Aerosol characterization in a Central‑West site of Brazil: infuence of farming activities and toxicity

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Received: 26 May 2023 / Accepted: 2 November 2023 / Published online: 13 December 2023 © The Author(s), under exclusive licence to Springer Nature B.V. 2023

Abstract

The Central-West region of Brazil presents three important and large ecosystems: the Amazon, the *Cerrado*, and the *Pantanal* biomes. Diferent anthropogenic activities (e.g., biomass burning and land use) afect this area, emitting particulate matter (PM) that can be transported to urban sites, adding to the local vehicular sources. Sampling of atmospheric particulate material with a size less than and equal to 10 μm (PM_{10}) was carried out in the medium-sized city of Cuiabá (Brazil), between 2008 and 2014. The maximum concentrations of PM_{10} were found in the dry season, surpassing the recommended levels by the World Health Organization. A slight seasonal variation was found between the concentrations of organic carbon, elemental carbon, elements, and water-soluble ions (WSI), with higher levels in the dry season, enhanced by biomass burning and dust resuspension. Polycyclic aromatic hydrocarbons, their nitrated and oxygenated derivatives (nitro and oxy-PAHs), and some *n*-alkanes showed similar behaviors in the dry and rainy seasons, with higher abundance of carcinogenic PAHs compared to the rest of the polyaromatics. Total incremental lifetime cancer risks due to exposure to PAHs were found to exceed the safety level. Based on the application of diagnostic ratios and the positive matrix factorization receptor model, biomass burning, soil and road dust resuspension, vehicular exhaust, and mining activities were pointed out as emission sources. These results allow us to better understand the aerosol sources that contribute to the worsening of air quality in a growing urban area.

Keywords Biomass burning · Atmospheric particulate matter · Organic pollutants · Water-soluble ions · Air mass trajectories

Introduction

Exposure to airborne particles and the diferent chemical species associated with them can cause harmful efects on human health, fauna, and fora (de Oliveira Alves et al. [2020](#page-17-0); Fajersztajn et al. [2017;](#page-18-0) Gurjar et al. [2010\)](#page-18-1). These particles can contribute

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to radiative forcing, as they can absorb or scatter light (Myhre [2013\)](#page-19-0). Approximately 92% of the world's population lives in regions where air pollution levels exceed WHO guidelines. On the South American continent, especially in growing Brazilian cities, air pollution is a great challenge. In Brazil, air pollution is responsible for more than 51,000 deaths per year. It may lead to premature deaths, lung, and vascular diseases, as well as to the development of diferent types of cancer and other diseases (PAHO [2018;](#page-19-1) Sant'anna et al. [2021](#page-20-0)). Another aspect directly afected by air pollution is the Brazilian economy, registering losses in agricultural productivity (Roy and Braathen [2017](#page-20-1)).

Crop and forest fres are the main sources of air pollutant emissions in the regions of central Brazil and the Amazon. Biomass burning associated with deforestation and pasture management releases greenhouse gases and large amounts of particulate matter (Artaxo et al. [2013;](#page-17-1) Liu et al. [2020](#page-19-2)), increasing in the dry period, from July to October (Artaxo et al. [2013](#page-17-1); de Oliveira Alves et al. [2015;](#page-17-2) de Oliveira Galvão et al. [2018](#page-17-3)). The central area of Brazil (including parts of the

Legal Amazon) is not only home to savannas and tropical rainforests (Sisenando et al. [2011](#page-20-2)) but also hosts one of the greatest soy productions in the world (FAO [2022\)](#page-18-2). In the last decades, mineral exploration, industry, agriculture, and livestock have grown throughout this area and have caused an increase in fres used as a pretext for indiscriminate slaughter and burning for the development of agricultural or pastoral lands (Piromal et al. [2008](#page-20-3)). Urban areas have grown in this Brazilian region, where the studied city of Cuiabá is located. These growing urban areas in Brazil and other Latin American countries need further studies on air quality, given that most of the monitoring is concentrated in metropolises such as São Paulo and Rio de Janeiro (Squizzato et al. [2021\)](#page-20-4).

Many health and environmental effects can be associated with the composition of particulate matter (PM). $PM_{2.5}$ and PM_{10} (PM with an aerodynamic diameter smaller than 2.5 and 10 μm, respectively) constituents include organic carbon (OC) and elemental carbon (EC) (Gurjar et al. [2010\)](#page-18-1), potentially toxic metals and metalloids, such as As and Pb, and water-soluble secondary ions, as ammonium, sulfate, and nitrate (Pereira et al. [2017](#page-19-3); Pereira et al. [2023a](#page-19-4)). EC is an important solar radiation absorber and is emitted mainly by the incomplete combustion of fossil fuels, including vehicular exhaust (especially heavy-duty vehicles) and biomass burning (Cao et al. [2021;](#page-17-4) de Oliveira Alves et al. [2015](#page-17-2); Pio et al. [2011\)](#page-19-5). Another important component of atmospheric aerosols is OC, representing up to 70% of the fne aerosols' total mass. It is related to diverse organic species such as aliphatic compounds and polycyclic aromatic hydrocarbons (PAHs), among others (Ding et al. [2009,](#page-18-3) [2019](#page-18-4)). PAHs represent a much studied class of contaminants since some of these species present carcinogenic and mutagenic properties (de Oliveira Galvão et al. [2018](#page-17-3); Vasconcellos et al. [2011\)](#page-20-5).

This study aimed at evaluating seasonal variations of PM_{10} concentration during the years 2008–2014, assessing the chemical composition of PM_{10} , estimating cancer risks resulting from exposure to elements and PAHs, and apportioning the contribution of diferent emission sources using diagnostic ratios, correlations between species, and the PMF receptor model.

Material and methods

Study area and fre maps

The studied site (coordinates: 15° 34′ 11′′ S, 56° 04′ 27′′ W) shown in Figure S1 corresponds to the parking lot of the Secretary of State for the Environment (SEMA) in Cuiabá (Capital of Mato Grosso State, Brazil). The sampling site is surrounded by several main avenues and large parking lots (light and heavy-duty vehicles). The industrial district is about 13 km away. The vegetation around is diverse, with a predominance of the *Cerrado*, similar to savanna biome (Valente et al. [1982\)](#page-20-6). The site is characterized by a tropical super-humid monsoon, with a high average annual temperature above 24 °C and high rainfall (2000 mm per year), concentrated in the wet season (Cavalcanti et al. [2009](#page-17-5)). The fres in the state occur mainly in the dry season, from May to October. Data from heat sources (fres) are detected by the National Oceanic and Atmospheric Administration (NOAA) satellite and are available from the National Institute for Space Research (INPE).

PM₁₀ sampling

One hundred forty-six PM_{10} samples (Table S1) were collected between 2008 and 2014 with high-volume samplers (107 samples in the dry season and 39 samples in the wet season, one sample collected every three days, at a flow of 1.13 m³ min⁻¹). Quartz fiber filters (20 cm \times 25 cm, Millipore, US) were used to collect the samples, which were previously treated at 800 °C for 8 h to eliminate organic contamination. The quartz fber flters were stabilized (50% humidity) and then weighed on an analytical balance. The mass concentrations of PM_{10} were obtained by gravimetry (weighing before and after sampling). Once weighed, they were packed in aluminum foil, labeled, and stored at 5 °C until analysis (Boonyatumanond et al. [2007](#page-17-6); Caumo et al. [2018](#page-17-7)).

Chemical characterization

To determine the organic carbon (OC) and elemental carbon (EC) content, the thermo-optical methodology detailed in Custódio et al. ([2014](#page-17-8)) and Pio et al. ([2011](#page-19-5)) was followed. The calculation of the uncertainty of this method (less than 5%) was based on the triplicate analysis of the flters. The detection limits were 30 ng m^{-3} for OC and 3 ng m^{-3} for EC. Organic matter (OM) was estimated by multiplying the OC concentrations by a factor of 1.6 (Pio et al. [2008\)](#page-20-7).

Eight water-soluble inorganic species (WSI) were determined (Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, Cl⁻, NO₃⁻, and SO₄²⁻) using the procedure described by Custódio et al. ([2016](#page-17-9)). The determination of these species was carried out using four 9 mm circles cut from the filters and subjected to extraction with 5 mL of Milli-Q ultrapure water under an ultrasonic bath for 15 min. Subsequently, the liquid extracts were fltered through a 0.45 μm pore PTFE flter to remove insoluble particles. The diferent cations and anions were determined using an ion chromatograph (DIONEX, ICS-2500/2000). The method presents detection limits ranging from 0.1 to 1 ng $m⁻³$.

Elemental determination was performed by inductively coupled plasma mass spectrometry (ICP-MS).

Approximately $\frac{1}{8}$ of each filter was acid digested (5 mL HF, 2.5 mL HNO₃, and 2.5 mL HClO₄) by mechanical agitation (5 h, 115 rpm at room temperature). Prior to ICP-MS analysis, samples were fltered through PTFE syringe flters with a pore size of 0.45 μm (Amato et al. [2016;](#page-16-0) Querol et al. [2001](#page-20-8)).

Elements' hazard quotient (HQ), for Mn, Cu, Co, Ni, Cd, and Pb, were calculated with Eqs. (1) (1) , (2) (2) , and (3) (3) and indicate the non-carcinogenic risk of a single contaminant. The hazard index (HI), calculated with Eq. [4](#page-2-3), which represents the total number of non-carcinogenic risks of the diferent contaminants for the three forms of exposure (ingestion, inhalation, and dermal contact) was also estimated (Hu et al. [2012](#page-18-5); Jadoon et al. [2020](#page-18-6); Zhou et al. [2014\)](#page-21-0). HI is a non-cancerous risk due to multiple pathways. If $HI > 1$, it indicates that the metal may represent a non-carcinogenic risk for the public. However, if $HI \leq 1$, it can be concluded that the risk is insignificant. RfD_o is the reference dose and RfC_i reference concentration for inhalation, which means the maximum dose required to avoid an adverse reaction when absorbed, per unit time and per unit weight (Men et al. [2018](#page-19-6); Gao et al. [2013\)](#page-18-7). GIABS is a gastrointestinal absorption factor. SLF is the cancer slope factor, UIR is the metal inhalation unit hazard. RfD_{o} , RfC_{i} , SLF, GIABS, and IUR were downloaded from the US EPA site and provided in Table S2 (EPA [2023\)](#page-18-8).

$$
HQ_{Ingestion} = \frac{DIM_{Ingestion}}{RfDo}
$$
 (1)

$$
HQ_{Inhalation} = \frac{EC_{Inhalation}}{RfCi \times 1000 \,\mu g \, \text{m}^{-3}}
$$
 (2)

$$
HQDermal = \frac{DADDermal}{RfDo \times GIABS}
$$
 (3)

$$
HI = \sum HQ_{(Ingestion/Inhalation/Dermal)}
$$
 (4)

Daily metal intake (DIM) was calculated with Eq. ([5](#page-2-4)), dermal adsorption dose (DAD), with Eq. [\(6](#page-2-5)), and the exposure concentration (EC) , with Eq. (7) (7) (7) , in order to assess exposure through ingestion, dermal contact, and inhalation $(mg kg^{-1} day^{-1})$ (Hu et al. [2012;](#page-18-5) Jadoon et al. [2018](#page-18-9)). Cs is the element concentration (mg kg^{-1}) in PM₁₀ (EPA [2023](#page-18-8)), IR_{ing} is the ingestion rate, EF is the exposure frequency, ED is the exposure duration, BW is the average body weight, AT is the average time of illness development, CF is the conversion factor, IR_{inh} is the inhalation rate, PEF is the particle emission factor, SA is the surface area of the skin exposed to the airborne particles, AF is the dermal adherence factor for the air particulates, and ABS is dermal absorption factor. The values and units of all these parameters are given in Table S3.

$$
DIM_{Ingestion} = \frac{(C_{UCL} \times IR_{ing} \times EF \times ED)}{BW \times AT \times CF}
$$
 (5)

$$
ECInhalation = \frac{(CUCL x IRinh x EF x ED)}{BW x AT x PEF}
$$
 (6)

$$
DAD_{\text{Dermal}} = \frac{(C_{\text{UCL}} \times SA \times AF \times ABS \times EF \times ED)}{BW \times AT \times CF}
$$
 (7)

The incremental lifetime cancer risk (ILCR) was calculated for Cd, Cr, Ni, and Pb with Eqs. [8,](#page-2-7) [9](#page-2-8), and [10.](#page-2-9) In the current study, it is assumed that all metal risks were additive; therefore, it is possible to calculate the cumulative risk of cancer (Eq. [11](#page-2-10)) (Table S3). The tolerable risk for regulatory purposes is in the range of 1×10^{-6} – 1×10^{-4} provided by Jadoon et al. [\(2018](#page-18-9)), Men et al. [\(2018\)](#page-19-6), and Zhang et al. ([2017\)](#page-21-1).

$$
ILCRInsestion = DIM x SLF
$$
 (8)

$$
ILCRDermal = DAD x \left(\frac{SLF}{GIABS}\right)
$$
 (9)

$$
ILCRInhalation = IUR \times EC
$$
 (10)

$$
ILCRTotal = \Sigma ILCR_i
$$
 (11)

The organic material deposited on the flters was extracted by sonication with dichloromethane (80 mL) from circular portions (9 mm in diameter), with three cycles of 20 min. Then, the extract was concentrated to 1 mL in a rotary evaporator (Pereira et al. [2017](#page-19-3)). A glass column containing 3.2 g of silica gel and 1.8 g of alumina was used to separate the diferent classes of compounds in the organic extracts. Two fractions were collected, the frst contained alkanes (40 mL of hexane), and the second, PAHs and derivatives (50 mL of hexane + 50 mL of methylene chloride); then, each fraction was evaporated until 1 mL. The extracts were dried using a low and constant flow of $N₂$ at room temperature (Caumo et al. [2018;](#page-17-7) Křůmal et al. [2013](#page-19-7)). PAHs, nitro-PAHs, and oxy-PAHs were quantifed in a gas chromatograph coupled to a mass spectrometer (GC-MS) (Agilent Technology) equipped with a VF-5ms (30 m \times 0.25 mm \times 0.25 µm) column. The qualitative and quantitative analyses of PAHs and their derivatives were performed using the methodology detailed in de Oliveira Alves et al. ([2015](#page-17-2)). *N*-alkane $(C_{16}-C_{40})$ concentrations were determined using a gas chromatograph with a fame ionization detector (GC-FID, Shimadzu, 2010) equipped with a SH-Rtx-5 column (30 m \times 0.32 mm \times 0.25 mm). Other details are described in Caumo et al. [\(2018\)](#page-17-7).

Fifteen PAHs were quantifed, including fuorene (Flu), phenanthrene (Phe), and anthracene (Ant) with 3 rings;

fuoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), and chrysene (Chry) with 4 rings; benzo[b]fuoranthene (BbF), benzo[k]fuoranthene (BkF), benzo[e]pyrene (BeP), benzo[a] pyrene (BaP), and dibenzo[a,h]anthracene (DahA) with 5 rings; and indeno[1,2,3-cd]pyrene (InP) and benzo[ghi]perylene (BghiP) with 6 rings and coronene (Cor) with 7 rings. These PAHs can be classifed according to their molecular weight: low (3-ring LMW-PAHs), medium (4-ring MMW-PAHs), and high (5, 6, and 7-ring HMW-PAHs). In addition, nine nitro-PAHs and four oxygenated PAHs were determined. They were 9-nitrophenanthrene (9-NPhe), 6-nitrochrysene (6-NChry), 1-nitropyrene (1-NPyr), 4-nitropyrene (4-NPyr), 3-nitrofluoranthene (3-NFlt), 2-nitrofluorene (2-NFlu), 7-nitrobenzo[a]anthracene (7-NBaA), 6-nitrobenzo[a]pyrene (6-NBaP), 5-nitroacenaphthene (5-NAce), 9,10-anthraquinone (9,10-AQ), 9-fuorenone (9-FO), 2-methylanthraquinone (2-MAQ), and benzo[a]anthra-7,12-quinone-(7,12-BAQ).

Analytical standards were used to construct calibration curves to determine analyte concentrations. The recovery percentages for the determined organic compounds varied between 65 and 102%, 69 and 112%, 98 and 114%, and 70 and 99 % for PAHs, nitro-PAHs, oxy-PAHs, and *n*-alkanes, respectively. The linearity of the curve was $(R^2 > 0.99)$ for all compounds.

Benzo[a]pyrene equivalent carcinogenicity and mutagenicity

The benzo[a]pyrene (BaP) carcinogenic (BaP-TEQ) and mutagenic (BaP-MEQ) equivalents were calculated (de Oliveira Alves et al. [2015;](#page-17-2) Jung et al. [2010](#page-18-10)) by multiplying the PAH concentrations and the respective carcinogenicity (TEQ) or mutagenicity (MEQ) potential (Durant et al. [1996;](#page-18-11) Nisbet and LaGoy [1992](#page-19-8); Jung et al. [2010](#page-18-10)), according to Eqs. [12](#page-3-0) and 13. To estimate the BaP equivalent carcinogenicity for nitro-PAHs $(BaP-TEQ_{nitro-PAH})$, their concentrations were multiplied by the respective carcinogenic equivalent factors (TEQ) (de Oliveira Alves et al. [2015](#page-17-2); Jung et al. [2010\)](#page-18-10), as shown in Eq. [14](#page-3-1).

$$
BaP - TEQ = ([BaA] \times 0.1) + ([Chry] \times 0.01) + ([BbF] \times 0.1) + ([BkF] \times 0.1)
$$

$$
+ ([BaP] \times 1) + ([InP] \times 0.1) + ([DBA] \times 5) + ([BghiP] \times 0.01)
$$

BaP − MEQ = ([BaA] × 0.082) + ([Chry] × 0.017) + ([BbF] × 0.25) + ([BkF] × 0.11) + ([BaP] × 1) + ([InP] × 0.31)

$$
+ ([\text{DBA}] \times 0.29) + ([\text{BghiP}] \times 0.19)
$$

$$
BaP - TEQnitro - PAHs = ([1NPyr] \times 0.1)
$$

+ ([4NPyr] \times 0.1)
+ ([6NChry] \times 10) (14)

The incremental lifetime cancer risk (ILCR) was calculated to quantitatively estimate the risk of exposure through inhalation, ingestion, and dermal uptake routes to environmental PAHs that are reported to be carcinogenic and mutagenic by applying the US EPA standard models (Eqs. [15](#page-3-2), [16,](#page-3-3) and [17\)](#page-3-4) (EPA [2011;](#page-18-12) [1993](#page-18-13); Goudarzi et al. [2021](#page-18-14); Yang et al. [2015\)](#page-21-2). CS is the sum of BaP equivalent concentrations of individual PAHs, which were calculated based on the toxic equivalency factors (TEF) listed in Table [2](#page-7-0) (μ g kg⁻¹) (Nisbet and LaGoy [1992\)](#page-19-8), CSF is the carcinogenic slope factor $(mg kg⁻¹ day⁻¹)⁻¹$, BW is the body weight (kg), AT is the average life span (day), EF is the exposure frequency (day year⁻¹), ED is the exposure duration (years), IR_{Inhalation} is the inhalation rate $(m^3 \text{ day}^{-1})$, $IR_{Insection}$ is the soil intake rate (mg day⁻¹), SA is the dermal surface exposure $(cm²)$, AF is the dermal adherence factor (mg $cm⁻² h⁻¹$), ABS is the dermal absorption fraction, and PEF is the particle emission factor $(m^3 \text{ kg}^{-1})$. CSF_{Ingestion}, CSF_{Dermal}, and CSF_{Inhalation} of BaP were taken as 7.3, 25 , and 3.85 (mg kg^{-1} day⁻¹)⁻¹, respectively. These values were determined by the cancer-causing ability of BaP (Goudarzi et al. [2021;](#page-18-14) Minnesota Department of Health [2016;](#page-19-9) Peng et al. [2011](#page-19-10)). Cancer risks were estimated for three age groups: childhood (0–10 years), adolescence (11–18 years), and adulthood (19–70 years) (Table S3).

$$
ILCR_{Ingestion} = \frac{CS \times \left(CSF_{Ingestion} \times \sqrt[3]{\frac{BW}{70}} \times IR_{Ingestion} \times EF \times ED\right)}{BW \times AT \times 10^6}
$$
\n(15)

$$
ILCR_{\text{Dermal}} = \frac{CS \times \left(CSF_{\text{Dermal}} \times \sqrt[3]{\frac{BW}{70}} \times SA \times SAF \times ABS \times EF \times ED \right)}{BW \times AT \times 10^6}
$$
(16)

$$
ILCRInhalation = \frac{CS \times \left(CSFInhalation \times \sqrt[3]{\frac{BW}{70} \times IRInhalation \times EF \times ED} \right)}{BW \times AT \times PEF}
$$
 (17)

Data treatment

(12)

(13)

Diferent diagnostic ratios between PAHs (Fla, Pyr, BaA, BbF, BkF, BaP, BghiP, and InP) are generally calculated to assign the main emission sources (Oliveira et al. [2011](#page-19-11); Pereira et al. [2017\)](#page-19-3). The carbon preference index (CPI) is also a diagnostic source ratio. When applied to *n*-alkanes, it is a proportionality ratio between homologs with an even carbon number and those with an odd carbon number (Eq. [18](#page-3-5)). It indicates whether the *n*-alkanes are of biogenic or anthropogenic origin. Likewise, C_{max} (the most abundant *n*-alkane in the homologous series) provides indication of biogenic or anthropogenic contributions (Caumo [2020](#page-17-10); Simoneit [1984](#page-20-9); Simoneit et al. [1990\)](#page-20-10).

$$
CPI = \frac{\Sigma \text{Concentration of odd carbon homologs}}{\Sigma \text{Concentration of even carbon homologs}} \tag{18}
$$

Fig. 1 Concentrations of PM_{10} collected during the whole period and in the dry and wet seasons (2008–2014)

The enrichment factor (EF) was used to identify the degree to which an element in the aerosol is enriched, by applying Eq. [19](#page-4-0), where C_x/C_{Fe} is the ratio of elements in the PM_{10} and in the crust reported in Lee ([1999](#page-19-12)). The element Fe was used as reference crustal metal to calculate the EFs. EFs below 2 indicate minimal enrichment, between 2 and 5, moderate enrichment, between 5 and 20, significant enrichment, between 20 and 40 very high enrichment, and above 40, extremely high enrichment (Yang et al. [2016\)](#page-21-3).

$$
EF = \frac{\left(C_x/C_{\text{Fe}}\right)_{\text{PM10}}}{\left(C_x/C_{\text{Fe}}\right)_{\text{Crust}}}
$$
\n(19)

In this study, the receptor model positive matrix factorization (PMF) was employed for source apportionment. The US EPA PMF v5 software was applied. The species that retain a signifcant signal were separated from those dominated by noise, following the signal-to-noise (S/N) criterion defned by Paatero and Hopke (2003) . Species with S/N < 0.2 are generally defned as poor variables and removed from the analysis, and species with $0.2 < SN < 2$ are typically defined as weak and weighted variables (increasing the uncertainty by a factor of 3). However, since the S/N is very sensitive to sporadic values above the noise level, the data percentage above the detection limit was used as an additional criterion. A set of 142 samples and 25 chemical species were used as input for the model.

The aerosol composition was examined by means of statistics and correlation analysis using the RStudio Free Software 2013 (Free Software Foundation's GNU General Public License) and Microsoft Excel 2013 (Microsoft Corp. USA). To compare (signifcant diferences) the results obtained in the studied seasons, the Student's *T* test and the Mann-Whitney *U* test were used following the distribution. The distribution of the data was verifed using the Shapiro-Wilk normality test. A signifcance level of 0.05 was used for the statistical tests.

Results and discussion

PM10 concentrations and air mass trajectories

The PM_{10} concentrations in Cuiabá ranged between 1 and 666 μg m⁻³, averaging 70 \pm 66 μg m⁻³ (Fig. [1](#page-4-1)). Comparing the average concentration obtained in this study with the values recommended by the new WHO guidelines [\(2021\)](#page-21-4) (45 μ g m⁻³), the levels were higher in 69% of the samples. On the other hand, the limit of 120 μ g m⁻³ imposed by the Brazilian legislation (CONAMA [2018](#page-17-11)) was exceeded in 58% of the samples.

A mean value of 87 μ g m⁻³ was registered in the dry season, during which 87% of the samples presented values surpassing the WHO guideline. On the other hand, the mean obtained for the wet period was 27 μ g m⁻³, with 16% of the samples above the value recommended by the WHO ([2021](#page-21-4)). The signifcant lower concentrations (Mann-Whitney; *p* < 0.05) found in the wet season may be due to the greater frequency of rains, which favor the wet deposition of the particulate material by washout and rainout processes, keep the soil wet and thus limit dust resuspension, and prevent fres because of the high moisture content of biomass. It has been reported that, in the rainy season, during which natural emissions predominate, the mass concentration of PM_{10} in Amazonian regions ranges from 10 to 30 μ g m⁻³ (Artaxo et al. [2002](#page-16-1); de Oliveira Alves et al. [2015;](#page-17-2) Santanna et al. [2016](#page-20-11)). Artaxo et al. ([2013\)](#page-17-1) obtained a PM_{10} concentration of 57 μ g m⁻³, during a period of strong drought in 2010 in Rondônia. De Oliveira Alves et al. ([2015](#page-17-2)) found a mean of 30 μ g m⁻³ in that site (dry season), between 2011 and 2012. In rural areas of Cuiabá (2004–2005), a concentration of 20 μ g m⁻³ was recorded for the same season. The value obtained in this work $(87 \mu g m^{-3})$ was higher than in those previous studies, but it is lower than that registered during

Fig. 2 Number of fres per year in Mato Grosso and Cuiabá (2008–2018) (INPE, [2022](#page-18-17))

the dry season several years before (100 μ g m⁻³) by Maenhaut et al. ([2002](#page-19-14)). Values also reached high levels (between 15 and 600 μ g m⁻³) during the dry season in Alta Floresta, in the north of Mato Grosso state, and in Rondônia (Artaxo et al. [2002](#page-16-1)). According to Artaxo et al. [\(2002](#page-16-1)), the high concentrations of atmospheric particulate matter during the dry season result from the fres that occur in Alta Floresta and Rondônia, whose smoke spreads over an area of 5 million km². Therefore, the effects of these emissions exceed the local scale and afect regions far from the sources on a regional and global scale.

Fig. [2](#page-5-0) presents the fres reported between 2008 and 2014 in the state and its capital. The annual values exceeded 17,000 fres in Mato Grosso, representing approximately 14% of the total detected in the country during the studied period. Only 0.4% of the fres detected in Mato Grosso correspond to those registered in the Cuiabá municipality during the analyzed period (2008-2014).

The hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model was used to calculate the air mass backward trajectories (96 h) for each sampling period. Similar trajectories were grouped by cluster analysis (Draxler and Hess [1998\)](#page-18-15). Fig. [3b](#page-6-0), c shows that higher concentrations in the two seasons are observed when air masses originated in the southern and eastern sectors, suggesting the infuence of pollution from these regions on aerosol mass loadings in Cuiabá. On August 13, 2014, the PM_{10} concentration was the highest (666 μ g m⁻³). This high value may be related to the huge number of fres registered in Mato Grosso state on that day (6200 fres), 3 to 4 times higher than on the other sampling days (Fig. [3a](#page-6-0)). Fig. [3d](#page-6-0), e shows the average trajectories of the four clusters obtained for the two seasons. For both the dry and wet seasons, the highest PM_{10} loads were associated with air masses from the East and South,

accounting for 61 and 34% of the backward trajectories, respectively. However, in the wet season, air masses coming from the north were also signifcant.

Carbonaceous species, water‑soluble inorganic ions, and elements

The mean concentrations, standard deviations, and ranges of OC, EC, OM, and TC are presented in Table [1.](#page-6-1) OC and EC concentrations ranged, respectively, from 0.1 to 24.7 and from 0.1 to 10.5 μ g m⁻³, representing 9 and 4% of the total PM_{10} mass. During the dry period, the concentration of OC $(6.6 \,\mu g \text{ m}^{-3})$ and EC (2.9 $\mu g \text{ m}^{-3}$) were significantly higher than those obtained in the wet season (Mann-Whitney; *p* < 0.05), but the contribution of these species to PM₁₀ was lower in this period, which may be attributed to a higher share of inorganic constituents in the dry season due to dust resuspension (Alves et al. [2018\)](#page-16-2).

The OC/EC ratio in the present study was 2.6 ± 1.3 (2.6) in the dry season and 2.8 in the wet season, respectively). Values from 2 to 5 are found in urban background atmospheres and may indicate a signifcant contribution from secondary organic aerosol (Pio et al. [2011\)](#page-19-5), while ratios near or less than one may reflect fresh traffic emissions (Alves et al. [2015](#page-16-3); Pio et al. [2011](#page-19-5); Pereira et al. [2023a\)](#page-19-4). Authors such as Amato et al. [\(2016](#page-16-0)) and Pereira et al. ([2017](#page-19-3)) have reported ratios between 1 and 2 for urban environments. Alves et al. ([2015](#page-16-3)) and Gonçalves et al. ([2016\)](#page-18-16) observed that higher values in remote forested locations in the Amazon may be associated with biogenic organic aerosols and biomass burning. Therefore, the values now obtained can be attributed to contributions from secondary aerosols and biomass burning.

Higher EC and OM concentrations in the dry season compared to the wet season are probably a result of emissions

Fig. 3 Number of fres in Mato Grosso in the 12/08/2014–13/08/2014 period. (INPE, [2022](#page-18-17)) (**a**). Plots of backward trajectories as a function of PM10 concentrations (μg m-3) (**b, c**). Cluster with trajectories of air masses (**d, e**)

from fres and agricultural and forestry activities in the southern Amazon basin. On the other hand, the decrease in concentrations in the wet season can be attributed to unfavorable climatic conditions for dust resuspension and dispersion of particulate matter due to heavy rains (Custodio et al. [2019](#page-17-12); Gonçalves et al. [2016;](#page-18-16) Santanna et al. [2016;](#page-20-11) Yamasoe et al. [2000](#page-21-5)).

The water-soluble inorganic species (WSI) determined in this study are shown in Table 2 . Na⁺ was the WSI with highest concentrations. It is well known that $Na⁺$ and Cl⁻ are **Table 2** Total and seasonal concentrations of elements and water-soluble ions (ng m^{-3}) in PM₁₀ for Cuiabá (LD-detection limit)

the main sea spray components (Custódio et al. [2016](#page-17-9)), but both ions can also be incorporated into particulate matter through biomass burning and dust resuspension (Seinfeld and Pandis [2006](#page-20-12)). Cl−/Na+ ratios were below 0.2 in both seasons, rather lower than the 1.8 ratio found in sea salt (Fu et al. [2004;](#page-18-18) Souza et al. [2014](#page-20-13)), corroborating to other sources of sodium and/or the depletion of Cl⁻ (Pereira et al. [2017](#page-19-3)). The other water-soluble species that presented high concentrations were K^+ and Ca^{2+} , being slightly higher during the dry season. K^+ is found in biomass burning emissions (de Oliveira Alves et al. [2015](#page-17-2); Vasconcellos et al. [2007\)](#page-20-14) and soil resuspension (Amato et al. [2016](#page-16-0); Pereira et al. [2017](#page-19-3)). On the other hand, Ca^{2+} is associated with soil resuspension (Castanho and Artaxo [2001](#page-17-13); Othman et al. [2021\)](#page-19-15).

The relatively high concentrations of SO_4^2 and NO_3^- in the two seasons may be related to a contribution of secondary formation from anthropogenic-emitted gaseous precursors (industrial activities and vehicle emissions) (Pereira et al. [2017](#page-19-3); Vasconcellos et al. [2011](#page-20-5)) (Table [3](#page-8-0)). Furthermore, higher year-round temperatures may reduce the formation and relative contribution of particulate nitrate in the studied site (Ianniello et al. [2011](#page-18-19)). The low molar concentrations of NH_4^+ during the studied period (1.2 nmol m^{-3}) may indicate that less than 2 % of H₂SO₄ could be

neutralized by ammonia. When the molar ratio $[NH_4^+]$ / $[SO_4^2]$ is higher than 2, excess NH_4^+ may indicate that $HNO₃$ may be also neutralized by ammonia (Sharma et al. [2016](#page-20-15)). Due to low ammonium concentrations, the neutralization of these acids could be carried out mainly by aerosols of carbonated minerals coming from the soil, especially in the dry season. The ammonium availability index (J) is calculated as follows:

$$
J = \frac{\left[\text{NH}_4^+\right]}{2 \times \left(\left[\text{SO}_4^{2-}\right]) + \left(\left[\text{NO}_3^{-}\right]\right)}\tag{20}
$$

in percent related to the amount of ammonia available to neutralize acids. Considering ammonia as the only basic component of PM capable of neutralizing these acids, the *J* index can be used to estimate the acidity of the aerosol (Singh et al. [2021\)](#page-20-16). The very low *J* index in the present study (below 2%) may indicate that the aerosol is considerably acidic throughout the campaign.

The WSI presented a larger contribution to the mass of PM_{10} in the dry season (22%) compared to the wet season (11%), which may be associated with the greater number of fres and enhanced dust resuspension in the most arid period (Artaxo et al. [2002](#page-16-1); Martin et al. [2010](#page-19-16)). Na⁺, SO₄²⁻,

Table 3 Total and seasonal element diagnostic ratios for Cuiabá

Ratio	Total	Dry season	Wet season
Fe/Cu	32	34	15
Fe/Ca^{2+}	12	13	
EC/Cu	11	11	

 $NO₃$ ⁻, Ca²⁺, and K⁺ showed significantly higher concentrations (Mann-Whitney; $p < 0.05$) during the dry season and together are often associated with crustal and soil resuspension sources (Pereira et al. [2017](#page-19-3)), apart from secondary formation for SO_4^2 and NO_3 . The other species presented less diference when compared to the wet period.

Overall, the most abundant elements were $Fe > Cu > Sr$ $> Mn > Rb > Pb$. This profile is similar to that observed in Latin American urban sites such as São Paulo, Lima (Perú), and Medellín (Colombia) in the last decades (La Colla et al. [2021;](#page-19-17) de Oliveira Alves et al. [2020;](#page-17-0) Pereira et al. [2019](#page-19-18); Pereira et al. [2017](#page-19-3)). The predominance of elements such as Fe and Cu have been associated with emissions from vehicles powered by ethanol and gasohol, widely used in Brazil (Brito et al. [2013](#page-17-14)). These elements have also been associated with non-exhaust sources (brake abrasion and road dust resuspension) (Thorpe and Harrison [2008\)](#page-20-17). Pb emissions were recently linked to the Brazilian HDV fleet (Pereira et al. [2023a](#page-19-4)). Fe and Cu have been related to engine corrosion that increases with the use of ethanol fuel in Brazilian LDVs, while Cu is also present in ethanol (Ferreira da Silva et al. [2010](#page-18-20); Pereira and Pasa [2005\)](#page-19-19). Another abundant element, strontium has been associated with road dust in the coarse mode (Behera et al. [2015](#page-17-15); Pereira et al. [2019\)](#page-19-18). rubidium may be associated with soil and biomass burning emissions (Saide et al. [2020](#page-20-18); Massimi et al. [2020](#page-19-20)).

Enrichment factors are displayed in Fig. [4](#page-8-1). Overall, Be, V, Mn, Co, and Ni presented minimal enrichments. Some of these species, such as V and Ni, are often attributed to anthropogenic sources (e.g., fuel combustion), but showed low EFs here, which may be due to the regional characteristics of the soil. Mn is abundant in the crust (Lee [1999\)](#page-19-12) and is therefore often associated with dust resuspension. However, it has also been related to vehicular sources (Pant and Harrison [2013\)](#page-19-21). Pb, Cu, and As presented signifcant to very high enrichments. Copper has been described as an element of LDV emissions in Brazil (Brito et al. [2013](#page-17-14)), while As has multiple sources (Hedberg et al. [2005\)](#page-18-21). Arsenic-rich particles have also been found in road dust afected by agricultural activities, which can release this element by livestock dips, pesticide application, organic manure, and fertilizers (Candeias et al. [2020;](#page-17-16) Punshon et al. [2017\)](#page-20-19). Cadmium was extremely enriched and often originated from industrial sources (e.g., metal smelting, electroplating, and mining) (Zhong et al. [2020](#page-21-6)). The study of Csavina et al. [\(2011](#page-17-17)) associated the presence of toxic elements such as As, Cd, and Pb, to mining activities. In the dry season, overall, lower EFs were observed, suggesting a higher contribution of soil resuspension.

The diagnostic ratios between the elements are presented in Table [3](#page-8-0). The average Fe/Cu ratio was 31, higher than that observed in a tunnel study in São Paulo in 2018 (4 and 9 for the Jânio Quadros and Rodoanel tunnels) (Pereira et al. 2023a), suggesting a greater infuence of soil resuspension for iron. The observed values are also higher than those attributed to brake wear debris in dynamometer studies from two decades ago (Fe/Cu = 14) (Sanders et al. 2003) and in an urban road tunnel in Portugal (Fe/ $Cu = 21$) (Pio et al. [2013](#page-20-21)). The Fe/Ca ratio (considering Ca^{2+}) was, on average, 12. A Fe/Ca value of 20 was documented for emissions from

Fig. 4 Total and seasonal element enrichment factors for Cuiabá

Table 4 Non-cancerous hazard or risk index (HI) for each metal in Cuiabá (dry and wet seasons)

light vehicles (Pereira et al. [2023b](#page-19-22)), while a ratio of 1.38 was pointed out as typical of crustal materials (He et al. [2008](#page-18-22)). A mean EC/Cu ratio of 11 was obtained, which is close to that observed in tunnels for LDVs (varying between 5 and 8), whereas values above 80 were reported for emissions from HDVs (Pereira et al. [2023a\)](#page-19-4).

In all the studied periods in Cuiabá (dry and wet seasons) and for the three groups studied, the values obtained for the hazard quotients (HQ) were higher for dermal contact, followed by ingestion and inhalation (Table S4). Hazard quotients for elements were in the following order, for dermal contact $Mn > Cd > Pb > Cu > Ni > Co$, for ingestion Pb > $Cu > Cd > Mn > Co > Ni$, and for inhalation $Mn > Cd >$ $Ni > Co > Cu > Pb$ (Table S4). The non-cancer hazard or risk index (HI) of all quantifed elements (Cu, Mn, Pb, Co, Ni, and Cd) was lower than 1, indicating negligible non-carcinogenic risk for residents in Cuiabá (Table [4](#page-9-0) and Fig. [5a](#page-9-1)).

Cancer risks from ingestion, inhalation, and dermal due to exposure to PM_{10} -bound Cu, Cd, Co, Mn, Ni, and Pb are summarized in Table S5. The mean cancer risks by all routes of exposure in PM_{10} for elements are presented in Table S5 and Fig. [5b](#page-9-1). The ILCR values for the three exposure routes and the total for all ages were below 10^{-6} and considered insignifcant by the US EPA.

PAHs, nitro‑PAHs, and oxy‑PAHs

On average, the total PAH concentration (ΣPAHs) was higher in the dry season (39 ng m⁻³) than in the wet sea-son (29 ng m⁻³) (Fig. [6\)](#page-10-0). The most abundant compound for both seasons was BkF, representing 16 and 21% of ΣPAHs, respectively. The second most abundant in the dry season was Chry, with a mean of 5.8 ng m^{-3} , followed by BeP > $InP > BbF > DahA$. In the wet season, the second most

Fig. 6 Concentrations of PAHs studied in the dry and wet seasons

abundant PAH was Chry with a mean of 5.8 ng m-3, followed by BeP, DahA, and InP. Thus, similar profles were observed for the major compounds in both seasons. Most of them are HMW compounds (except Chry), tend to be concentrated in the particulate phase (Kim et al. [2013](#page-19-23)) and are dominant in emissions from gasoline-powered LDVs (Pereira et al. [2023a;](#page-19-22) Ravindra et al. [2008](#page-20-22)). As observed in a study performed at the Metropolitan Area of São Paulo in 2018, the source profles of organic carbon were characterized by four-ring PAHs (Chry and Pyr) and five-ring PAHs (BeP and BaP), while in a more HDV-impacted tunnel, higher LMW-PAH abundances were observed (Pyr, Flt, and Phe) (Pereira et al. [2023a](#page-19-4), [2023b](#page-19-22)). Flu, Phe, and Pyr have been documented as major PAHs in emissions from biomass burning, while Chry, DahA, and BaA have been linked to stationary sources (Magalhães et al. [2007\)](#page-19-24).

The largest contributions to total PAHs in both seasons were from 5-ring PAHs (51%), followed by the 4-ring PAHs (28%), while the lowest contributions were from 6- and 3-ring PAHs, accounting for 11% and 10%, respectively. LMW and HMW compounds represented 37% and 63% of ΣPAHs, respectively. This may refect the predominance of pyrogenic sources (Zhang et al. [2008](#page-21-7)).

In a study carried out in Porto Velho, a city located in the western Amazon, total concentrations of 3 and 1 ng m-3 were observed in the dry and wet seasons (de Oliveira Alves et al. [2015](#page-17-2)), an order of magnitude lower than those found in the present study. Diferences between PAH concentrations may vary according to the sampling site, the geography of the area, the meteorological conditions, and the emission sources. BaA, Chry, BbF, BkF, and BaP were among the most abundant PAHs reported by de Oliveira Alves et al.

([2015](#page-17-2)). In another study by Vasconcellos et al. ([1998\)](#page-20-23) in an Amazon Forest area (Alta Floresta, Mato Grosso), the highest concentrations were obtained for BkF, BeP, BghiP, InP, and Chry.

Table [5](#page-11-0) shows the concentration range of the nitro-PAHs investigated. According to previous results, concentrations of nitro-PAHs range from 2 to 1000 times lower than those of their precursor PAHs (Bamford and Baker [2003](#page-17-18)). 4-NPyr was the species with the highest concentrations all year round, reaching up to 1.2 ng m⁻³ in both seasons. This compound presents greater carcinogenic potential than BaP (IARC [2010\)](#page-18-23). 1-NPyr, which is highly mutagenic (IARC [2010\)](#page-18-23), achieved concentrations up to 0.8 ng m^3 . 6-NBaP and 6-NChry, compounds emitted by diesel and gasoline combustion (Ringuet et al. [2012\)](#page-20-24), were also identifed.

The sum of oxy -PAH was 3.8 ng m⁻³ in the dry season, period during which the highest concentrations were recorded. Of the four oxy-PAH determined, 2-MAQ showed the highest values in both seasons, reaching a peak concentration of 2.4 ng m^{-3} , followed by 9,10-AQ and 9-FO. This compound is suspected of being carcinogenic to humans and is related to biomass burning (Gori et al. [2009\)](#page-18-24). Oxy-PAHs are not uniquely produced during incomplete combustion processes, but are also formed when PAHs undergo photochemical reactions with hydroxyl radicals, nitrate radicals and ozone (de Oliveira Alves et al. [2020](#page-17-0); Chen and Zhu [2014;](#page-17-19) Finlayson-Pitts and Pitts [1999\)](#page-18-25). Higher proportions of oxy-PAHs have also been attributed to the emissions of diesel-powered HDVs in a tunnel study in São Paulo (Pereira et al. [2023a\)](#page-19-4).

Values obtained for BaP-TEQ, BaP-MEQ, and BaP- $TEQ_{nitro-PAHs}$ in the dry and wet seasons for the studied site

Table 5 Range and frequency of detection of PAH derivatives in Cuiabá.

Compound	Season		
	Dry	Wet	
	$(ng m-3)$		
Nitro-PAHs			
$2-Flu$	$0.2 - 2.2(94%)$	$0.6 - 1.2(82%)$	
9-NPhe	$0.3 - 2.9(95%)$	$0.2 - 2.7(97%)$	
$3-NFlt$	$0.6 - 2.7(93%)$	$0.4 - 1.2(95%)$	
4-NPyr	$0.8 - 2.4(94%)$	$1-1.6(95%)$	
1-NPyr	$0.4 - 1.4(96\%)$	$0.2 - 1.2(95%)$	
6-NChry	$0.6 - 2.2(88%)$	$0.7 - 1.7(85%)$	
7-NBaA	$0.1 - 2.6(100\%)$	$0.6 - 1.5(92\%)$	
6-NBaP	$0.5 - 1.7(94%)$	$0.3 - 1.7(92\%)$	
5-NAce	$0.2 - 1.7(96%)$	$0.2 - 1.1(92%)$	
Oxy-PAHs			
$9,10$ -AO	$0.5 - 1.7(94%)$	$0.3 - 1.7(92\%)$	
$9-FO$	$0.2 - 1.7(96%)$	$0.3 - 1.1(92\%)$	
2-MAO	$0.4 - 2.3(98%)$	$0.2 - 2.1(92\%)$	
$7,12-BAO$	$0.3 - 1.3(96\%)$	$0.4 - 1.1(95%)$	

are presented in Fig. [7.](#page-11-1) Estimated ILCR values for inhalation, dermal, and ingestion exposure routes are shown in Fig. [8](#page-12-0). In the whole period, the values were 19, 6, and 10 ng m^{-3} for BaP-TEQ, BaP-MEQ, and BaP-TEQ_{nitro-PAHs}, respectively. The concentrations of BaP-TEQ and BaP-MEQ in the dry season were higher than those in the rainy season, showing significant differences (Mann-Whitney; $p < 0.05$), which can be attributed to climatic conditions less favorable to the dispersion of pollutants and the greater infuence of biomass burning. The concentrations of BaP-TEQ_{nitro-PAHs} were similar in both seasons (Mann-Whitney; $p > 0.05$).

The values obtained for BaPeq in this work were higher than those obtained by Gregoris et al. ([2014\)](#page-18-26), in an Italian region in 2009 and 2012. The PAHs that most contributed to the calculated BaP equivalents (carcinogenic and mutagenic) were DahA, BaP, and InP, including species more associated with the emissions of LDVs (Pereira et al. [2023a](#page-19-4)).

The total ILCR for children, adolescents, and adults were 1.4×10^{-4} , 2.2×10^{-3} , and 1.6×10^{-4} , respectively. Regardless of age, dermal exposure is the route that presents the highest risks. Zhang et al. [\(2019\)](#page-21-8) classified ILCR $< 1.0 \times 10^{-6}$ as a very low cancer risk, 1.0×10^{-6} < ILCR < 1.0×10^{-4} low risk, 1.0 $\times 10^{-4}$ < ILCR < 1.0×10^{-3} moderate risk, 1.0×10^{-3} < ILCR $< 1.0 \times 10^{-1}$ high risk, and ILCR $> 1.0 \times 10^{-1}$ very high risk.

Total ILCR values were higher in the dry season than in the wet season. Total ILCR values higher than those suggested by the USEPA (1.0 \times 10⁻⁶ to 1.0 \times 10⁻⁴) were recorded in both seasons. This is an indicator that the daily inhalation, ingestion, and dermal contact dose of PAHs bound to PM_{10} particles and cancer risks for children, adolescents, and adults in Cuiabá are well above tolerable levels. Zhang et al. ([2019\)](#page-21-8), in a study in Wuhan (China), reported values much higher than those obtained in this work.

Concentration of n‑alkanes

The predominant aliphatic species during the entire period studied were C₂₉ (24 ng m⁻³), C₃₀ (23 ng m⁻³), C₂₈ (23 ng m^{-3}), and C_{27} (19 ng m⁻³). Higher concentrations of long chain odd n-alkanes (C_{27} , C_{29} , C_{31} , and C_{33}) are indicative of emissions from vegetable waxes (Ding et al. [2009](#page-18-3); Simoneit et al. [1990\)](#page-20-10), which may be related to biogenic emissions and/ or biomass burning (Simoneit [2002](#page-20-25)). The sum of n-alkanes between C₁₆ and C₂₅ (lighter) was 59 ng m⁻³ (24% of the total), while the heaviest homologs $(C_{26}-C_{40})$ totaled 179

Fig. 8 Cancer risk due to PAHs exposure in the PM_{10} collected in the capital of Mato Grosso (Cuiabá)

ng m-3 (76% of the total). *n*-Alkanes with lower molecular weight $(C_{20}-C_{26})$ are more associated with the exhaust of vehicles (Alves et al. [2020\)](#page-16-4). The molecular distribution of the *n*-alkanes investigated here in the dry and wet seasons is shown in Fig. [9.](#page-13-0)

The concentrations of the homologs followed the same behavior in the two studied seasons, except for C_{40} , whose concentration was, on average, higher in the wet season. C_{30} was the homolog with highest concentrations in both periods, and the sum of the $C_{26}-C_{40}$ concentrations was higher in the dry season compared to the rainy period. In the dry season, CPI was 1.4, a value higher than that found in the wet period (1.0). The CPI values were similar to those obtained previously (0.9 and 1.4) in periods of intense and moderate biomass burning, pointing to an increase of biogenic emissions in the wet period (de Oliveira [2014\)](#page-17-20).

Source apportionment

PAH diagnostic ratios

The diagnostic ratio between low and high molecular weight (LMW-PAHs/HMW-PAHs) can be infuenced by several factors (pyrogenic and petrogenic sources, diesel and gasoline exhausts, and the gas-particle partition of PAHs). The values obtained for this ratio in the two seasons were below 1, indicating the contribution of pyrogenic sources (Zhang et al. [2008](#page-21-7)) (Table [5\)](#page-11-0). Lower LMW-PAHs/HMW-PAHs can also be attributed to a higher contribution of gasoline

compared to diesel. The study of Pereira et al. ([2023a\)](#page-19-4) found tenfold lower ratios for a gasoline-impacted tunnel (0.7) compared to a diesel and gasoline-impacted road underground infrastructure (7.5). Therefore, the ratios found here refect mixed contributions from pyrogenic and gasoline exhaust emissions.

Other diagnostic ratios were also studied to assess the main sources of PAHs, such as InP/(InP+BghiP), BaA/ (BaA+Chry), Flt/(Flt+Pyr), BaP/BghiP, and Ant/(Ant+Phe) (Table [6](#page-13-1)). The results for these ratios were similar in both seasons, indicating pyrogenic emissions, corroborating the fact that the urban site is often infuenced by biomass burning aerosols.

A parameter that can diferentiate the contribution from primary sources is the total index (Eq. [18](#page-3-5)). It is defned as the sum of some previously calculated diagnostic ratios. A total index (TI) higher than 4 denotes that the PAHs were generated by high-temperature processes (Bootdee et al. [2016](#page-17-21)).

$$
TI = \frac{\text{Flt}/(\text{Flt} + \text{Pyr})}{0.4} + \frac{\text{Ant}/(\text{Ant} + \text{Phe})}{0.1} + \frac{\text{BaA}/(\text{BaA} + \text{Chry})}{0.2} + \frac{\text{InP}/(\text{InP} + \text{BghiP})}{0.5}
$$
(21)

The total indexes for the dry (10) and wet (9) seasons in Cuiabá were found to be much higher than 4. This result indicates that PAHs were emitted in high-temperature combustion processes. In general, all the diagnostic ratios studied suggested that coal, wood, and oil burning, as well as vehicular emissions, are the primary sources of particlebound PAHs in the studied site.

Table 6 Diagnostic molecular reasons for PAHs at the two seasons

a Zhang et al. ([2008\)](#page-21-7)

^bKatsoyiannis et al. ([2011\)](#page-19-25)

^cYunker et al. ([2002\)](#page-21-9)

^dAkyüz and Çabuk [\(2010](#page-16-5))

e Ravindra et al. ([2008\)](#page-20-22)

^fde la Torre-Roche et al. ([2009\)](#page-17-22)

Polar plots and correlations between species

Polar plot graphs were constructed with the concentration values of PM_{10} , OC, EC, water-soluble species, elements, PAHs, and wind speed and direction. Correlations were also made between the concentrations of the aforementioned species (Figures S2 and S4 (dry season) and Figures S3 and S5 (rainy season)).

OC was correlated with EC in the two seasons $(R^2 = 0.64)$ and 0.73). The slightly lower correlation for the wet period

may indicate diferent emission sources, atmospheric reaction pathways, or removal processes between seasons.

The dry season showed a good correlation between almost all the water-soluble inorganic species that were determined. The low correlation between Na⁺ and Cl⁻ (R^2) $= 0.34$) during the wet season could be explained by the distance of the sampling site from the Atlantic Ocean and by the contribution of $Na⁺$ from sources such as soil and biomass burning (Custodio et al. [2019\)](#page-17-12). Biomass burning is one of the most important sources of Cl⁻ containing species in the atmosphere (Lobert et al. [1999](#page-19-26)). In Figures S2 and S3, it can be observed that these species show diferent wind dependent patterns, and the trajectories of the air masses are mainly from the continent (Figs. [4](#page-8-1)d, e). $Na⁺$ presented a high correlation with $NO₃⁻ (0.8)$, which can be related to the formation of $NaNO₃$, associated with the depletion of chloride and sea-spray aging (Cesari et al. [2018\)](#page-17-23).

During the two periods studied it was possible to observe moderate to strong correlations between SO_4^2 and $NO_3^$ with EC, OC, K^+ , Na⁺, Ca²⁺, and Mg²⁺ (Figures S4 and S5). In the dry season, these correlations were higher, pointing to a common origin associated with the same wind direction (Figures S2 and S3). Coarse mode nitrate and sulfate can result from heterogeneous reactions of $HNO₃$ and H_2SO_4 with alkaline surfaces of soil particles (Tang et al. [2016;](#page-20-26) Wang et al. 2016). The interaction of $SO₂$ and concrete or calcareous (e.g., from construction sources) may lead to the formation of sulfate particles containing Ca and Na (Bourotte et al. [2006\)](#page-17-24). During the wet season, NH_4^+ is well correlated with NO_3^- and relatively well correlated with SO_4^2 ⁻, suggesting an increase in the interaction of NH₃ and $HNO₃$ in this season (Ianniello et al. [2011](#page-18-19)). The correlations of secondary formation species appear to be more predominant in the wet season, under higher relative humidity. The formation of sulfate and nitrate in clouds and fog droplets may be related to the heterogeneous aqueous transformation of sulfur and nitrogen oxides under high relative humidity (RH) (Huang et al. [2016\)](#page-18-27). The neutralization of the acids $HNO₃$ and $H₂SO₄$ may be rather linked to carbonated minerals since the molar ratio $[NH_4^+]/[SO_4^2]$ is much lower than 2.

The correlations between Mg^{2+} and Ca^{2+} were significant in both seasons and presented similar patterns (Figures S2, S3, S4, and S5). These species showed signifcant correlations with both EC and K^+ , which could indicate that they are emitted by similar sources, probably by the resuspension of soil and biomass burning emissions, that may increase in dry periods (Custodio et al. [2019](#page-17-12)) and can also have the same removal processes. In the dry season, most of the elements presented high correlations with each other (*r* > 0.7), suggesting similar sources, or sources that increase with similar meteorological conditions. Ca^{2+} was correlated with Mn and Fe, which are present in the crust and also in vehicular emissions (Pereira et al. [2023a;](#page-19-4) Lee [1999\)](#page-19-12). These species correlated with EC and OC $(r > 0.7)$, suggesting that species anthropogenically emitted can settle onto the soil and then be resuspended along with crustal material.

Depending on the season, PAHs showed diferent patterns (Figure S2 and S3), especially when lighter PAHs (Flu, Phe, Ant, Flt, and Pyr) are compared with heavier PAHs (InP, DBA, and BghiP). Correlations between PAHs and other species were higher in the dry period than in the wet season, refecting diferent emissions sources and meteorological conditions.

PMF receptor model

Source apportionment of the samples $(n = 120)$ was carried out by applying the PMF receptor model. Twenty-two chemical species were set as "strong" variables, vanadium was set as "weak" variable, and the others were set as "bad" and excluded from the model, as recommended by Paatero and Tapper [\(1994\)](#page-19-27). The concentration of PM_{10} particulate material was set as the total variable. Three- to eight-factor runs were made, with the fve-factor run presenting the best results (base model displacement and bootstrap method, Tables S6 and S7). Extra uncertainties of 5% were added to avoid the discard of poor-quality data, as reported by Paatero and Hopke (2003) (2003) . Profiles of the source contributions $(\%)$ to PM_{10} obtained in the PMF analyses and the polar plots and seasonal distribution of the PMF factor contributions are shown in Fig. [Fig. 10.](#page-15-0)

Factor 1 contributed to only 8% of PM_{10} and presented loadings of Cd, Cs, and lesser amounts of Pb, Rb, and Li. As, Cd, and Pb have been related to mining activities (Csavina et al. [2011\)](#page-17-17). High Li, Sr, and Rb loading have been previously linked to urban works (Amato et al. [2009\)](#page-16-6). Thus, this factor seems to be related to mining or dust generating activities (e.g., urban works) (MI), it increases with winds coming from areas in the outskirts with exposed soil and constructions (west) and mining areas in the surroundings (northeast), although it also increases with winds coming from the city center (south). This infuence should be further investigated.

Factor 2 was one of the most dominant and was attributed to vehicular exhaust (VE), presenting loadings of great amounts of OC and EC, and also relatively lower amounts of Ca^{2+} , SO_4^2 , Fe, Ba, Ga, and V. It accounted for 33% of the PM_{10} concentrations, increasing with southwestern winds that passed through the downtown area. Factor 3 is not clear, as it may be related to soil resuspension (SR) due to the presence of species found in trace amounts as Ba, Sr, Li, and Rb (Calvo et al. [2013](#page-17-25)), but also presents SO_4^2 , which is mostly related to secondary formation and may be due to the reaction of secondarily produced H_2SO_4 and the carbonated minerals in the soil; however, barium is often found in the abrasion of

brake pads (Thorpe and Harrison [2008](#page-20-17)). This factor accounts for only 4% of PM_{10} and increases with winds coming from the southeast.

Factor 4 was related to road dust resuspended by traffic (RD), accounting for 23% of PM_{10} . It included species emitted in the exhaust of vehicle tailpipes, as well as in particles from brake and tire wear (non-exhaust emissions), such as Fe, V, Mn, Ni, and As (Pant and Harrison [2013\)](#page-19-21). Additionally, species related to road dust resuspension, such as Sr, and Rb, were also part of factor 4. OC and EC were more associated with Factor 2, rather than Factor 4, which may suggest lower vehicle exhaust component in the latter. This factor contribution increases with winds coming from the northeast, where there is a main road connecting to the outskirts.

Factor 5 was associated with biomass burning (BB) due to the presence of K^+ and OC, however nitrate was also found.

 $NO₃$ and $K⁺$ have been associated with biomass burning plumes in the Amazon area (Gonçalves et al. [2016\)](#page-18-16). Potassium and nitrate was also related to agricultural activities in the state of São Paulo (Allen et al., [2010](#page-16-7)). Nitrate may also be related to NO formed in the burning conditions (Vicente et al. [2013\)](#page-21-11). The presence of calcium suggests that it is also mixed with a soil source (Pereira et al. [2017\)](#page-19-3). It accounted for 32% of PM_{10} and together with vehicular emissions were major sources. Combustion sources as those may play an important role in both oxidative stress and genotoxicity (Guascito et al. [2023\)](#page-18-28). Diferently from what was observed in studies performed in São Paulo, it was not possible to observe a separated secondary formation factor (Serafeim et al. [2023](#page-20-27); Pereira et al. 2017). NO_3^- and SO_4^2 ⁻ are likely more related to soil resuspension in the present study as $HNO₃$ and $H₂SO₄$ may react with carbonated minerals in the soil, as pointed in "Polar plots and correlations between species." No industrial sources were identified; this type of source is difficult to be quantified by receptor models, with a high variability (Belis et al. [2020](#page-17-26)).

Conclusions

This study presented the results obtained for the concentration of PM_{10} and its chemical characterization, which includes diferent classes of compounds such as OC, EC, WSII, PAHs and derivatives, and n-alkanes in a region impacted by biomass burning, traffic emissions, and industrial and agricultural activities. Higher concentrations of OC, EC, and WSII were registered in the dry season, possibly due to biomass burning. PAHs, nitro-PAHs, and oxy-PAHs showed a similar behavior in the dry and rainy seasons. However, the concentrations were higher in the dry season, during which molecular weight compounds predominated. For n-alkanes, there were no signifcant diferences between seasons. According to the results of PAH diagnostic indices and the correlations between all determined species, the main pollutant emissions sources were biomass burning (wood, coal, and grass), vehicles, and soil resuspension. The lifetime cancer risks (inhalation, dermal, and ingestion) due to PAHs' exposure estimated for the two seasons far exceeded the value stipulated by the WHO, showing that children, adolescents, and adults in Cuiabá are exposed to concentrations well above the tolerable levels. The results shown by the PMF model pointed to biomass burning and vehicular emissions as the major sources of PM_{10} . This work provides knowledge about the sources of aerosols in a less studied region highly impacted by anthropogenic activities, which often presents high carcinogenic and mutagenic potential risks for human health, especially for the most vulnerable groups.

Supplementary Information The online version contains supplementary material available at<https://doi.org/10.1007/s11869-023-01467-1>. **Acknowledgements** The authors acknowledge the Ministry of the Environment of the State of Mato Grosso (SEMA) for the samples (especially to Sérgio Batista de Figueiredo).

Funding Yendry Jomolca Parra thanks CNPq (project: 155685 / 2016-3, Project 870031 / 2003-1) for the grants. Guilherme M. Pereira thanks FAPESP for grants #16/18438-0, #18/07848-9, and 19/01316- 8. The fnancial support to CESAM by FCT/MCTES (UIDP/50017/2 020+UIDB/50017/2020+ LA/P/0094/2020), through national funds, is also acknowledged. Pérola C. Vasconcellos thanks CNPq (grants 301503/2018-4).

Data Availability The datasets generated during and/or analyzed during the current study are available upon request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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