

WSOC and Its Relationship with BC, Levoglucosan and Transition Metals in the PM_{2.5} of an Urban Area in the Amazon

Karenn S. Fernandes,^{1a} Erickson O. dos Santos,^a Carla E. Batista,^b Igor O. Ribeiro,^b Victor P. Piracelli,^c Maria Cristina Solci,^{1b} Sergio Duvoisin Jr.,^d Scot T. Martin,^e Rodrigo A. F. Souza^d and Cristine M. D. Machado^{1b}*,^a

^aDepartamento de Química, Universidade Federal do Amazonas, Av. General Rodrigo Octavio Jordão Ramos, 1200, Coroado I, 69067-005 Manaus-AM, Brazil

^bPrograma de Pós-Graduação em Clima e Ambiente (CLIAMB, INPA/UEA), Instituto Nacional de Pesquisas da Amazônia, Av. André Araújo, 2936, Campus II, Aleixo, 69060-001 Manaus-AM, Brazil

^cDepartamento de Química, Universidade do Estado de Londrina, Rodovia Celso Garcia Cid, PR-445, Km 380, 86057-970 Londrina-PR, Brazil

^dEscola Superior de Tecnologia, Universidade do Estado do Amazonas, Av. Darcy Vargas, 1200, Parque 10 de Novembro, 69065-020 Manaus-AM, Brazil

^eSchool of Engineering and Applied Sciences, Harvard University, 02138 Cambridge, MA, USA

Water-soluble organic carbon (WSOC) makes up a large mass fraction of the organic carbon in the aerosol and can influence important cloud processes in the atmosphere. The capacity of WSOC to form metallic complexes with transition metals is well known; however, its influence on the aerosol of urban areas in the Amazon region is not very well known. In this study, we investigated the relationship between WSOC, black carbon (BC), levoglucosan (LEV) and transition metals (Fe, Cu and Mn) present in the PM_{2.5} (particles with a diameter smaller than 2.5 μm) of an urban environment during the dry season in the central Amazon. Oxalic acid (C2) was used to identify the influence of transition metals on WSOC. The mean mass concentration value of the PM_{2.5} was 14.72 μg m⁻³ (2.11-31.68 μg m⁻³). The WSOC made up 58.34% of the PM_{2.5} mass, followed by BC (20.28%), and LEV (2.62%). The WSOC showed significant correlation with the transition metals analyzed (> 0.56), especially Mn with C2 (linear coefficient (R²) = 0.74). A multiple linear regression with WSOC, BC and LEV showed a strong linear correlation between them (R² = 0.86), indicating the influence of biomass burning and vehicle traffic on the organic aerosol.

Keywords: water-soluble organic carbon, PM_{2.5}, transition metals, levoglucosan, black carbon

Introduction

Fine particulate matter (PM_{2.5}) (particles with a diameter smaller than 2.5 μm) stands out among the atmospheric pollutants due to its influence on atmospheric processes.^{1,2} Studies have shown that approximately 10-80% of the total urban PM_{2.5} mass is composed of organic carbon.^{3,4}

More than 90% of organic aerosol in urban environments is composed of secondary organic aerosol (SOA).⁵ Among the SOA, water-soluble organic carbon (WSOC) are

responsible for 40-80% of the mass fraction of organic carbon present in the aerosol.³ WSOC are highly oxidized organic compounds and are the most soluble species formed by photochemical reactions.^{6,7} In addition to contributing to the formation of SOA, WSOC are an important class due to their ability to influence the density of the cloud condensation nuclei (CCN), cloud formation and the radioactive balance of the atmosphere.⁸⁻¹⁰ It is known that WSOC are primarily emitted by the combustion of fossil fuels and biomass. They are also produced secondarily by the photo-oxidation of volatile organic compounds, aromatic or high molecular weight compounds from anthropogenic and biogenic sources.^{3,11}

*e-mail: cristinemachado@ufam.edu.br

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Among the WSOC, dicarboxylic acids (DCAs) stand out as one of the most abundant.^{4,12} They have low volatility and high solubility due to their two carboxyl groups in their chain. DCAs have the ability to affect the hygroscopicity and surface tension of $PM_{2.5}$.^{13,14} In urban aerosols, oxalic acid (C2) is the main representative of the lower molecular weight DCAs, and accounts for 50-70% of the total mass of DCAs.^{13,15}

Graham *et al.*^{16,17} studied the organic aerosol in Balbina (metropolitan region of Manaus), during the dry season, in an area with low human activity that was close to the forest. Graham *et al.*^{16,17} determined that among the DCAs, C2 was the most abundant (56.99-619 $ng\ m^{-3}$) in the two years studied. Kubátová *et al.*,¹⁸ while analyzing the aerosol from the same region, quantified, and characterized DCAs formed by gas-particle conversion, which are markers of photochemical processes of atmospheric oxidation. Thus, the authors concluded that the analyzed DCAs would be incorporated into cloud droplets and carried over long distances.

It has been reported that the formation of complexes between organic ligands and transition metals (mainly Fe, Cu and Mn) increase the absorption of polar organic compounds, both in atmospheric water and in the aerosol.¹⁹ Aqueous transition metal ions play an important role in the formation of oxidants (such as H_2O_2) and important radicals (HO^\bullet , HO_2/O_2^- , etc.) that will act in the transformation of the most diverse organic and inorganic pollutants in the atmosphere.²⁰ These radicals and oxidant agents will affect the composition of clouds and the aerosol, and contribute, for example, to the formation of acid rain in a region.²¹ WSOC, especially low molecular weight DCAs, are the main candidates for atmospheric binders.²⁰⁻²²

Black carbon (BC) is a unique type of carbonaceous material that is formed primarily in flames and is emitted directly into the atmosphere.²³⁻²⁵ As BC comes solely from combustion-related processes, its main sources are the burning of diesel fuel by vehicular and/or industrial engines, the burning of solid fuels (coal and biomass) and forest fires.^{23,26} BC is the main marker of the influence of anthropogenic burning processes in an urban environment. BC aerosol plays a unique and important role in the Earth's climate system, since it alters cloud properties at regional and global scales and affects population health and visibility in large cities.²³

Another important and recognized indicator of burning is levoglucosan (1,6-anhydro- β -D-glucopyranose) (LEV). This monosaccharide is primarily emitted by the pyrolysis (temperature above 300 °C) of cellulose.²⁷ LEV is photo-oxidation stable (no degradation for at least 10 days) and, therefore, it can be transported by air masses and travel

long distances from its place of emission.²⁸ Ribeiro *et al.*²⁹ measured the concentration of LEV during the dry season in Manaus in 2015 and 2016 and reported a mass concentration value of between 196-996 $ng\ m^{-3}$. The authors related that the increase in human activities that involve fire during the dry season increased the concentration of LEV during the studied period.

The population of the metropolitan region of Manaus (located in the central Amazon) exceeds 2.5 million people and, in the year of this study, Manaus (the capital of the State of Amazonas) had the 7th largest gross domestic product among all the Brazilian states.³⁰ However, studies on organic aerosol in a large urban environment in the Amazon, such as the Manaus, are still very scarce. There is a lack of understanding of how the WSOC emitted in Manaus are influenced by the burning of biomass and fossil fuels, and the role of transition metals in the production of WSOC. Thus, the mass concentration value of $PM_{2.5}$, WSOC, BC, LEV and metals of fine particles emitted by the city of Manaus was measured and, through the results, we sought to understand the relationship and influence/impact of transition metals and biogenic and fossil fuel burning markers to the origin of the WSOC.

Experimental

Description of sampling site

The city of Manaus (capital of the state of Amazonas, Brazil) has approximately 785,047 vehicles, of which 38.1% run only on gasoline, 1.9% run on alcohol only, 49.9% can run on both fuel types, and 7.9% are diesel powered.³¹ Manaus is located in the central Amazon, and its upper limit is the Amazon Rainforest, and its lower limit is the Negro and Solimões River (Figure 1).

Regarding the climate, Manaus has a tropical, rainy-type climate with a tropical monsoon subclimate (Köppen climate classification), and is characterized by having a large, accumulated annual precipitation, with the existence of a short dry period between the seventh and ninth month (at least one month with accumulated precipitation less than 60 mm).³² Manaus is only 355 km (in a straight line) from the Equator, which gives the city a low annual variation in temperature, in relative air humidity and in wind speed. The industrial district in Manaus (called the Zona Franca de Manaus) is responsible for approximately 42% of the capital's income. It has several sectors (metallurgy, automotive, beverages, etc.) and the electronics and communication equipment manufacturing sector are the most relevant (24% of total jobs).³³

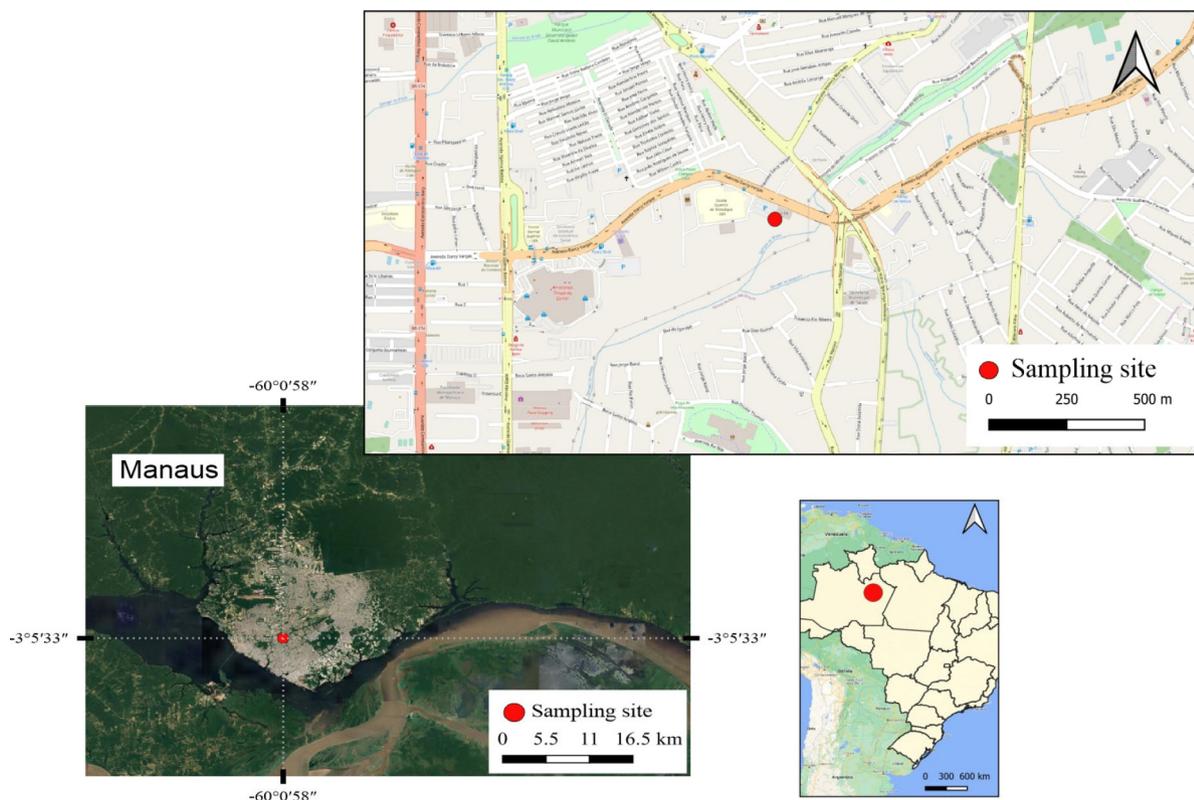


Figure 1. Location of Manaus and in the upper right corner the sampling site (red dot) and its surroundings (in yellow are the main avenues).

PM_{2.5} sampling

PM_{2.5} samples were collected on the roof of two shipping containers (6 meters above ground levels) (3.0913° S, 60.0172° W) located on the campus of the Amazonas State University (Manaus, Brazil). The university campus is close to avenues and overpasses with regular traffic throughout the day (Figure 1).

The sampling was performed using active sampling via a large-volume sampler (Energética®, São Paulo, Brazil) at a flow rate of 1.13 m³ min⁻¹. A total of 18 quartz microfibre filter (Tissuquartz™ filters, grade 8, QM-A, 8 × 10 inches, Whatman Corporation, Merck, Darmstadt, German) samples were collected during the dry season (August and September 2017). The filters were pre-baked at 500 °C for 12 h to remove any possible contaminants. Soon after calcination and after sampling, the filters were placed in aluminum envelopes, also pre-baked (500 °C/12 h), then stored in antistatic bags with silica gel sachets to control and reduce humidity and stored at -18 °C until use.

Chemical analysis

Two clean filters were used to obtain the laboratory blank and field blank. Both clean filters also were pre-baked (500 °C/12 h). The filter used as a “laboratory blank” was

kept in the refrigerator until the moment of extraction and analysis. The filter used as “field blank” was placed in the turned off equipment for 10 min, and then stored again in the refrigerator (-18 °C) until the moment of extraction.⁷

All the filters (samples and blanks) were carried out by the same chemical extraction and analysis to correct possible contamination. Data obtained from the sample filters were subtracted from blanks values. Four disks (47 mm) were obtained from each filter to perform the chemical analysis described below.

Metals analysis

The extraction of metals from the 47 mm disk taken from the filter was done by microwave digestion.³⁴ The quartz disk was placed in a Teflon tube followed by the addition of 10 mL of the extraction acid solution (5.55% HNO₃ (double-distilled acid)/16.75% HCl (Suprapur®, Sigma-Aldrich, Saint Louis, USA)) as recommended by EPA Compendium Method IO-3.4³⁵ (recovery > 76.1%, relative standard deviation (RSD) < 6.2%) and reported by Ventura *et al.*³⁶ as efficient acid solution (with recovery and accuracy equivalent to only nitric acid extraction). After digestion, the Teflon tube was rinsed with deionized (DI) water (< 0.05 μS cm⁻¹) to completely remove the extract from the walls of the tube. The extract was then filtered (syringe filter, 0.2 μm) and transferred to a 50 mL

flask filled with DI water. Metal analysis (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Zn) was performed using a simultaneous inductively coupled plasma atomic emission spectrometer (ICPE-9800, Shimadzu®, São Paulo, Brazil). Concentration was obtained through external calibration with certified standards (LGC Standards Ltd., Manchester, USA).

WSOC analyses

One disk from the filter was placed in a 20 mL vial and filled with DI water. Then, the solution was subjected to ultrasonication for 30 min. The ultrasonically treated solution was filtered with a syringe filter (0.2 µm) and placed in a new, clean vial.³⁷ WSOC was analyzed with a total carbon analyzer (TOC-V_{CPN}, Shimadzu®, São Paulo, Brazil). The TOC method described by Alcaide *et al.*³⁸ was used in this study.

BC analyses

Another 47 mm disk of the quartz filter was used for BC analysis via reflectance analysis on an EEL 43D smoke stain reflectometer (Diffusion Systems Ltd., London, UK). This followed the method described by Piracelli *et al.*³⁹ Initially, the linearity of the reflectance measurement was checked by adjusting the “zero” (no reflectance) with the sensor disconnected from the control unit, followed by the adjustment of “100” (total reflectance) by measuring a blank filter supplied with the equipment. Then, the linearity was confirmed with the measurement of a standard filter supplied with the equipment.

Levoglucosan and oxalic acid analyses

For the analysis of levoglucosan (LEV) and oxalic acid (C2), the method described by Ribeiro *et al.*,²⁹ briefly described below, was followed. One disk from the filter was inserted into a 20 mL scintillation vial for extraction. The samples were extracted in methanol (J.T. Baker, 99.9%, Pennsylvania, USA) using ultrasonic agitation (45 min), followed by filtration of the extracts with a syringe filter (Teflon membrane, 0.2 µm) and drying with pure nitrogen (99.999%) using an evaporator (TS-18826 Reacti-Vap III Evaporator with TS, 18823 Reacti-Therm heating/stirring Module, Thermo Fischer Scientific, Massachusetts, USA). Then, the dried residue was derivatized (*N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with trimethylchlorosilane (TMCS) (99:1 v/v, Supelco, Merck, Darmstadt, Germany), and pyridine (98%, anhydrous, Sigma-Aldrich, Saint Louis, USA) (70 °C for 1 h) and later transferred into amber vials for chemical

analysis with a gas chromatograph (Agilent 7890B GC, California, USA) coupled with an electron ionization quadrupole mass spectrometer (Agilent 5977A MSD, California, USA) (GC-MS).

LEV and C2 concentration in the PM_{2.5} samples were quantified using an external standard. (1S)-(+)-Ketopinic acid (Sigma-Aldrich, St. Louis, MO, USA) was used as the recovery standard. It is commonly used to verify the efficiency of derivatization carried out on field samples using GC-MS.⁴⁰ A typical recovery of 96% (LEV) and 111% (C2) was determined and applied to all the GC-MS analyses.

PM_{2.5} mass concentration and meteorological data

PM_{2.5} mass concentration data were measured using an automatic air quality station (airpointer®-mlu-recordum, Environmental Monitoring Solution GmbH, Germany) equipped with a nephelometer with a lower limit of detection (< 1 µg m⁻³). Meteorological data (temperature, relative humidity, and precipitation) were obtained through an automatic meteorological station installed at the sampling site.⁴¹

Results and Discussion

Meteorological conditions

The dry season in the region comprises the months of July–October.⁴² In the Amazon, rainfall is regular in both seasons (wet and dry season); however, it is sparser and of low volume during the dry season. In the period studied, only 27% of the sampling days had rain volume of above 1 mm. The cumulative rainfall was 42.5 mm (0–18 mm). The highest value (18 mm) was recorded in a single day during a rain shower. The average temperature and average relative humidity were 29 °C (26–32 °C) and 69% (55–87%), respectively.

Air mass backward trajectory clusters (96 h) for the sampling period (Figure 2) were obtained using the HYSPLIT model,⁴³ via the READY (Real-time Environmental Applications and Display sYstem)⁴⁴ and HYSPLIT Program (version 5.1.0) from NOAA (National Oceanic and Atmospheric Administration, USA).⁴³ The height set on the model was 1000 m due the convective boundary layer's average height above the Amazon region.⁴⁵

A total of 149 backward trajectories (CDC1 meteorological data) were obtained for the entire sampling period. These were combined into five clusters. In all, 58% of the air mass (clusters 1 and 3) that reached the sampling site came from the northeastern-western direction. The Amazon region is influenced by the Intertropical Convergence Zone (ITCZ).

During the beginning of the dry season, the ITCZ changes the air mass directions from northeast to east-southeast (changes are gradual until the end of the dry season).⁴⁶ Therefore, during the dry season, Manaus is highly influenced by the polluted air mass (biomass burning and others anthropogenic sources) from northeastern Brazil.

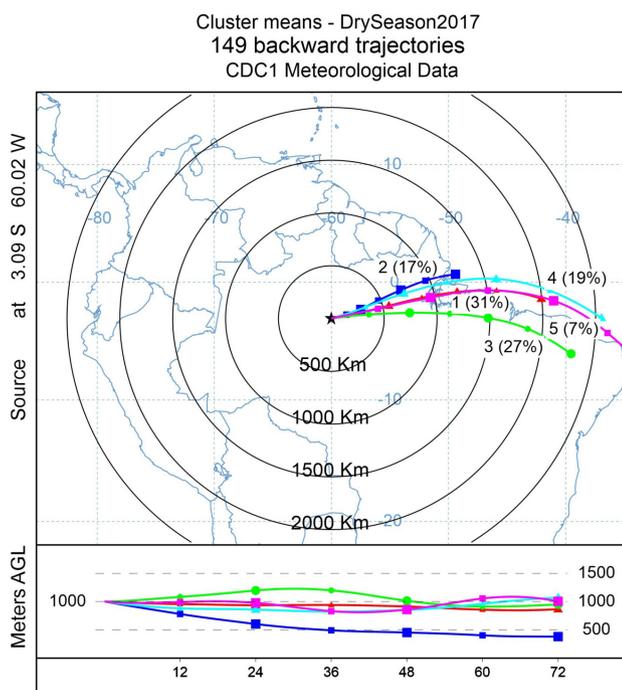


Figure 2. Air mass backward trajectory clusters (96 h) for the sampling site (the star on the map).

PM_{2.5} mass concentration

Figure 3 shows the diurnal variations of PM_{2.5} mass concentration. The average PM_{2.5} value was $14.72 \pm 7.55 \mu\text{g m}^{-3}$ and ranged between 2.11 and $31.68 \mu\text{g m}^{-3}$. In general, most PM_{2.5} levels were lower than

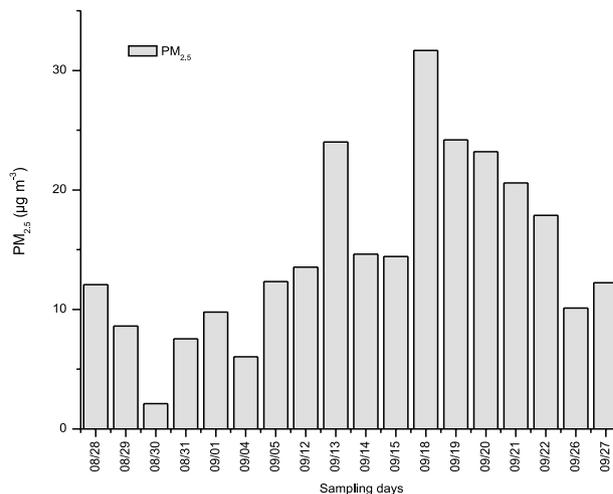


Figure 3. Diurnal variations of PM_{2.5} mass concentration.

the World Health Organization (WHO, $25 \mu\text{g m}^{-3}$ over 24 h) guidelines.⁴⁷ Only on 09/18 the PM_{2.5} level was higher than the WHO guideline.

The mean mass concentration value of the PM_{2.5} measured in this study was higher than the value of $11.6 \pm 7.8 \mu\text{g m}^{-3}$ that was obtained during the dry season in 2014,⁴⁸ and $6.7 \pm 3.3 \mu\text{g m}^{-3}$ recorded in the dry season in a study carried out in Iranduba (26 km southwest of Manaus).⁴⁹ The main sources of origin of PM_{2.5} in these studies were vehicular emission, exhaust and non-exhaust emission, and soil resuspension.

However, the PM_{2.5} values of this study were below those reported by Paralovo *et al.*,⁵⁰ ($21.6 \pm 14.6 \mu\text{g m}^{-3}$) in their study carried out in the dry season in Manacapuru (71 km southwest of Manaus). The higher values were attributed to biomass burning and urban emissions that are carried in and by the Manaus plume. Compared to other Brazilian cities, PM_{2.5} mass concentration in this work was generally lower, especially concerning big cities (Table 1).

Table 1. Comparison between PM_{2.5} mass concentrations values of this work and values reported for other Brazilian cities

Site	Sampling period	PM _{2.5} mean / ($\mu\text{g m}^{-3}$)	Sampling site	Reference
This work	August-September/2017	14.72	urban area	—
São Paulo	July/2014	45	near an important expressway	Pereira <i>et al.</i> ⁵¹
São José do Rio Preto	March-June/2017	10.88	near main state and federal highways	Franzin <i>et al.</i> ⁵²
Tangará da Serra	2008	42	municipality strongly influenced by plume of pollution from the arc of deforestation ^a	de Oliveira <i>et al.</i> ⁵³
Rio de Janeiro	January-April/2009	29.2	urban area influenced by vehicle emissions	Loyola <i>et al.</i> ⁵⁴
Belo Horizonte	2007-2008	14.7	central region of the metropolitan area	de Miranda <i>et al.</i> ⁵⁵
Rio de Janeiro	2016	10	central regions of the metropolitan area	Gioda <i>et al.</i> ⁵⁶

^aAmazon region is known for intense biomass burning activity. PM_{2.5}: fine particulate matter (particles with a diameter smaller than 2.5 μm).

Mass concentration of WSOC, BC, levoglucosan (LEV) and metals

The mean and the maximum and minimum values of mass concentration of WSOC, BC, LEV, and the metals determined in the PM_{2.5} are shown in Table 2. The WSOC average was $8.59 \pm 3.18 \mu\text{g m}^{-3}$ ($4.53\text{-}15.27 \mu\text{g m}^{-3}$). The lowest WSOC values, obtained on 09/22 ($4.99 \mu\text{g m}^{-3}$); 09/26 ($4.53 \mu\text{g m}^{-3}$) and 09/27 ($5.15 \mu\text{g m}^{-3}$), were related to the highest rainfall events (8.9 and 18 mm). The same happened on 09/05 and 09/12, when the occurrence of rain caused a decrease in the WSOC concentration (Figure 4).

The mean WSOC value in this study was lower than that reported by Graham *et al.*¹⁷ ($17.3 \mu\text{g m}^{-3}$) in the dry season in the Amazon (Rondônia, Brazil) in a pasture highly affected by biomass burning. However, the mean WSOC value for Manaus was similar to that determined during the summer ($8.1 \pm 2.8 \mu\text{g m}^{-3}$) in the city of Beijing (China)⁵⁷ and higher than WSOC values reported for Rio de Janeiro State (RJ) (Brazil) ($0.8\text{-}4.9 \mu\text{g m}^{-3}$), whose WSOC concentration was related to vehicle fleet traffic and industrial activities.⁵⁸

Thus, this similarity in WSOC values between Manaus and Beijing (China) and Manaus's WSOC values higher than related to RJ indicate that the WSOC collection was strongly influenced by urban primary sources (exhaust and non-exhaust emissions, traffic-related sources, etc.).

However, the data showed that the WSOC concentration was highly variable in the studied period. This variability of WSOC values indicates the occurrence of sporadic and diverse sources, which may be influenced by other primary and secondary origin (not in the subject of this work). This makes sense since the WSOC sources are diverse, with a significant participation also from secondary formation.⁵⁹

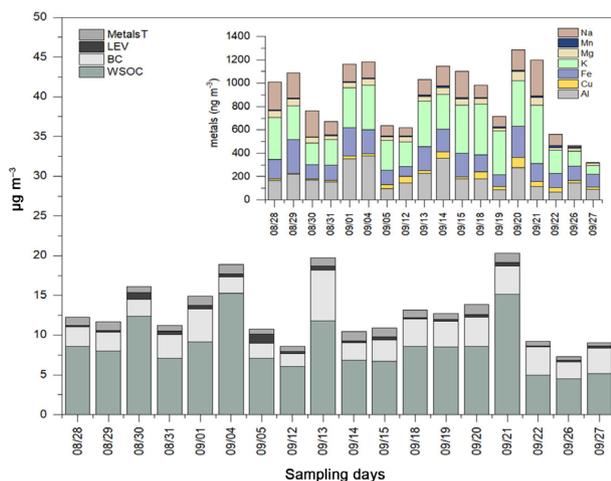


Figure 4. Daily variation of mass concentration (ng m^{-3}) of water-soluble organic carbon (WSOC), black carbon (BC), levoglucosan (LEV), and metals in PM_{2.5}. The term "MetalsT" refers to the total mass concentration value of the analyzed metals.

Table 2. Mean, standard deviation (SD), minimum (Min), and maximum (Max) concentrations of water-soluble organic carbon (WSOC), black carbon (BC), levoglucosan (LEV), and metals. The enrichment factor (EF) is calculated only for metal concentrations (Fe was chosen as the soil contribution reference metal)

	Mean	SD	Min	Max	EF
WSOC / ($\mu\text{g m}^{-3}$)	8.59	3.18	4.53	15.27	–
BC / ($\mu\text{g m}^{-3}$)	2.99	1.10	1.61	6.33	–
LEV / ($\mu\text{g m}^{-3}$)	0.37	0.26	0.11	1.15	–
	Metal / (ng m^{-3})				
Al	189.13	95.57	64.27	377.03	0.70
Cu	32.14	21.96	8.89	87.37	198.12
Fe	165.79	59.46	83.89	289.88	–
K	303.06	115.71	74.65	498.13	3.70
Mg	43.83	16.04	20.87	75.54	0.65
Mn	11.43	2.89	5.64	15.41	4.05
Na	148.84	74.75	10.81	309.21	1.60

The mean value of BC and LEV concentrations was 2.99 ± 1.10 and $0.37 \pm 0.26 \mu\text{g m}^{-3}$, respectively. The concentrations of BC and LEV in this study were higher than that reported by Barbosa and co-workers⁴⁶ ($2.4 \mu\text{g m}^{-3}$ BC) and Ribeiro *et al.*²⁹ ($0.20 \mu\text{g m}^{-3}$ LEV) for the same region and in the same season.

A low coefficient of variation (37%) indicates the presence of a regular source of BC, which is probably the vehicular traffic since (i) incomplete fuel combustion is the main regular source of BC^{23,25} and (ii) the proximity of the site sampling to important avenues. Levoglucosan (LEV) is a specific marker of cellulose burning and, therefore, an important ally in the identification of the aerosol source.^{60,61}

The elements Ca, Cd, Co, Cr, Mn, Ni, P, Pb, Zn had more than 50% of their values below the limit of detection (specified as the smallest point on the calibration curve = $4.8 \mu\text{g L}^{-1}$). The metals analyzed in this study according to greatest presence was K ($303.06 \pm 115.71 \text{ ng m}^{-3}$) > Al ($189.13 \pm 95.57 \text{ ng m}^{-3}$) > Fe ($165.79 \pm 59.46 \text{ ng m}^{-3}$) > Na ($148.84 \pm 74.75 \text{ ng m}^{-3}$) > Mg ($43.83 \pm 16.04 \text{ ng m}^{-3}$) > Cu ($32.14 \pm 21.96 \text{ ng m}^{-3}$) and, finally, Mn with an average of $11.43 \pm 2.89 \text{ ng m}^{-3}$.

In order to assess the origin (anthropogenic sources or soil) of the metals analyzed, the enrichment factor (EF) was calculated using Fe as a reference element.^{19,56} The values of the elements in soil was taken from Mason.⁶² EF was calculated by:

$$EF = \frac{(C_X C_R)_{\text{particles}}}{(C_X C_R)_{\text{soil}}} \quad (1)$$

where C_X is the concentration of metal of interest and C_R is the concentration of the reference element. EF indicates whether the concentration of a particular element is greater

than expected to come from the soil.⁶³ $EF > 1$ indicates that the soil was the only source of that element. EF between 1 and 5 indicates the contribution of anthropogenic sources. $EF > 5$ shows anthropogenic sources as the main source of the element for the particulate matter.⁶⁴

Al and Mg were the metals that came only from the soil (Table 2). K (3.70) and Mn (4.05) had significant EF values, which demonstrate their natural origin, but also the influence of anthropogenic sources. K is generally pointed out as being a marker of biomass burning, but it can also originate from primary biogenic sources and other anthropogenic origins. Thus, the relationship between LEV and K must be investigated to establish the strength of the non-biomass burning sources of K.²⁷ In this study, K and LEV did not show a statistically significant relationship through linear correlation, neither through Pearson correlation. Thus, the EF value of K (3.70) (Table 2) indicates a strong influence of non-biomass burning sources of K (industrial activities, diesel and gasoline vehicles, leaf respiration, etc.).^{27,65}

Mn is used as an additive in gasoline; therefore, vehicular traffic is its main anthropogenic origin in the particulate matter.⁶⁶ Cu showed a high EF value (198.12), and this demonstrates a strong influence of anthropogenic sources for this element. Cu comes from industrial activities and mainly from activities related to vehicular traffic (oil combustion, brake wear, fuel combustion, etc.).^{67,68}

Cu had a moderate Pearson correlation (R) with Mn (0.50), which confirms the influence of joint anthropogenic sources for these elements. PM_{2.5} showed important correlations with K ($R = 0.54$), Cu ($R = 0.62$), Mn ($R = 0.63$) and BC ($R = 0.55$). These R values show that there was influence caused by burning (vehicular/industrial) sources in the origin of the particulate matter mass in this study.

The WSOC had a 58.34% contribution to the PM_{2.5} mass, followed by BC (20.28%), total metals analyzed (MetalsT) presented a 6.02% contribution and LEV (2.62%) (Figure 5). Although the LEV is a WSOC its PM_{2.5} mass contribution shows the influence of biomass burning on the mass of collected particles. Other unanalyzed aerosol components (organic carbon, elemental carbon, soluble ions, etc.) were responsible for 12.73% of PM_{2.5} mass. The relative WSOC mass contribution value to the PM_{2.5} is in agreement with other studies carried out in the Amazon region where the WSOC had an average contribution of 56% to the total carbon of the collected PM_{2.5}.⁶⁹

Influence of transition metals on the WSOC

Transition metals (Fe, Cu, and Mn in this study) have an important role in the particle's aqueous phase. These

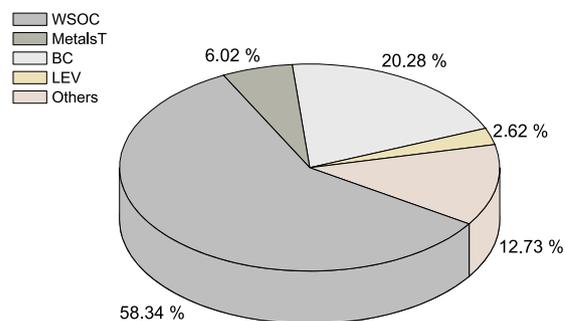


Figure 5. Relative contribution of mass concentration of water-soluble organic carbon (WSOC), black carbon (BC), levoglucosan (LEV), metals and others different species to the composition of the PM_{2.5}. The term "MetalsT" refers to the total mass concentration value of the analyzed metals.

metals are the principal ones to form the WSOC complex, having a critical influence on the oxidation of sulfur species in cloud droplets, being also an important sink of oxalic in the atmosphere.^{70,71} To better understand this relationship, a linear regression between WSOC and transition metals analyzed in this study was constructed.

Figure 6 show that WSOC had significant correlations with the transition metals demonstrating statistical dependence between them. Mn and Fe had the same linear coefficient value (R^2) with the WSOC; however, the slope of the regression equation between WSOC and Mn (709.27) was 14.8 times greater than the WSOC and Fe (47.75). Therefore, Mn had a greater influence on WSOC formation during the studied period.

Transition metals can influence the formation of free radicals in the aerosol and influence the hygroscopicity, as well as the action of the aerosol as cloud condensation nuclei (CCN).⁷¹ Dicarboxylic acids (DCAs) are the biggest contributors to the WSOC. Among them, oxalic acid (C2) is the major component of DCAs and is also an important key to understanding secondary aerosol formation.^{22,72,73} As such, the relationship between transition metals and C2 was observed in order to understand how these metals influence the WSOC.

Oxalic acid can form metal oxalate complexes in the aerosol by reacting with metal ions present in the particle or in the liquid film of the aerosol, since the aqueous phase is a reaction field for complexation.^{22,64} Furthermore, it is estimated that most of the oxalate present in the aerosol is complexed with some metallic ligand.²²

In this work, C2 had significant linear correlations with Fe ($[C2] = 2.74 [Fe]$; $R^2 = 0.60$), Mn ($[C2] = 45.05 [Mn]$; $R^2 = 0.74$), and Cu ($[C2] = 11.97 [Cu]$; $R^2 = 0.55$). Mn had the highest correlation with C2, followed by Fe and Cu. The atmosphere is an important source of organic-metal complexes.^{74,75} Low molecular weight DCAs, C2 being the majority among them, are effective atmospheric

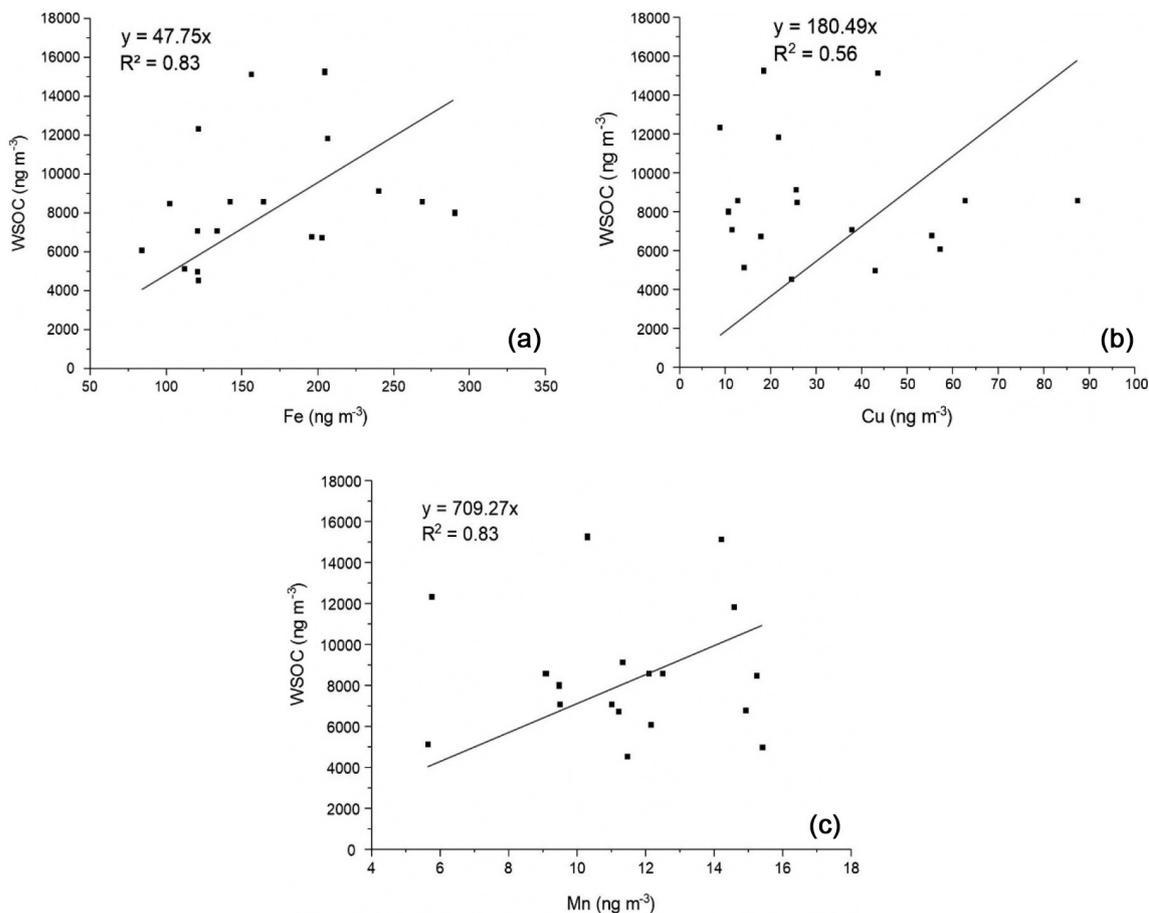


Figure 6. Linear correlation between WSOC and (a) Fe, (b) Cu and (c) Mn.

binders because they have (i) high stability constants in the atmosphere and (ii) they are highly soluble (high constant of Henry's Law). Thus, it is estimated that oxalic acid is present in the aerosol mainly in the form of metal oxalate complexes.^{20,74}

Although Fe was not the main agent in C2 formation, the photolysis of Fe^{III}-oxalate complexes is an important source of hydrogen peroxide (H₂O₂) for the aerosol. H₂O₂ plays an important role in decreasing the pH or acidification of clouds and rainwater, through the fast oxidation of SO₂ forming H₂SO₄.²¹ Honório *et al.*⁷⁶ reported a pH of 4.1 in the rainwater collected in Manaus. The author related no significant relationship between the low pH value, conductivity and the sulfate anion dissolved in rainwater. Therefore, the influence of Fe on C2, as well as the other metals studied and its ability to form stable complexes with oxalate, may influence the pH of clouds and rainwater, as well as the formation of aerosol in the region.

WSOC and the burning processes

WSOC had a significant linear correlation with BC ($R^2 = 0.82$) and LEV ($R^2 = 0.69$). A multiple linear

regression (MLR) with WSOC, BC and LEV was performed to observe the relationship between these variables together. The equation constructed was as follows:

$$[\text{WSOC}] = 1.88[\text{BC}] + 6.57[\text{LEV}] \quad (2)$$

BC ($p = 3.03 \times 10^{-4}$) and LEV ($p = 0.03$) were significant in the model and had strong linear correlation with WSOC ($R^2 = 0.86$). This demonstrates that burning processes, whether from fossil or non-fossil fuels, were important sources of the WSOC during the period studied. Other studies also confirm the occurrence of relationships between WSOC, BC and LEV. Urban *et al.*²⁷ studied the relationship between WSOC and LEV in a region affected by sugarcane burning and observed a linear positive correlation ($R^2 = 0.54$) between them. However, the author indicates that there was no direct relationship between WSOC and LEV on the day with the highest concentration of LEV. Park *et al.*⁷⁷ collected PM_{2.5} at a roadway site and observed positive correlations between BC and LEV, which indicates that emissions from fossil fuel burning sources were significant in the collected WSOC. It is important to note that WSOC have a greater

dependence on the LEV (red part of the Figure 7 and a higher slope value in equation 2), which indicates that biomass burning was significant in the chemical composition of the aerosol collected. The red area in the upper right corner of Figure 7 predicts that the increase in BC and LEV emission will also lead to an increase in the WSOC concentration in the aerosol.

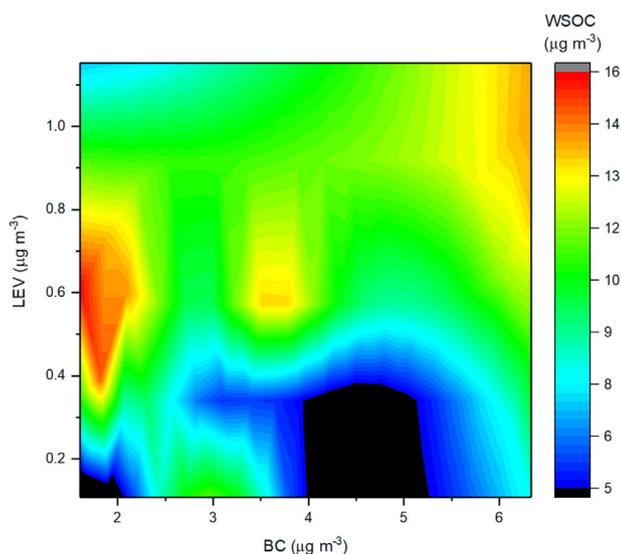


Figure 7. Dependence of levoglucosan (LEV) and black carbon (BC) on water-soluble organic carbon (WSOC) in PM_{2.5}.

Conclusions

In this study, it was possible to observe the great relative contribution of the WSOC to the mass concentration of PM_{2.5} (58.34%) in the urban area of the Amazon under study. A dependence equation between WSOC, BC and LEV was constructed, and indicated that BC and LEV primary sources emitted WSOC. Biomass burning origin had the greater impact as indicated by the highest slope of LEV in the equation. However, how the increase in the BC and LEV primary sources and the emission of their associated species will influence the WSOC composition is still not clear and needs further study.

The influence of the studied transition metals on the WSOC and evidence of the formation of metal oxalate complexes was also observed. The oxalate-complexes can affect the formation and composition of clouds, forming free radicals acting in various atmospheric reactions, and also improve the formation of acid rain that has been described in the literature for the city of Manaus.

Finally, this study contributes to the knowledge of the organic aerosol in an urban environment in the Amazon and the atmospheric organic chemistry of the region. It also collaborates by aiding in the understanding of the influence that the city of Manaus has on the composition

of the aerosol in the region, and how this urban aerosol can change the environment to which it will be transported by air masses.

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Author Contributions

Karenn S. Fernandes was responsible for writing of original draft; conceptualization, data curation, formal analysis; Erickson O. dos Santos for data curation, writing-review and editing; Carla E. Batista for data curation, formal analysis, writing-review and editing; Igor O. Ribeiro for data curation, formal analysis; Victor P. Piracelli for data curation, formal analysis; Maria Cristina Solci for methodology; resources; Sergio Duvoisin Jr. for methodology, resources; Scot T. Martin for methodology, resources; Rodrigo A. F. Souza for methodology, resources; Cristine M. D. Machado for conceptualization, writing-review and editing, supervision, project administration.

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