

## IMPACT OF BIOMASS BURNING ON AEROSOLS PHYSICAL-CHEMICAL PROPERTIES IN BRAZILIAN PANTANAL

# IMPACTO DA QUEIMA DE BIOMASSA NAS PROPRIEDADES FÍSICO-QUÍMICAS DE AEROSSÓIS NO PANTANAL BRASILEIRO

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**Abstract**: The Brazilian Pantanal is a complex forest with increasing agricultural production and has suffered heavily from droughts and fires whose emission impacts cloud formation, radiation scattering, air quality and human health with few in situ studies. The current work analyzed the impact of wildfires on the physical-chemical properties of aerosols in a natural reserve. Particulate material (PM) was collected in filters during seven months in the dry season and optical properties were retrieved from AERONET Cuiabá-Miranda site in the year of 2012. Chemical speciation was performed with X-ray fluorescence by energy dispersion and reflectometry for quantification of equivalent black carbon (eBC). The results indicate a shift in the predominance of trace elements from crustal (AI, Si, Fe and P) to biomass burning related (eBC, S, K), once wildfires occur, along with the particles average size reduction, verified by gravimetry and AERONET volumetric size distribution. The PM mass concentration mean value of  $6,7\pm5,56$  µg.m-3 for coarse mode and  $5,98\pm2,18$  µg.m-3 for fine mode. Equivalent BC had a mean concentration of  $0,59\pm0,53$  µg.m-3 in the whole period, and during a wildfire episode, reached 1,68 µg.m-3 in fine mode. Results showed the direct relation between optical groups of strong absorption and lower size and the increase of eBC concentration.

Keywords: Wetland. Black Carbon. Absorption and Scattering Angstrom Coefficient. AERONET

Resumo: O Pantanal brasileiro é uma floresta complexa com grande importância no controle do fluxo de água na Bacia do Rio Paraguai, apresentando crescente produção agropecuária e tem sofrido fortemente por queimadas cuja emissão impacta a formação de nuvens, espalhamento da radiação, qualidade do ar e a saúde humana. Por isso, para analisar o impacto das queimadas nas propriedades físico-químicas dos aerossóis em uma reserva natural no Pantanal Norte, material particulado foi coletado em filtros, durante sete meses de amostragem na estação seca. A caracterização química foi realizada com fluorescência de raios-X por dispersão de energia e refletômetria para quantificação de black carbon equivalente(eBC). As propriedades óticas obtidas do sítio Cuiabá-Miranda da AERONET como: Profundidade Ótica de Aerossol (AOD), Expoentes de Angstrom de absorção e espalhamento (EAE, AAE, SAE), Albedo de Espalhamento Único (SSA) e Distribuição de Tamanho Volumétrico, foram usadas para caracterizar e classificar oticamente os aerossóis. Os resultados indicam forte impacto da emissão de queimadas nas propriedades óticas, com aumento das médias de AOD, SSA, AAE e SAE. Observou-se a alteração do perfil químico dos elementos traços, que em sua maioria é AI, Si, Fe e P, na estação chuvosa; e BC equivalente, S, K, ao quando há maior incidência de queimadas. Houve redução do tamanho médio das partículas coletadas verificada pela massa coletada nos filtros e pelo produto de inverso de distribuição volumétrica da AERONET. O valor médio da concentração de massa PM de 6.7±5.56 µg.m<sup>-3</sup> para a moda grossa e 5,98±2,18 µg.m<sup>-3</sup> para a moda fino. A concentração média de eBC foi de 0,59±0,53 µg.m<sup>-3</sup>, e durante um episódio de incêndio florestal, atingiu 1,68 µg.m-3 na moda fina. Os resultados

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mostraram a relação direta entre agrupamentos óticos de alta absorção e de menor tamanho e o aumento da concentração de eBC.

Palavras-chave: Áreas Úmidas. Black Carbon. Coeficientes de Angstrom de Absorção e Espalhamento. AERONET.

## **1 INTRODUCTION**

Located southwest of the Mato Grosso State, in Brazil, the Brazilian Pantanal is a wetland area that extends for approximately 140,000 km<sup>2</sup>, corresponding to 1.6% of the national territory. The Pantanal comprises a complex vegetation system, including grass-dominated savanna, upland woodlands, forests, and cattle pasture, and is seasonally flooded (Vourlitis et al., 2013). The geophysical structure of the Pantanal is composed of large alluvial plains and deltas in the Paraguay basin (Curado et al., 2012). The region shelters the headwaters of rivers that feed the Plata Basin, for example, Cuiabá and Paraguay Rivers. The climate is austral dry winter and rainy summer. In Brazil, the Savanna, or simply Cerrado, covers about 24% of the country, and its dominant vegetation is over areas subjected to prolonged dry seasons (Rodrigues et al., 2014; Vourlitis et al., 2014). In the summer, those rivers are fed by rains originated from the South Atlantic convergence zone and by clouds generated in the Amazon Basin (Kodama, 1992). North of the Mato Grosso State integrates the region known as Arc of Deforestation of the Amazon Basin (Pacifico et al., 2015), that together with Cerrado, has suffered intensive agriculture, deforestation, cattle ranching, urban growth, and mining, resulting in the changes in the soil occupation in the past years, causing an increase of fire spots, average temperature, aerosol concentration, drought season duration, and reduction of CO<sub>2</sub> absorption (Aragão et al., 2018; Blunden; Arndt, 2016; Fonseca et al., 2019; Fu et al., 2013; Nobre et al., 2016)

During the dry season in South America, deforestation and wildfires release massive amounts of gases and biomass burning aerosols into the atmosphere, more frequently from August until October (Crutzen; Andreae, 1990). Black carbon is one of the main components optically absorptive of the biomass burning aerosols, and 5,63 Tg are launched annually in the atmosphere (Jacobson; Hansson, 2000). They are the third main atmospheric radiative absorption element (Boucher; Randall, 2013). The north's smoke plume is transported to the south (De Miranda *et al.*, 2016), enriching the soot concentration, compromising air quality and human health (Da

Silva *et al.*, 2010; Jacobson *et al.*, 2014; Machado-Silva *et al.*, 2020; Smith *et al.*, 2014), decreasing the amount of photosynthetic radiation to varying canopy levels, affecting sensible and latent heat fluxes on the surface(Yamasoe *et al.*, 2006), and altering the radiative forcing (Atmospheric aerosols in Amazonia and land use change: From natural biogenic to biomass burning conditions Artaxo *et al.*, 2013; Procopio *et al.*, 2004; Rosário *et al.*, 2011; Sena *et al.*, 2013). It was also observed the increase of the dry season length and the reduction of rain precipitation in the Plata and Amazon Basins (Camponogara *et al.*, 2014; Coelho *et al.*, 2012).

The main local aerosol aspects are regulated by the hydrological seasons: in the wet season, coarse biogenic and dust particles are the majority of aerosol composition, with little fossil-fuel soot; in the dry season, biomass burning, soil resuspension, dust, and urban aerosols enhance their participation in the composition (Leslie, 1981; Maenhaut et al., 1999; Rothmund et al., 2018; Santanna et al., 2016; Santos et al., 2016). Other works have deepened the characterization of local aerosols. It was observed that in wildfires episodes and the dry period, the burnt vegetation changes the type and efficiency of combustion(Ward, 1992), and these factors influence aerosols morphology, size distribution, and optical properties (Martins et al., 1998; Martins et al., 1998; Reid; Hobbs, 1998). Cluster analysis of intensive optical properties separate particles from dry and rainy seasons according to radiation absorption and scattering spectral aerosol optical depth dependency (Cazorla et al., 2013; Russell et al., 2010). In the rainy season, larger particles tend to be less radiation absorptive and more scattering, and in the dry season, there are smaller particles that are less scattering and have greater absorption (Palácios et al., 2020).

Previous works reported the average PM concentration and black carbon weight fraction in a fine mode in dry season varied around 1.2-50  $\mu$ g.m<sup>-3</sup> and 6.7-16% respectively (Artaxo *et al.*, 1998; Maenhaut *et al.*, 1999; Santanna *et al.*, 2016). It was observed that the Absorption Aerosol Optical Depth (AAOD) in the Cuiabá-Miranda AERONET site was 67% higher than the average AAOD, and the lowest single scattering albedo of seven different sites in the Brazilian Amazon and Cerrado (Palácios *et al.*, 2020; Rothmund *et al.*, 2018), even though the black carbon concentration is lower than other sites in the Arc of Deforestation in the dry season (Artaxo *et al.*, 2002; 2013b; Maenhaut *et al.*, 2002).

To further investigate the relation between aerosol optical properties with chemical composition, the present work analyzed the chemical composition of collected particle matter, meteorological data, and the optical properties retrieved from Aerosol Robotic Network (AERONET) (Holben *et al.*, 1998) in a tropical wetland forest area during the dry season. We combined the field campaign data to apply a methodology to estimate absorbing aerosol types using intensive optical properties (Russell *et al.*, 2010). The main goals of this study were to characterize the chemical trace species and the intensive optical properties evolution over time and the impact of meteorological and environmental events over them; to classify the optical groups, and; to analyze the impact of chemical species on those groups determined from stacked filters.

### **2 MATERIAL AND METHODS**

### 2.1 Sampling

#### Instrumentation and location

The sampling site is located in the Baía das Pedras Park, within the Private Natural Heritage Reserve – RPPN SESC (16°39' S; 56°47' W) in the Poconé municipality and bordering the municipality of Barão de Melgaço (about 160 km from the capital Cuiab´a) in the State of Mato Grosso, Brazil. The campaign lasted from April until October 2012. Meteorological data was provided by the university's Advanced Base station, National Institute for Space Research (INPE, 2020), and National Institute of Meteorology (INMET, 2020), as shown in Table 1.

The particulate matter was collected by inertial impact on two Nuclepore® polycarbonate filters arranged in series. The first stage retains the coarse fraction particles using a coarse filter with pores of 8 µm in diameter. The fine fraction particles were retained in the second stage using a filter with pores of 0.4 µm in diameter. Both filters are 47 mm in diameter. The typical flow during sampling was 14 liters per minute. Twenty-seven particulate samples were collected in 2012, starting on April 12<sup>th</sup> until October 24<sup>th</sup>. The integration time of each filter set was seven days in April and May, and 48 hours in the rest of the time.

Month	Precipitation(mm)*	T <sub>max</sub> (°C)*	T <sub>min</sub> (°C)*	Fire Outbreaks**	AERONET Inverse products daily average data at Level 1.5.	Filters samples
April	51.1	33.79	22.8	2,877	10	3
May	264.2	32.2	19.4	9,421	20	5
June	33.3	31.0	18.4	24,163	20	4
July	0	32.0	16.2	27,012	26	2
August	0	35.5	17.1	90,913	27	5
September	40.3	38.0	19.9	155,038	19	4
October	26	36.8	22.7	46,824	17	4

Table 1 - Meteorological and sampling monthly data

\*Data provided by (INMET, 2020). \*\*Data provided by (INPE, 2020)

The mass of aerosols collected in the filters was determined by gravimetric analysis, performed on a scale (Mettler) with nominal precision of 1 µg, capable of quantifying the mass variation of each filter before and after the collection process. Polycarbonate filters were exposed to a radioactive polonium source (<sup>210</sup>Po) for 24 hours before each weighing. This process was performed to neutralize the static electric charges attached to the surface of each filter, so that these charges did not influence the weighing results. The place where the procedure was performed kept the temperature controlled at 20 °C and humidity below 40%.



### 2.1.2 Chemical composition

We used the optical reflectance technique before and after the collection of aerosol particles to determine equivalent black carbon (eBC) concentrations. This process is based on the incidence of light from a tungsten (W) lamp on the sample, which reflects an intensity inversely proportional to the amount of black carbon present. As black carbon particles absorb light with high efficiency, the greater the amount present in the sample, the lower the intensity of light reflected and detected by the photosensor. The device was adjusted with white filters for 100% reflection (Martins, 1999; Rizzo, 2002). The equipment used was a reflectometer, brand Diffusion System Ltd., model Smoke Stain Reflectometer – Model 43. The calibration curve of the light reflected by the amount of black carbon was obtained empirically according to Equation 1, which indicates that from the reflectance measured, the mass of black carbon present in the sample.

$$BC = \left[ (30.9 \pm 0.15) - (14.454 \pm 0.007) \times \log R \frac{A}{v} \right]$$
(1)

Where:

BC is the concentration in µg.m<sup>-3</sup>; R is the Reflectance (%); A is the Filter Area (14.4 cm<sup>2</sup>); V is the Sampled Volume (m<sup>3</sup>).

The black carbon reflectance takes the measurement of the entire sample under light exposure and does not differentiate other forms of carbon that may be in the sample and also absorb light, as well as other chemical elements such as iron, overestimating the presence of elemental carbon and the like (Reisinger *et al.*, 2008). Absorbent organic carbon, brown carbon (BrC), can also be present in the sample. Therefore, the literature suggests calling the BC found in this way as equivalent Black Carbon or eBC.

The elemental analysis was performed by Energy Dispersive X-ray fluorescence (EDXRF) to determine the aerosol chemical composition of each sample using an Epsilon 5, PANalytical B.V. instrument as reported in (Arana *et al.*,

2014). The filters of fine and coarse mode, the total number of 27 each, were analyzed for black carbon and 25 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Cd, Sb, and Pb) and the detection limits for each element, following Santos and collaborators (2016), can be seen in (ARANA *et al.*, 2014). The X-ray tube anode operates with accelerating voltages of 25–100 kV and currents of 0.5–24 mA, with a maximum power of 600 W. The primary target is Sc/W, and the 11 secondary targets (Mg, Al, Si, Ti, Fe, Ge, Zr, Mo, Ag, CaF<sub>2</sub>, and CeO<sub>2</sub>) can be chosen for measuring different ranges of elements. A Si(Li) detector with a resolution of 126 eV for Mn K $\alpha$  was used. Each filter was submitted to EDXRF, and spectral counting was accumulated for 600 s for elements from Na to K and 300 s for elements from Ca to Pb.

## 2.1.3 Aerosol Optical Properties

We retrieved optical data from Cuiabá-Miranda AERONET site photometer (15.73°S 56.02°W), located about 20 km from the urban perimeter of Cuiabá, Capital of Mato Grosso State, which is in the Cerrado-Pantanal transition zone and 140km north from the University's Advanced Base. The radiometer for this site is located approximately, in a region with small trees and twisted branches, directly influenced by local fossil fuel emissions throughout the year and biomass burning in the dry season. Table 1 shows the retrieved data from AERONET during the sampling period.

The AERONET network follows a protocol for data quality assurance, divided according to the level of processing, which varies between 1.0, 1.5, and 2.0. Level 1.0 data represents gross measurements, with no corrections and with all points acquired by the photometer. Level 1.5 has processed measures that eliminate cloud and rain contamination. At the 2.0 level, a cut is made for the optical depth of the aerosol in the channel of 440 nm, the Aerosol Optical Depth (AOD) measured in 440 nm must be greater than 0.4, which minimizes uncertainty for AOD values ranging from 0.01 to 0.02 (Eck *et al.*, 1999).

The obtained data coincide with the filter sampling days, for each sample, a mean value is calculated from daily average products. The daily means of the following products: Aerosol Optical Depth, Single Scattering Albedo (SSA), Absorption Angström Exponent (AAE), Extinction Angstrom Exponent (EAE) were

retrieved in Level 1.5. The Volumetric Size Distribution was retrieved from level 2.0 as monthly averages as shown in Table 1. The products supplied by AERONET are available online at http://AERONET.gsfc.nasa.gov/, which contains all the information about the monitoring system. (Eck *et al.*, 1999; Holben *et al.*, 1998).

### 2.2 Methodology

#### 2.2.1 Cluster Analysis

The Extinction (EAE), Absorption (AAE), and Scattering Angstrom (SAE) Exponents are variables regarding the spectral dependency of AOD, AAOD, and SAOD, respectively, and can be related by as a power-law fit and can be calculated with Equations 1-3. The slope number depends on the aerosol material and dominant size. The AAE is associated with the chemical composition. and the Literature reports some typical values regarding common aerosols: AAE equal one for black carbon; AAE between 1 and 1,5 for the mixture of BC and BrC particles and coated with non-absorbing components; AAE>1.5 for particles with absorption on shorter wavelengths, for example, dust and BrC; and AAE larger than 2 for a complex mixture of urban, industrial and desert dust. SAE is related to the dominant size mode of the aerosol at its inverse proportionality. Larger values are associated with smaller particles, and lower numbers suggest the dominance of coarse mode particles (Bergstrom *et al.*, 2007).

$$EAE(\lambda_1, \lambda_2) = -\frac{\ln\left(\frac{AOD_1}{AOD_2}\right)}{\ln\left(\frac{\lambda_1}{\lambda_2}\right)}$$
(1)

$$AAE(\lambda_1, \lambda_2) = -\frac{\ln\left(\frac{AAOD_1}{AAOD_2}\right)}{\ln\left(\frac{\lambda_1}{\lambda_2}\right)}$$
(2)

$$SAE(\lambda_1, \lambda_2) = -\frac{\ln\left(\frac{SAOD_1}{SAOD_2}\right)}{\ln\left(\frac{\lambda_1}{\lambda_2}\right)}$$
(3)

Cluster analysis of intensive optical properties was reported as a method to identify and classify aerosol types, sources, and an indication of chemical composition (Bahadur *et al.*, 2012; Dubovik *et al.*, 2002; Russell *et al.*, 2010). The method consists in plotting EAE vs AAE or AAE vs SAE, thus typical values

mentioned before serve as guidelines to separate regions associated with different absorbing aerosol types called Angstrom Matrix. The wavelengths chosen were  $\lambda_1$ =440,  $\lambda_2$ =870 nm, used by AERONET to determine the AAOD and SAOD.

Cazorla and co-authors (2013) described eight denominations to common intensive optical properties combinations, for AAE<1 and SAE< 1.5 as Coated Large Particles, as low absorbing and with large size; AAE<1 and SAE>1.5 as Elemental carbon (EC) dominated, for fine size and low spectral dependency. But if the particles are fine but absorb highly at short wavelengths, are rich in organic carbon, or closer to brown carbon definition (Andreae; Gelencsér, 2006), they are nominated as Organic Carbon (OC) and enclosed at AAE>1.5 and SAE>1.5. Dust-dominated particles have similar optical behavior as OC, but a larger mean size. Between those four main classifications, there are the mixtures: Dust/EC, Dust/OC, EC/OC, and Mixture.

### **3 RESULTS AND DISCUSSION**

### 3.1 Meteorological and environmental events

Figure 2 shows optical parameters from AERONET photometer as Aerosol optical depth (AOD), Extinction Angstrom Exponent (EAE), Single Scattering Albedo (SSA), gravimetric data from particle matter (PM) mass deposition in filters, and the local station's meteorological data.

The transition from the rainy season to the dry season is noticeable: from April to June, temperatures are lower, the relative humidity oscillates around 75%, and the particles collected are mostly in coarse mode and in low concentrations, with few fires' spots. From July to October, during the transition from spring to winter, there is an increase in temperature, a reduction in relative humidity that reaches desert levels, and an increase of wild fires.

This transition is verified in the increase of AOD, the collected mass of particulate material, with predominance of the fine mode; in the average of the EAE, which represents the AOD spectral dependency, and is calculated as Equation 1. The Angstrom exponent is often used as a qualitative indicator of aerosol particle size, with values greater than 2 indicating small particles associated with combustion origin, and values less than 1 indicating large particles like sea salt, crustal dust, and

biogenic (Schuster *et al.*, 2006). On the first period, it varied around 1.25, accompanying the PM coarse mode share, and reduced to the lowest point in August, then increased as other variables related with the biomass burning emissions. Another hint of particle size transformation is the AERONET Volumetric Size Distribution Inversion Product presented in Figure 3 as monthly average. In April-August there is the predominance of coarse particles; but as soon the winter ends, the increase of fine particles is perceptible, and the volume coarse mode reduction.

Chapada dos Guimarães National Park is located 80km north from the photometer site and 220km from the University Advanced Base, frequently has vast areas destroyed by wildfires. In September 2012, 130 km<sup>2</sup> were burned in this park, releasing smoke plume over Cuiabá and surrounding areas, including the AERONET site and the University Advanced Base (INPE, 2020), enhancing eBC, SSA, AOD, and PM fine and coarse, additionally, the Angstrom Exponent raised to 1.8 with the wildfires and smoke plumes release intensification, reducing the coarse weight fraction to 29% on September 22<sup>nd</sup>. By the middle of September, a cold front arrived from the south/southeast of Brazil reducing the aerosol concentration, increasing humidity, and the SSA, but at the same time reduced AOD and PM concentration.

The Cuiabá-Miranda site has the higher imaginary refractive part (absorptive) index on wet and dry seasons, the lowest value of SSA, and more spectral dependency than all the other Amazon and Cerrado sites (Palácio *et al.*, 2020). Although, other sites have higher BC concentrations in the dry season (Artaxo *et al.*, 2002; 2013a; Maenhaut *et al.*, 1999, 2002). In Porto Velho, for example, such component is found around 2.801±2.922 and 0.222±0.230 µg.m<sup>-3</sup> in the dry season in fine and coarse mode, respectively, and in forest sites, moldering phase combustion is preponderant (Artaxo *et al.*, 2013, Ward, 1992). Those facts suggest a microstructure and chemical composition quite different from the other sites, which can be due to the proximity of the AERONET site location with urban plume, aerosol average age, and combustion phase. Probably, the aerosols detected in August are more relative to fossil fuel and urban emissions, suggesting that the aerosol is richer in biomass burning and urban soot (Russell *et al.*, 2010).



Figure 2 – Meteorological and optical data obtained from INMET in 2012



Figure 3 – Monthly average Volume distribution AERONET Inversion Product at level 1.5

### 3.2 Chemistry of Aerosol

Trace elemental concentration is presented in Figure 4. As shown in figure 1, coarse mode aerosol is predominant from April until mid-August for practically all elements, except BC and S. Crustal dust elements like AI, Si, and Fe are dominant in the coarse mode aerosols in greater weight fraction, and Ca, P and Cl are found in minor proportions. Phosphorous is a biogenic tracer, in this study its participation in coarse mode compared with fine mass is always dominant, with major contributions at a higher relative humidity as reported by Santanna et al. (2016). It should be stated that the average soil concentration of the region is Al<sub>2</sub>O<sub>3</sub> 16%, SiO<sub>2</sub>75%, Fe<sub>2</sub>O<sub>3</sub> 4 %, K<sub>2</sub>O 2%. CaO, MgO, TiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub> comprise less than 2% in weight fraction (Coringa et al., 2014). In forest sites, it is observed the biogenic emission of ions like K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, almost exclusive in coarse mode (Andreae, 1983; Crutzen; Andreae, 1997; Pöhlker et al., 2012).

In tropical forests and savannas in the Southern Hemisphere, the chemical composition of aerosols follows the change from dry to wet seasons. In rainy seasons, and most of them are caused by anthropogenic activities and aerosols are largely (Gregory et al., 1986; Pöhlker et al., 2012; Pöschl et al., 2010), and may suffer influence of nearby urban plumes (Fraund et al., 2017) and advective episodes of ocean wet fronts (Artaxo *et al.*, 1998; Marengo *et al.*, 1997; Reid; Hobbs, 1998; Ward, 1992) or intercontinental transportation (Rizzolo *et al.*, 2016, 2017). The most common chemical elements are those related to emissions of biogenic and volatile organic compounds (henceforth C, H, O, N, S), saline ions (K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, phosphates). When entering the dry season, organic aerosols are overcome by aerosols from fire and soil dust, and the most frequent elements are: Al, Si, Fe, S, K, Na, and black carbon and non-graphitic carbonaceous.

Calcium and Magnesium provide dubious information regarding their emission source. Some studies correlated these elements to soil resuspension, biomass burning, and biogenic origin (Arana; Artaxo, 2014; Artaxo *et al.*, 2013; Santos *et al.*, 2016). Magnesium in SCAR-B experiment was more related to biogenic sources since its concentration in the soil is very low in most parts of Pantanal and Cerrado, but it could be provided from biomass burning if found at smaller particles (Artaxo *et al.*, 1998; Reid *et al.*, 1998).

Iron and Potassium are largely predominant in coarse mode over the observed period, mainly originated from crustal dust and biogenic emissions, respectively. However, once fires increase, those two elements have their concentrations highly elevated in two size modes. Potassium is a biomass burning tracer (Andreae, 1983), so can be used as an indicator of fires at the flaming phase (Echalar *et al.*, 1995), although there are important limitations in the use of this marker because soil dust resuspension and fertilizers can be major sources of potassium found in the atmosphere (Urban *et al.*, 2012). In Central Amazonia, potassium is more likely to be found in coarse mode, provided from biogenic emissions in the wet season, and is increased by biomass burning in the dry season (Arana; Artaxo, 2014; Brito *et al.*, 2014; Pöhlker *et al.*, 2012). The overall increase of elements in coarse mode from August to October can be due to whirlwinds occurrence in wildfires and typical wind increase in these months.

Iron in fine mode originated from fires and urban pollution is a possibility in this study, and has been the focus of recent studies as a source of soluble metals and radiative forcing enhancement (Ito *et al.*, 2019; Ito; Shi, 2016; Li *et al.*, 2017; Moteki *et al.*, 2017; Rizzolo *et al.*, 2017). Biomass burning elements (eBC, K, S, and Zn), which are more present in fine mode, had their concentration raised, accompanying the intensity of the fire. AOD, fine mass, and volume of accumulation mode had the

same behavior during this period. Other trace elements that comprised less than 3% of mean mass distribution.



Figure 4 - Trace elements concentration in collected filters over the 2012 dry period.

Sodium, which is probably associated to soil or anthropogenic sources had no clear relation with Chloride and precipitation. Sodium was found on 21 filters in coarse mode, and 19 in fine, and higher concentrations in fine mode, and the Chloride was found only in 15 and 19 filters, in fine and coarse, respectively, and

more in coarse mode. Heavier metals (Z>26) which are urban emissions tracers had their concentrations from July to September.

# 3.3 Aerosol optical classification

The scatter plots between the scattering Angstrom exponent (SAE) and the absorption Angstrom exponent (AAE), the so-called Angstrom matrix, provide indications of the possible sources for the aerosols. The methodology reported (Bahadur *et al.*, 2012; Cazorla *et al.*, 2013; Russell *et al.*, 2010) was applied to corroborate the aerosol physical and chemical characterization the intensive properties retrieved from the AERONET site. Figure 5 shows the Angström Matrix plot, as AAE vs SAE that presents the chemical nature and size dependency of aerosol particles of the entire period of the study. The wavelength chosen in the Angström Matrix plot were 440 and 870nm, due to the direct product given by AERONET.

Figure 5 – Aerosol optical classification of Angstrom Matrix in 2012 at AERONET Cuiabá-Miranda site, level 1.5.



The trend of the Angstrom Matrix is not different from other sites in dry season in Brazil. It's separated into four major groups and four other mixtures. The Coated large particles group is dominant from April until June, and in the same period, and lower frequency of Dust, Dust-EC, EC and Mixture groups; meanwhile trace elements labeled as crustal and biogenic are the chemical majority from April until August as observed in Figure 4. Analyzing cluster optical results of similar sites, most aerosols are classified as coated large particles or biogenic as well in that same period (Rothmund *et al.*, 2018). Dust group was irrelevant in this study, despite the crustal elements concentration as shown.

From August to October, group related to smaller and more absorptive particles, labeled as EC, EC/OC, and Dust/EC, outnumber the coated large and dust particles. The EC/OC group was dominant in August-October, with a reduction of EC, Dust-EC, and the absence of OC. At that period, the frequency of EC/OC group increased from 48 to 89%, and there was a reduction of Mix (15 to 5%) and Dust/Ec groups (30 to 0%), which is corroborated by the increase of biomass burning tracers, the size distribution of collected particles and, as the coarse mode fraction diminished, and the enhancing of fine mode particles' total number. The Dust-EC group was relevant between July and August, probably due to the higher presence of coarse crustal elements that reached 64% of all trace elements in August, and then reduced to 30% in October. The EC diminutive proportion and the OC absence enlighten the chemical nature of absorptive carbon analyzed in the AERONET site. Despite the location close to the city of Cuiabá, pure fossil fuel emissions were not dense enough to mark out the optical interaction (EC), whose frequency, in this study, not occurred more than once per month. At the other hand, non-graphitic carbon, named optically as OC, was not registered once at that period, indicating that the arguments regarding the combustion phase and aerosol age are pertinent.

The Cuiabá-Miranda AERONET site is located twenty kilometers from the city center and is close to a highway, and there may be bias due to urban plume, which may correspond to the greater observation of optical groups related to soot and urban dust in the Angstrom Matrix, in comparison with the same groups that would have been observed in chemical analysis. The AERONET data used in this work, was daily average points which reduced the sampling and temporal resolution. Analysis of in-*situ* equipment, could make the sampling of optical properties more realistic and sophisticated.

The offline collection filters facilitate the determination of trace elements of higher atomic weight; however, information regarding lower atomic numbers compounds is missing and are the major part of the composition of aerosols. The collections in late summer and early autumn showed low particulate concentrations and needed more time for a minimum sample to be analyzed, which reduced the number of filters' analyses.

The Angstrom Matrix methodology provided important information regarding the content and size of aerosols. The transition from winter to spring had intense wildfires with smoke transportation from the North. For example, the trend in reduction of crustal elements such as AI, Si, and Fe accompanied the reduction of associated optical class (CLP and Dust). And the same fashion, but in a reverse direction, was observed in the elemental carbon classes.

## **4 CONCLUSION**

Aerosol physical-chemical and optical properties were quantified to investigate the impact of biomass burning in aerosols in a wetland forest during the dry season by observing micrometeorological data and the relation with aerosol optical properties and chemical elements concentrations.

The months with low biomass burning emissions were considered as coarse mode dominant, with AI, Si, Fe, P and K as the majority of trace elements. Chemical components related to biomass burning (eBC, S, K, Fe) had their concentration elevated with the increase of wildfires, from August until October, with the size reduction; it was observable possible impact of the urban plume over the AERONET photometer. The Angstrom Exponents AAE and SAE identified the aerosols changes in size, chemical composition, and spectral dependency. Classes related to elemental carbon had their participation enhanced on the same trend of biomass burning trace elements.

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