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HIGHLIGHTS

- PM_{10}, OC, EC, anhydrous sugars and PAHs were quantified in Western Amazonia.
- Results are representative of the deforestation arc, home of over 10 million people.
- Factor analysis identified Biomass Burning, Fossil Fuel and Mix sources.
- During the dry season, the lung cancer risk largely exceeded the WHO guideline.

ARTICLE INFO

ABSTRACT

The Brazilian Amazon represents about 40% of the world's remaining tropical rainforest. However, human activities have become important drivers of disturbance in that region. The majority of forest fire hotspots in the Amazon arc due to deforestation are impacting the health of the local population of over 10 million inhabitants. In this study we characterize western Amazonia biomass burning emissions through the quantification of 14 Polycyclic Aromatic Hydrocarbons (PAHs), Organic Carbon, Elemental Carbon and unique tracers of biomass burning such as levoglucosan. From the PAHs dataset a toxic equivalence factor is calculated estimating the carcinogenic and mutagenic potential of biomass burning emissions during the studied period. Peak concentration of PM_{10} during the dry seasons was observed to reach 60 $\mu g\ m^{-3}$ on the 24 h average. Conversely, PM_{10} was relatively constant throughout the wet season indicating an overall stable balance between aerosol sources and sinks within the filter sampling resolution. Similar behavior is identified for OC and EC components. Levoglucosan was found in significant concentrations (up to 4 $\mu g\ m^{-3}$) during the dry season. Correspondingly, the estimated lung cancer risk calculated during the dry seasons largely exceeded the WHO health-based guideline. A source apportionment study was carried out through the use of Absolute Principal Factor Analysis (APFA), identifying a three-factor solution. The biomass burning factor is found to be the dominating aerosol source, having 75.4% of PM_{10} loading. The second factor depicts an important contribution of several PAHs without a single source class and therefore was considered as mixed sources factor, contributing to 6.3% of PM_{10}. The third factor was mainly associated with fossil fuel combustion emissions, contributing to 18.4% of PM_{10}. This work enhances the knowledge of aerosol sources and its

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1. Introduction

The Brazilian Amazon embraces contains about 40% of the world's remaining tropical rainforest, covering 5.5 million km^2, corresponding to 61% of the area of Brazil. It is the largest and most species-rich biome of the planet. This region plays vital roles in maintaining biodiversity, regional hydrology and climate equilibrium, and terrestrial carbon storage (Malhi et al., 2008; Soares-Filho et al., 2006). However, agricultural expansion and climate variability have become important agents of disturbance in the Amazon basin (Davidson et al., 2012).

Fires have been consistently used in the Amazon as a clearing tool used to burn trees from recently cut forests so that agricultural or pastoral lands may be developed, being a major source of particulate matter (PM) during the Amazon dry season (Artaxo et al., 2013; Ten Hoeve et al., 2012). The majority of forest fire hotspots in the Amazon takes place in the deforestation arc, an area of roughly 500 000 km^2, with a population of over 10 million inhabitants (IBGE, 2014). Such large population suffers regularly from high level of pollutants resulting from biomass burning emissions (Andreae et al., 2004; Brito et al., 2014), with significant increase of occurrence of respiratory diseases during these periods (Carmo et al., 2010; Jacobson et al., 2014).

Carbonaceous material, a significant fraction of particle-phase emission from fires (Brito et al., 2014; Kondo et al., 2011), can be classified as organic carbon (OC) and elemental carbon (EC). While OC can be directly emitted to the atmosphere or formed from the oxidation and condensation of organic vapors, EC is primary and emitted from combustion sources. EC is known as an important contributor to radiative heating of the atmosphere (Cabada et al., 2004). An important group of organic compounds found in the atmosphere is composed by Polycyclic Aromatic Hydrocarbons (PAHs). They are emitted from a large variety of sources, including vehicular emissions (Brito et al., 2013; Martins et al., 2012), tobacco smoke (Ding et al., 2008), industrial activities (Lakhani, 2012; Wang et al., 2014) and biomass burning (Alves et al., 2011; De Oliveira Alves et al., 2014). The speciation of PAHs in ambient air is an increasing concern due to their associated carcinogenic and mutagenic potential (Samanta et al., 2002). The US Environmental Protection Agency has listed 16 PAHs as priority pollutants for control, however the health risk posed by PAHs exposure suggests a continuing need for their control through air quality management (Kim et al., 2013). Furthermore, PAHs may overcome large distances affecting sites far from where these pollutants are generated (Ravindra et al., 2008).

Mutagenic and DNA damage effects (Teixeira et al., 2012; Umbuzeiro et al., 2014) of PM are mainly associated to PAHs. A recent study in Greece shows that particles emitted from biomass combustion are more toxic than PM emitted from other sources, in particular to PAH levels. Moreover, higher lung cancer risk was estimated for infants and children (Sarigiannis et al., 2015). Other works assessed the lifetime cancer risks related to contributions of diet and inhalation to the overall PAH exposure of the population of Beijing in China and showed that diet accounted for about 85% of low-molecular-weight PAH (L-PAH) exposure, while inhalation accounted for approximately 57% of high-molecular-weight PAH (H-PAH) exposure of the Beijing population (Yu et al., 2015).

Here we characterize western Amazonia biomass burning emissions through the quantification of 14 PAHs, OC, EC and unique tracers of biomass burning such as Levoglucosan. From the PAHs dataset a toxic equivalence factor is calculated estimating the carcinogenic and mutagenic potential of biomass burning emissions during the period studied. Finally, the use of factor analysis on the dataset allows to not only apportion PM distinct sources affecting the sampling site, but to also characterize these sources in regarding to their PAHs content.

2. Methods

2.1. Site description and sample collection

Filter samples were collected in a governmental reservation located about 5 km north (usually upwind) of Porto Velho, a city in the state of Rondônia, western Amazon, a region with significant land use change since the 1980s. During the South American Biomass Burning Analysis (SAMBBA), which took place during the 2012 dry season period, fine organic aerosols mainly linked with biomass burning emissions, were observed with varying levels of atmospheric oxidation, in agreement with large number of fires distributed in the area (Brito et al., 2014).

The sampling was conducted during two distinct periods: the dry season (August–October/2011) and wet season (November/2011–March/2012). A high volume filter sampler (flow rate of 1.3 m^3 min^{-1}), sampling PM_{10} aerosols into quartz fiber filters, was deployed on the border of a 150 m radius grassland clearance at the southwest corner of 2000 ha of dense forest belonging to governmental reservation. The road that connects Porto Velho to governmental reservation cuts through large pasture areas and a handful of local businesses. No vehicular access is permitted within the biological reservation.

2.2. Instrumentation and analytical methods

Prior sampling, quartz fiber filters were pre-cleaned by heating in an oven at 800 °C for 8 h. Mass concentrations were obtained gravimetrically using an electronic microbalance with a readability of 1 μg (Mettler Toledo, model MX5) in a controlled-atmosphere room where filters were equilibrated for 24 h prior weighing.

OC and EC analysis was performed using thermal–optical transmittance (TOT) (Sunset Laboratory Inc.) (Birch and Cary, 1996). The filters were analyzed according to the EUSAAR2 protocol (Cavalli et al., 2010). The limit of detection to OC and EC were 5 μg cm^{-2} and 1 μg cm^{-2}, respectively.

Monosaccharide anhydrides, levoglucosan, mannosan, and galactosan, commonly used as tracers for biomass burning, were determined by high-performance anion-exchange chromatography with electrospray ionization mass spectrometry detection (HPAEC/ESI-MS). The analytical method is similar to the used in Saarnio et al. (2010), except that the used internal standard was methyl-β-D-arabinopyranoside (Saarnio et al., 2013). To examine the comparability of the great diversity of analytical methods used for analysis of levoglucosan, mannosan and galactosan in ambient aerosol filter samples, it is necessary to arrange intercomparison studies. The method used in this study has been twice

intercompared successfully. The first intercomparison study is published in Yttri et al. (2015).

The PAHs were extracted from the filters with dichloromethane using the Soxhlet apparatus during 24 h and then concentrated on a rotary evaporator. The different fractions were obtained using a silica gel column (2.5 g) and different solvents of increasing polarity following the procedure proposed by Wei et al. (2012). The quantitative and qualitative analyses were carried out by gas chromatography with mass spectrometer (Agilent 7820A). An inert 5% phenyl − methyl column, VF − 5 ms (30 m × 0.250 mm, 0.25 μm film thickness) was used for separation of the compounds and 1 μL of sample was injected in splitless mode. The GC conditions were: 1.3 mL/min helium flow; temperature programme: 80 °C, 4 min, increasing 20 °C/min until 200 °C, then 4 °C/min until 270 °C and 5 °C/min until 280 °C. The injector temperature was set 280 °C, the transfer line to 300 °C and the ion source to 200 °C. The identification and quantification of PAHs were done according to retention times with standard solutions. Calibration curves were prepared with different PAHs concentrations. The correlation coefficients of the calibrate curve for the different PAHs were $R^2 > 0.9996$.

Overall 14 PAHs were detected, as follows: phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PY), retene (RET), benz[a]anthracene (BaA), chrysene (CHRY), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indene[1,2,3-c,d]pyrene (IcdP), dibenz[a,h]anthracene (DahA) and benzo[g,h,i]pyrene (BghiP).

The results of both the recovery and repeatability of the analytical procedure for all the PAHs show that the quality control was very effective. Recoveries of the PAHs were determined using EPA 525 PAH Mix A (48953-U, Sigma), Benzo(e)pyrene (442475, Sigma) and Retene (483-65-8, Chemservice). The total recovery efficiencies of the compounds ranged from 72.1% to 104.7%. PAHs concentrations in laboratory and field blanks were consistently very low, and the data were not subjected to any blank correction. The limits of detection and quantification for the PAH compounds, calculated using 3.3 x s/S (s = standard deviation estimate of the response, and S = slope of the calibration curve) are presented in Table 1.

2.3. BaP-equivalent concentrations and lifetime lung cancer risk (LCR)

Carcinogenic and mutagenic equivalents (ng m^{-3}) were calculated by multiplying the concentrations of eight PAHs compound with its carcinogenic equivalency factors (TEF) (Nisbet and LaGoy, 1992) and mutagenic equivalency factor (MEF) (Durant et al., 1996). Carcinogenic equivalents (BaP-TEQ) (Eq. (1)) and mutagenic equivalents (BaP-MEQ) (Eq. (2)) concentrations levels for the sum of nonvolatile PAHs were calculated as follows (Jung et al., 2010):

$$(BaP-TEQ)_{\Sigma 8PAHs} = [BaA] \times 0.1 + [CHRY] \times 0.01 + [BbF] \times 0.1 + [BkF] \times 0.1 + [BaP] \times 1 + [IcdP] \times 0.1 + [DahA] \times 5 + [BghiP] \times 0.01. \quad (1)$$

$$(BaP-MEQ)_{\Sigma 8PAHs} = [BaA] \times 0.082 + [CHRY] \times 0.017 + [BbF] \times 0.25 + [BkF] \times 0.11 + [BaP] \times 1 + [IcdP] \times 0.31 + [DahA] \times 0.29 + [BghiP] \times 0.19. \quad (2)$$

Based on World Health Organization (WHO) data, the unit risk (UR) for PAHs, indicating the estimated lifetime lung cancer risk from exposure to atmospheric PAHs, is 8.7×10^{-5} (i.e., incidence of 8.7 cases per 100 000 people with chronic inhalation exposure to 1 ng m^{-3} BaP over a lifetime of 70 years) (WHO, 2000). In this work, the lifetime lung cancer risk (LCR) attributable to PAHs inhalation exposure was estimated by multiplying the sum of the individual BaP-TEQ or BaP-MEQ, respectively by the UR of exposure to BaP according to the formula: LCR = UR × BaP-TEQ and UR × BaP-MEQ according to Callén et al. (2014b).

2.4. Receptor model

Receptor models have been often used as a tool in source apportionments studies in a large variety of sites (Artaxo et al., 1998; Khairy and Lohmann, 2013). Appropriate source identification is fundamental as guidance of public policies for decision makers and providing foundations for health oriented studies (Brown et al., 2012; Callén et al., 2012). Among existing receptor models, positive matrix factorization (PMF, Paatero and Tapper (1994)) and Absolute Principal Factor Analysis (APFA, Thurston and Spengler (1985)) are some of the most used multivariate models. The database collected here has been analyzed through both techniques; however PMF has not resolved the data satisfactorily, probably due to the limited number of filters relative to speciated compounds. APFA, however, has yielded robust results and therefore has been used for source apportionment. The APFA model aims to reduce the number of factors that are independent and uncorrelated that could explain most of the original data variability. Whereas the factor-loading matrix represents the association between the analyzed elements and corresponding factor, the factor-scores are an indication of the strength of each sample to each retained factor.

3. Results and discussion

3.1. Aerosol loadings during the campaign

A summary of the PM$_{10}$, OC, EC, total carbon, monosaccharide anhydrides and individual PAHs concentrations are shown in Table 2. The average concentrations of PM$_{10}$ during dry and wet seasons were 30.20 ± 12.34 μg m^{-3} and 13.38 ± 3.15 μg m^{-3} respectively. It is noteworthy that 2011 was a anomalously wet year, with number of identified fires being approximately half of the period 1998−2011 mean (Gatti et al., 2014). However, PM$_{10}$ concentrations at the same site during the 2010 dry season, subject to a

Table 1
Detections and quantifications limits of PAHs monitored during the GC/MS analyses.

PAHs	DL	QL
	(ng m^{-3})	
Phenanthrene	0.0008	0.0028
Anthracene	0.0100	0.0303
Fluoranthene	0.0072	0.0217
Pyrene	0.0143	0.0432
Retene	0.0076	0.0231
Benz[a]anthracene	0.0087	0.0267
Chrysene	0.0082	0.0247
Benzo[b]fluoranthene	0.0052	0.0158
Benzo[k]fluoranthene	0.0010	0.0028
Benzo[e]pyrene	0.0024	0.0074
Benzo[a]pyrene	0.0007	0.0021
Indeno[1,2,3-c,d]pyrene	0.0019	0.0057
Dibenzo[a,h] anthracene	0.0007	0.0019
Benzo[g,h,i]perylene	0.0022	0.0068
Phenanthrene	0.0007	0.0019

PAHs: Polycyclic Aromatic Hydrocarbons.
DL: Detection Limit.
QL: Quantification Limit.

Table 2
Species concentrations observed at the sampling site. PM_{10}, Organic Carbon, Elemental Carbon and Levoglucosan are given in $\mu g\ m^{-3}$. Galactosan, Mannosan and PAHs are given in $ng\ m^{-3}$.

	Dry season		Wet season	
	Mean $\pm$ SD	Min—Max	Mean $\pm$ SD	Min—Max
PM_{10}	30.20 $\pm$ 12.34	13.06—58.60	13.38 $\pm$ 3.15	9.46—18.29
Organic carbon	10.66 $\pm$ 04.91	04.83—22.57	06.44 $\pm$ 1.41	3.30—09.82
Elemental carbon	0.99 $\pm$ 0.53	0.34—02.50	0.35 $\pm$ 0.15	0.10—0.86
Monosaccharides				
Levoglucosan ($\mu g\ m^{-3}$)	0.84 $\pm$ 01.05	0.02—004.32	0.02 $\pm$ 0.01	<DL—0.04
Galactosan ($ng\ m^{-3}$)	73.70 $\pm$ 74.80	24.90—322.60	3.30 $\pm$ 2.90	<DL—12.00
Mannosan ($ng\ m^{-3}$)	40.40 $\pm$ 64.50	0.60—262.20	0.90 $\pm$ 0.30	<DL—01.40
PAHs ($ng\ m^{-3}$)				
Phenanthrene	0.26 $\pm$ 0.25	0.10—1.02	0.28 $\pm$ 0.30	0.06—1.27
Anthracene	0.36 $\pm$ 0.25	0.04—0.77	0.27 $\pm$ 0.29	0.04—1.05
Fluoranthene	0.20 $\pm$ 0.18	0.03—0.61	0.14 $\pm$ 0.17	0.02—0.61
Pyrene	0.21 $\pm$ 0.19	0.03—0.62	0.13 $\pm$ 0.15	0.02—0.65
Retene	0.60 $\pm$ 1.17	0.05—4.91	0.30 $\pm$ 0.25	0.01—0.99
Benz[a]anthracene	0.22 $\pm$ 0.20	0.03—0.72	0.14 $\pm$ 0.18	0.02—0.81
Chrysene	0.21 $\pm$ 0.18	0.03—0.63	0.15 $\pm$ 0.19	0.02—0.81
Benzo[b]fluoranthene	0.12 $\pm$ 0.11	0.03—0.42	0.07 $\pm$ 0.07	0.01—0.30
Benzo[k]fluoranthene	0.13 $\pm$ 0.14	0.02—0.58	0.06 $\pm$ 0.07	0.01—0.26
Benzo[e]pyrene	0.25 $\pm$ 0.30	0.04—1.22	0.11 $\pm$ 0.11	0.02—0.43
Benzo[a]pyrene	0.18 $\pm$ 0.16	0.03—0.57	0.09 $\pm$ 0.10	0.02—0.41
Indeno[1,2,3-c,d]pyrene	0.21 $\pm$ 0.27	0.06—1.04	0.13 $\pm$ 0.17	0.04—0.82
Dibenzo[a,h] anthracene	0.30 $\pm$ 0.31	0.07—1.40	0.14 $\pm$ 0.13	0.03—0.60
Benzo[g,h,i]perylene	0.15 $\pm$ 0.14	0.04—0.62	0.08 $\pm$ 0.09	0.02—0.42
Total samples	19		31	

strong drought, was 56.6 $\mu g\ m^{-3}$ (Artaxo et al., 2013). Some years before, dry season average PM_{10} concentration of up to 100 $\mu g\ m^{-3}$ was reported by Maenhaut et al. (2002) on Amazonian site. Previous studies have already identified that even relatively low (25.2 $\mu g\ m^{-3}$ and dry season average) PM_{10} exposure levels of Amazonian biomass burning emissions cause mutagenic and genotoxic effects in human lung cell line and vegetable cells (De Oliveira Alves et al., 2014, 2011).

The time series of PM_{10}, OC, EC, levoglucosan and RET are depicted in Fig. 1. Two sharp peaks of PM_{10} levels (24-h average) were observed during the dry season, reaching concentrations close to 60 $\mu g\ m^{-3}$. Contrarily, PM_{10} was relatively constant throughout the wet season indicating an overall stable balance between aerosol sources and sinks within the filter sampling resolution. Similar behavior is identified for OC and EC components. Levoglucosan was found in significant concentrations only in filters collected prior October-2011 and, as such, such transition period was chosen to separate between dry and wet season. Interestingly, RET depicts a somewhat different profile during the wet season and shall be addressed in details in a later section.

The OC concentrations found in this study were similar to the results described in Rondônia in the dry season of 1999 (Artaxo et al., 2002), although the sampling system at the time used a 2.5 μm cut-off, not accounting for coarse-mode carbonaceous material. On the other hand, EC is significantly higher in the 1999 study rather than the 2011 study (considering dry season only) and depicts a similar contribution to PM_{10} in both studies (3.2% in 2011 versus 4.5% from 1999). The fraction of OC to total carbon (TC = OC + EC) reported from 1999 dry season was 0.72 whereas our ratio is 0.91, suggesting a significant contribution of coarse-mode OC to overall carbonaceous material.

The peak value of levoglucosan (Fig. 1c) was 4.32 $\mu g\ m^{-3}$, accounting alone for almost 8% of PM_{10}. Laboratory experiments of wood combustion have reported a ratio of levoglucosan to PM_{10} ranging from 4% to 15% (Schmidl et al., 2008b), comparable with ambient data reported here. Such high value illustrates the major role which biomass burning emissions play in regulating atmospheric aerosol concentration during the dry season in the region.

Correspondingly, the levoglucosan to OC ratio (on a carbon mass basis) (L: OC) was as high as 8.4% during peak concentrations. Previous measurements carried out in Rondônia as well have reported high levels of ambient levoglucosan: up to 6.90 $\mu g\ m^{-3}$ and 7.50 $\mu g\ m^{-3}$ in the dry season of 1999 and 2002, respectively. Such values, however, on a carbon mass basis accounted for 4.4% and 3.5% of OC only (Claeys et al., 2010; Graham, 2002), significantly
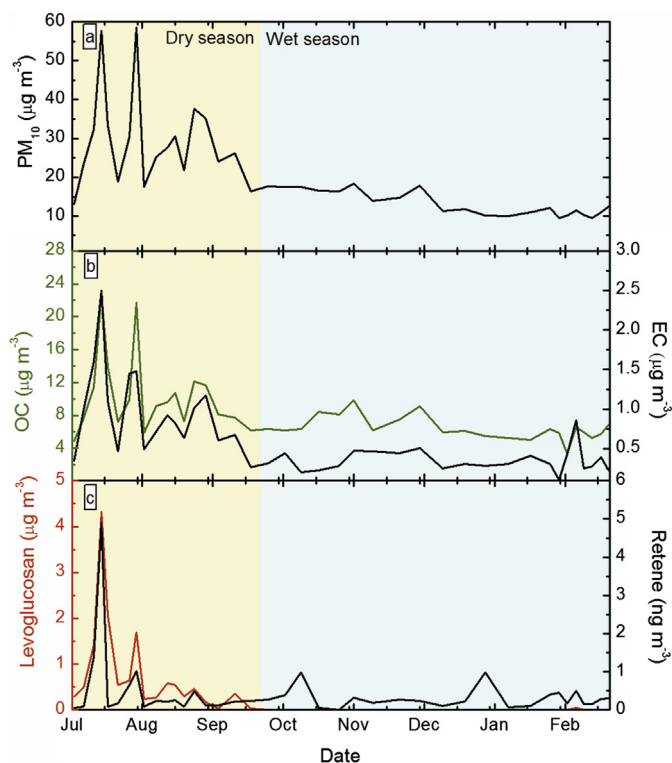

Fig. 1. Concentration time series of PM_{10} (a), OC and EC (b), and levoglucosan and retene (c).

lower than the 2011 data. It is interesting to note that the L: OC ratio has been reported to depend not only on the burning material, but on the Modified Combustion Efficiency (MCE, $\Delta CO_2/(\Delta CO + \Delta CO_2)$) of the fire as well (Sullivan et al., 2008).

Biomass combustion can be further characterized relating the concentration of levoglucosan relative to mannosan (L: M), and relative to galactosan (L: G). The former has been identified to separate between the combustion of hardwood (L: M ~15) and softwood (L: M ~3) (Schmidl et al., 2008b) while the latter has been linked to separate between wood combustion (L: G ~10–50) and leaf combustion (L: G ~1) (Schmidl et al., 2008a). During biomass burning peak, the ratio L: M was 16.5, showed somewhat similar values as observed during 1999 and 2002 campaigns (9.4 and 13.3, respectively), indicating typical ranges of hardwood fires. Correspondingly, the L: G ratio during the 2011 biomass burning was significantly lower (13.4) relative to 2002 data (28.8) and 1999 data (46.6). Although such values classify the three datasets as hardwood combustion, they depict the significant heterogeneity of fire sources impacting the same region in different years.

RET was the most abundant PAHs with an ambient concentration ranging between 0.01 and 4.91 ng m^{-3}, followed by the ANT, PHE and DahA. RET accounted on average to 25% of the total PAHs mass, being up to 50% during biomass burning peak. Although it correlates well with biomass burning, it is not emitted uniquely from such source, as it will be discussed in Section 3.2. The ensemble of carcinogenic PAHs (BaA, CHRY, BbF, BkF, BaP, IcdP and DahA) are responsible for 37% of the PAHs mass found during all analyzed period.

3.2. Retene as a marker for wood combustion

In early 1980s, RET has been proposed as a marker for wood combustion in ambient air (Ramdahl, 1983). This species is undoubtedly emitted from wood combustion (as our data indicates as well), and its use as a tracer for wood combustion (Shen et al., 2012) and it is also found in road dust (Bari et al., 2009), corn residue (Ding et al., 2012) and fireplace combustion of wood (pine, oak and eucalyptus) (Schauer et al., 2001).

Although it has been observed a significant reduction of aerosol concentration and associated biomass burning markers from the dry to the wet season, RET only decreased by a factor of two (0.60 ng m^{-3} to 0.30 ng m^{-3}), suggesting not to be uniquely linked to forest burning emissions at the site. Fig. 2 is a scatter plot of RET and levoglucosan concentrations, depicting a high correlation for levoglucosan values higher than 100 ng m^{-3} ($R^2 = 0.81$), which coincides with a L: M + G ranging from 5 to 8, typical of hardwood. Conversely, very poor correlation ($R^2 = 0.02$) is observed for low levoglucosan values, with low L: M + G values as well. Interestingly, L: M + G ratios of 1–3 have been previously observed to arise from the burning of bituminous coal (Kourtchev et al., 2011), which could be the dominating source of RET during the wet season. Such source could be linked to brickyard emissions which were previously reported to sporadically impact the sampling site (Brito et al., 2014).

3.3. Source apportionment by APFA model

Fig. S1 (Supplementary data) show a plot of the factor-loading matrix obtained by APFA model. Three factors were identified shown in Table 3, named Biomass Burning, Mix and Fossil Fuel for factor 1, 2 and 3, respectively. The biomass burning factor is found to be the dominating aerosol source, having 75.4% of PM$_{10}$ loading (Fig. 3). This factor also is shown to be the dominating source of carbonaceous material (76.4% of OC and 71.2% of EC). Curiously the model has apportioned RET entirely to the biomass burning factor,
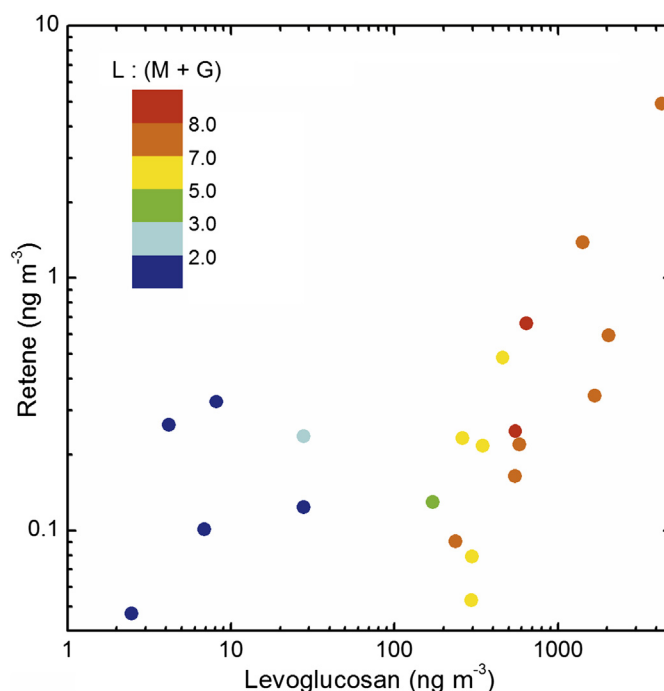

Fig. 2. Concentration of Levoglucosan vs. Retene and ratios of Lev/(Mann + Gal).

although it is clearly not uniquely emitted from the same sources as levoglucosan, as discussed above. BeP has been strongly associate (76.5%) with this factor as well, unlike BaP (36.4%).

The second factor contributes marginally to PM$_{10}$ (6.3%) and carbonaceous material (7.0% of OC and 8.5% of EC). However, it depicts an important contribution of several PAHs without a single source class and therefore was considered as mixed sources factor. It may be noted that due to the overlap of the source signatures, it is difficult to differentiate to individual source categories of PAHs (Dvorská et al., 2012; Wingfors et al., 2011).

The third factor was characterized by high contributions of IcdP

Table 3
Source apportionment of different species using APFA.

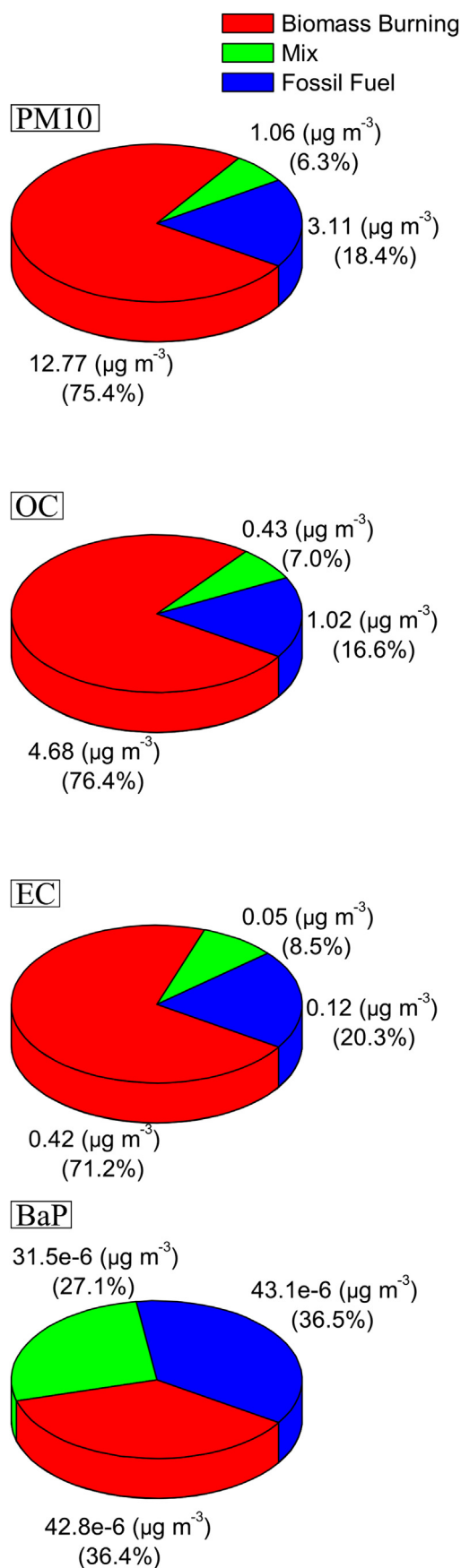|	Factor 1	Factor 2	Factor 3
	Biomass burning	Mix	Fossil fuel
μg m^{-3}			
PM$_{10}$	12.77	1.06	3.11
Organic carbon	4.68	0.43	1.02
Elemental carbon	0.42	0.05	0.12
Levoglucosan	0.53	0.00	0.00
Mannosan	0.31	0.00	0.00
Galactosan	0.40	0.00	0.00
ng m^{-3}			
Phenanthrene	0.03	0.04	0.10
Anthracene	0.09	0.08	0.05
Fluoranthene	0.05	0.04	0.05
Pyrene	0.05	0.04	0.05
Retene	0.51	0.00	0.00
Benz[a]anthracene	0.05	0.04	0.06
Chrysene	0.05	0.05	0.05
Benzo[b]fluoranthene	0.03	0.02	0.03
Benzo[k]fluoranthene	0.02	0.02	0.04
Benzo[e]pyrene	0.13	0.04	0.00
Benzo[a]pyrene	0.04	0.03	0.04
Indeno[1,2,3-c,d]pyrene	0.01	0.03	0.10
Dibenzo[a,h] anthracene	0.04	0.02	0.13
Benzo[g,h,i]perylene	0.02	0.01	0.06
%PM$_{10}$ contribution	80%	6%	14%

Fig. 3. Source apportionment of PM$_{10}$, OC, EC and BaP.

(~70%), DahA (~69%) and BghiP (67%). These PAHs are reported as dominant in fossil fuel combustion emissions (Ravindra et al., 2008). IcdP in particular has been previously linked to diesel emissions (Khairy and Lohmann, 2013; Simcik et al., 1999). This factor contributes to 18.4% of PM$_{10}$ and 16.6% and 20.3% of OC and EC, respectively. Such factor is probably a combination of vehicular emissions with diesel fueled thermoelectric power plants, the latter increasingly becoming important agents of disturbance in the Amazon basin (Hacon et al., 2014). Fig. 3 summarizes source apportionment of PM$_{10}$, OC, EC and BaP.

3.4. Carcinogenic and mutagenic risks potential of PAHs

The BaP-equivalent (BaP-TEQ and BaP-MEQ) concentrations calculated for sum of 8 PAHs (BaP, B[a]A, CHRY, BbF, BkF, IcdP, DahA and BghiP) and individual PAHs measured in this study are shown in Table 4. The meaning obtained for BaP-TEF in the dry season concerning the sum of the eight PAHs was 1.97 ± 0.47. Besides, this data was approximately four times higher compared with the study done in residences (outdoor and indoor) in the city of New York by Jung et al. (2010). Furthermore, the BaP-equivalent found in the Amazon region were much higher (3–10 times, depending on the period) that the values found in the study performed in urban area in the Rio Grande do Sul state, Brazil (Agudelo-Castañeda and Teixeira, 2014).

The largest contribution of individual PAHs to carcinogenic risk potential was the DahA, accounting for 83%. While the contribution of the BaP to carcinogenic risk was on average only 13%, their contribution to mutagenic risk was considerably higher (~49%).

Table 4
Assessment of BaP-equivalent carcinogenicity and mutagenicity in the Amazon region.

	BaP-TEQ (ng m^{-3}) for exposition to PAHs			
	Dry season		Wet season	
	TEF[a]	Mean ± SD[b]	TEF[a]	Mean ± SD[b]
∑8 PAHs	–	1.970 ± 0.47	–	0.840 ± 0.03
Benz[a]pyrene	1.00	0.260 ± 0.18	1.00	0.100 ± 0.10
Benz[a]anthracene	0.10	0.026 ± 0.21	0.10	0.015 ± 0.18
Chrysene	0.01	0.002 ± 0.19	0.01	0.001 ± 0.19
Benzo[b]fluoranthene	0.10	0.014 ± 0.12	0.10	0.007 ± 0.07
Benzo[k]fluoranthene	0.10	0.015 ± 0.15	0.10	0.006 ± 0.06
Indene[1,2,3-cd]pyrene	0.10	0.024 ± 0.30	0.10	0.014 ± 0.18
Dibenzo[a]anthracene	5.00	1.650 ± 0.34	5.00	0.700 ± 0.18
Benzo[g,h,i]perylene	0.01	0.001 ± 0.15	0.01	0.000 ± 0.09
Samples total		19		31
	BaP-MEQ (ng m^{-3}) for exposition to PAHs			
	Dry season		Wet season	
	MEF[c]	Mean ± SD[b]	MEF[c]	Mean ± SD[b]
∑8 PAHs	–	0.530 ± 0.62	–	0.230 ± 0.12
Benz[a]pyrene	1.000	0.260 ± 0.18	1.000	0.100 ± 0.10
Benz[a]anthracene	0.082	0.021 ± 0.20	0.082	0.012 ± 0.20
Chrysene	0.017	0.004 ± 0.18	0.017	0.002 ± 0.17
Benzo[b]fluoranthene	0.250	0.035 ± 0.13	0.250	0.017 ± 0.07
Benzo[k]fluoranthene	0.110	0.016 ± 0.14	0.110	0.006 ± 0.07
Indene[1,2,3-cd]pyrene	0.310	0.074 ± 0.33	0.310	0.043 ± 0.18
Dibenzo[a]anthracene	0.290	0.095 ± 0.39	0.290	0.040 ± 0.16
Benzo[g,h,i]perylene	0.190	0.030 ± 0.18	0.190	0.015 ± 0.08
Samples total		19		31

BaP-TEQ: Carcinogenic equivalents calculated from the cancer potency relative to BaP (TEF) multiplied by the concentration of PAH in a sample.
BaP-MEQ: Mutagenic equivalents calculated from the mutagenic potency relative to BaP (MEF) multiplied by the concentration of PAH in a sample.
∑8 PAHs: BaP, B[a]A, CHRY, BbF, BkF, IcdP, DahA and BghiP.
[a] TEF: Toxic equivalent factor.
[b] SD: Standard deviation.
[c] MEF: Mutagenic equivalent factor.

Similar results were also observed in the urban area of Amritsar, Punjab, India (Kaur et al., 2013). Other studies in urban areas have identified BaP as the largest contributor to carcinogenic (Jung et al., 2010; Mirante et al., 2013a; Ohura et al., 2004) and mutagenic (Jung et al., 2010) risks.

The inhalation lifetime lung cancer risk based on BaP-TEQ (LCR-BaP-TEQ) and BaP-MEQ (LCR-BaP-MEQ) was performed (Fig. 4). Such value provides a more accurate risk assessment from environmental exposure to PAHs than only considering BaP (Callén et al., 2014a). It was observed that during the dry season, the estimated lung cancer risk to BaP-TEQ in the sampling site, considered representative of the Amazonian deforestation arc, exceed significantly the WHO health-based guideline. In the case of mutagenic risk (BaP-MEQ), the values did not reach the WHO unit risk. Studies performed in New York (Jung et al., 2010) and Madrid (Mirante et al., 2013b) estimated the carcinogenic risk lower than standards established by environmental and health agencies. In a recent work by Callén et al. (2014a), in an urban area in Spain, the LCR has exceeded the unit risk only during episodic pollution peaks.

4. Conclusions

This study describes quantification of ambient OC, EC, anhydrous sugars and PAHs in a region strongly impacted by biomass burning in the Amazon Basin, representative of the arc of the deforestation, an area inhabited by over 10 million people. Even during an anomalously wet year, 2011, levoglucosan was observed in significant concentration, accounting up to 8% of PM_{10}. Peak concentration of PM_{10} during the dry seasons was observed to reach 60 μg m^{-3} on the 24 h average. Inversely, PM_{10} was relatively constant throughout the wet season indicating an overall stable balance between aerosol sources and sinks within the filter sampling resolution. Similar behavior is identified for OC and EC components. PCA analysis identified a three-factor solution, being

biomass burning, a mixed sources factor and fossil fuel combustion emissions. As expected, the biomass burning factor is the larger contributor to PM_{10}, OC, EC, levoglucosan and RET. Furthermore, the estimated lung cancer risk calculated during the dry seasons largely exceeded the WHO health-based guideline. This work enhances the knowledge of aerosol sources on an Amazon region highly impacted by anthropogenic activities with significant contribution on climate variability and carcinogenic and mutagenic potential risks to human health, especially for the most vulnerable groups. Despite the large area of the Amazon forest, the representative contribution of individual PAHs to carcinogenic human risk showed that this biome is not able to disperse the pollutants enough to reduce the impact of human exposure to negligible values.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.08.059.

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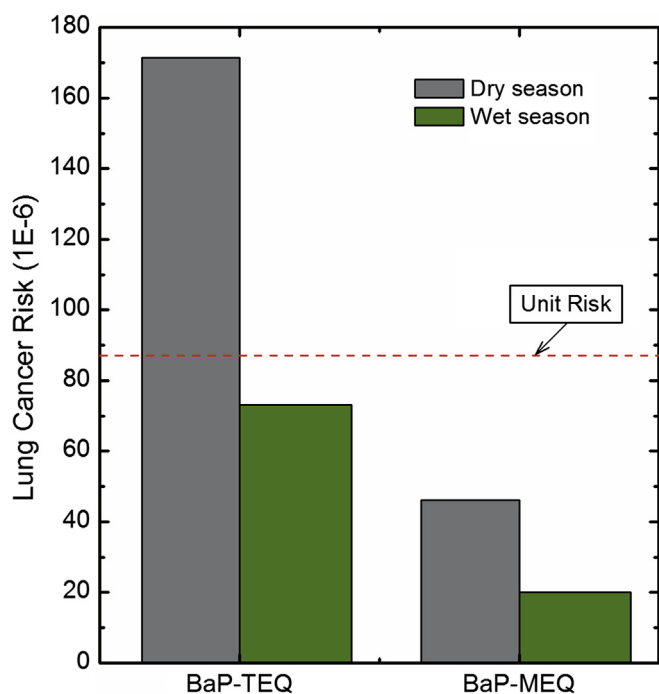
Fig. 4. Assessment of the lifetime lung cancer risk (LCR) from the BaP-TEQ (carcinogenic potential) and BaP-MEQ (mutagenic potential) during the dry and wet season in the Amazon region. The WHO Unit Risk = 8.7*10^{-5} (ng m^{-3}) was also remarked.

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