerosols. It was observed a clear seasonal pattern for both sites, with higher concentrations in the dry season. But the difference in seasonal concentrations observed for Porto Velho is much larger due to stronger anthropogenic influences. In Manaus during the wet season, very low concentrations of heavy metals, maybe the smallest measured in continental regions are reported. Positive Matrix Factorization (PMF) was used to separate the different aerosol components. In general, for fine and coarse mode and wet and dry season, 3 aerosol components could be observed: 1) Natural biogenic aerosol; 2) biomass burning component; 3) Soil dust both locally and long range transported Sahara dust

Keywords: Amazon, Atmospheric aerosol, Atmospheric chemistry, Heavy metals, optical properties.

Introduction

Central Amazonia is one of the few continental sites in the world where we can still observe very little impact of anthropogenic pollution (Davidson et al., 2012). Aerosol particles and trace metals show very low concentrations, because the air masses have travelled about 2.000 Km over pristine rainforest before being measure at sites North of Manaus (Martin et al., 2011).

Materials and Methods

Aerosol physical and chemical properties were measured in two sites in Amazonia since January 2008. The clean site is at central Amazonia and is located in a pristine Amazonian forest site. A second sampling site is located in Porto Velho, Rondonia, an area strongly affected by land use change and biomass burning emissions. Long term measurements, are being carried out in these two sites, as part of the AEROCLIMA (Direct and indirect effects of aerosols on climate in Amazonia and Pantanal) project. The dataset obtained encompass the first long term aerosol measurements ever performed in Amazonia. In the pristine central Amazonia, measurements were taken at the Cuieiras forest site, tower TT34, with coordinates 2°35'40"S and 60°12'33"W, above the

canopy (45m), under dry conditions (RH<40%) For site description see Kulmala et al., 2011, Martin et al., 2011. A MAAP 5012 absorption photometer in series with a 3-wavelengths nephelometer (TSI 3563) was used to measure aerosol absorption and scattering, respectively. Aerosol size distributions were measure using a Lund DMPS system, as well as a TSI SMPS system. Aerosol composition, trace elements, O₃, CO and CO₂ that helps to characterize aerosol sources were also measured. In Rondonia, a sampling station was installed close to the city of Porto Velho, in the at (8,69° S; 63,87° O). This region has important land use change and biomass burning emissions. In both sites Stacked Filter Units (SFU) are being used to collect aerosol particles in two size fractions: PM₁₀ and PM_{2.5}. The sampling time is 2 to 5 days depending on the aerosol loading in the atmosphere. Gravimetric analysis, black carbon as well as trace elements are being measured in the filters. X-ray Fluorescence using a PanAnalytical EDXRF Epsilon 5 instrument allows the detection of up to 24 trace elements.

Results and Discussion

In terms of optical measurements, in the pristine

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Amazonian atmosphere, aerosol scattering coefficients ranged between 1 and 200 Mm⁻¹ at 450 nm, while absorption ranged between 1 and 20 Mm⁻¹ at 637 nm. A strong seasonal behavior was observed, with greater aerosol loadings during the dry season (Jul-Nov) as compared to the wet season (Dec-Jun). Although the forest site is locally well preserved, it receives the influence of regional biomass burning emissions during the dry season.

During the wet season in Manaus, aerosol scattering (450 nm) and absorption (637 nm) coefficients averaged, respectively, 14 ± 22 and 0.9 ± 0.8 Mm⁻¹. Both optical coefficients were greatly increased during the dry season, averaging 58 ± 58 Mm⁻¹ and 4.1 ± 3.8 Mm⁻¹, correspondingly. Angstrom exponents for scattering were lower during the wet season (1.6 ± 0.4) in comparison to the dry season (1.9 ± 0.2) , which is consistent with the shift from biomass burning aerosols to biogenic and dust aerosols, predominant in the coarse mode. Single scattering albedo (at 637 nm), did not show a significant seasonal variation, averaging 0.86 ± 0.06 and 0.86 ± 0.04 , respectively for wet and dry season.

In Porto Velho, even in the wet season it was possible to observe a strong impact from anthropogenic sources. Very high biomass burning aerosols in the dry season were measured. PM_{2.5} aerosol concentrations of about 300 ug/m² were measured in August and September for most of the years. Black carbon were measured at 20 ug/m³ in the dry season, showing strong aerosol absorption. Very high aerosol light scattering coefficients above 300 Mm⁻¹ were measured.

In terms of trace elements, Table 1 provides the average elemental concentrations in ng/m³ for trace elements measured in Manaus. It is possible to observe the very low elemental concentrations for V, Ni, Pb and other tracers of anthropogenic pollution. PM refers to the aerosol mass concentration and BC for the black carbon component.

In Manaus during January-April a significant influx of Sahara dust aerosol was observed (Baars et al., 2011). This long range transport happens when the ITCZ is South of Manaus, allowing air masses from Tropical Africa to enter South America, transporting dust with smoke from biomass burning in Africa.

Tab.1 Average concentrations in ng/m^3 for trace elements in Manaus for wet and dry seasons. Fine mode fraction is represented by $PM_{2.5}$ (particles less than 2,5 micrometers). The term "Coarse Mode" refers to particles with diameter 2.5<dp<10 micrometers. PM refers to the aerosol mass concentration and BC for the black carbon component

		Wet s	eason	Dry season				
	PM _{2.5}		Coarse Mode		PM _{2.5}		Coarse Mode	
PM	1650	± 920	6190	± 2040	4870	± 2390	5950	± 2500
ВС	94	± 63	58	± 17	325	± 205	60	± 19
Mg	10	± 18	11	± 18			2,84	± 7,72
Al	80	± 106	78	± 99	28	± 22	44	± 30
Si	158	± 220	156	± 219	34	± 25	58	± 41
Р	3,27	± 2,23	27	± 7	2,49	± 1,76	22	± 13
S	91	± 51	44	± 15	228	± 145	50	± 33
CI	0,60	± 0,43	53	± 66	2,07	± 1,28	25	± 33
K	25	± 21	73	± 21	92	± 80	71	± 36
Ca	10	± 11	21	± 18	4,96	± 2,96	16	± 8
Ti	5,03	± 6,80	5,50	± 7,07	2,11	± 1,32	4,41	± 2,72
٧	0,32	± 0,61	0,02	± 0,06	0,30	± 0,36	0,29	± 0,36
Cr	0,12	± 0,20	0,19	± 0,25	0,23	± 0,27	0,28	± 0,24
Mn	0,65	± 0,67	0,77	± 0,85	0,32	± 0,22	0,54	± 0,29
Fe	33	± 44	36	± 47	19	± 14	35	± 22
Ni	0,27	± 0,33	0,05	± 0,06	0,24	± 0,30	0,03	± 0,04
Cu	0,07	± 0,10	0,20	± 0,11	0,80	± 2,32	0,24	± 0,15
Zn	0,35	± 0,21	0,76	± 0,27	1,26	± 0,63	0,89	± 0,37
Br	0,15	± 0,09	0,16	± 0,14	0,85	± 0,57	0,19	± 0,17
Pb	0,03	± 0,07			0,24	± 0,25	0,04	± 0,06

Tab.2 Average trace element concentrations in ng/m^3 for some selected trace elements in Manaus and Porto Velho and Manaus. Concentrations were measured for PM_{10} aerosols

	Port	o Velho	Manaus		
Element	Dry Season	Wet Season	Dry Season	Wet Season	
Cr	0.5 ± 0.5	0.1 ± 0.1	0.3 ± 0.2	0.4 ± 0.2	
Ni	0.1 ± 0.1	0.1 ± 0.1	0.4 ± 0.3	0.4 ± 0.3	
Cu	1.0 ± 0.4	0.4 ± 0.5	5.0 ± 8.6	5.1 ± 6.7	
Pb	2.7 ± 2.5	0.9 ± 0.7	1.9 ± 0.9	1.6 ± 0.7	
Al	121.4 ± 89.2	24.3 ± 21.4	14.8 ± 17.7	29.8 ± 30.9	
Fe	120.3 ± 86.6	36.3 ± 77.5	9.5 ± 10.5	127 ± 16	

The two sites show very different aerosol concentrations, as can be observed in Table 2. Lead concentrations from 1 to 3 ng/m³ were observed, and are associated with natural Pb levels in Amazonia. The fine mode aerosol concentration (PM2.5) for Manaus averages a low 1.9 \pm 1.3 $\mu g/m³$ and for Porto Velho, 8.7 \pm 7.0 $\mu g/m³$. For the coarse mode, we observed in Manaus a concentration of 4.2 \pm 2.2 $\mu g/m³$ and for Porto Velho 10 \pm 6.2 $\mu g/m³$. The fine mode black carbon concentrations show an even large difference between the two sites: 144 \pm 110 ng/m³ in Manaus and 861 \pm 520 ng/m³ for Porto Velho.

Positive Matrix Factorization (PMF) was used to separate the different aerosol components. In general, for fine and coarse mode and wet and dry season, 3 aerosol components could be observed: 1) Natural biogenic aerosol; 2) biomass burning component; 3) Soil dust both locally and long range transported Sahara dust.

Conclusions

This study presents long term trace element concentrations in two sites in Amazonia, one of them (Manaus) showing very low background concentrations. The site in Porto Velho, Rondonia shows that land use change increase aerosol concentrations very significant. But for some heavy metals such as lead, even in perturbed regions in Amazonia, concentrations are much lower than other continental regions. The aerosol in Amazonia is mostly organic (approx. 85% of aerosol mass) (Martin et al., 2010).

In July 2012, mercury measurements will start continuously in Manaus, in order to understand the natural and long range transported components of Hg, associated with aerosols and key trace gases.

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