Observations of atmospheric monoaromatic hydrocarbons at urban, semi-urban and forest environments in the Amazon region

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Abstract

An integrated experiment was conducted measuring the concentrations of the volatile organic compounds benzene, toluene, ethylbenzene and meta, ortho, para-xylene (known as BTEX), all of them regarded as pollutants with harmful effects on human health and vegetation, being also an important precursor of tropospheric ozone. Additionally, these compounds are known to play a major part in the formation of SOA, which can greatly influence the pattern of cloud formation, and thus the regional weather. The samples were collected in 2012/2013 at three different locations: (i) The Amazon Tall Tower Observatory (ATTO), a pristine rain forest region in the central Amazon Basin; (ii) Manacapuru, a semi-urban site located southwest and downwind of Manaus as a preview of the Green Ocean Amazon Experiment (GoAmazon 2014/15); and (iii) the city of Manaus (distributed over three sites). Results indicate that there is an increase in pollutant concentrations with increasing proximity to urban areas. For instance, the benzene, concentration range was 0.237 - 19.6; 0.018 - 0.313 and 0.036 - 0.948 $\mu\text{g m}^{-3}$ at Manaus, ATTO and Manacapuru, respectively. For toluene, they were 0.700 - 832; 0.011 - 4.93 and 0.091 - 2.75 $\mu\text{g m}^{-3}$ at Manaus, ATTO and Manacapuru, respectively. For ethylbenzene, they were 0.165 - 447; 0.047 - 0.401 and 0.018 - 1.20 $\mu\text{g m}^{-3}$ at Manaus, ATTO and Manacapuru, respectively. Remarkably, no significant difference was found between the pollution levels measured in dry season and wet season. Furthermore, it was observed that, in general, the city of Manaus seems to be less impacted by these pollutants than other cities in Brazil and in other countries, near the coastline or on the continent. A risk analysis for the health of Manaus' population was performed and specified that the measured concentrations indicated a truthful risk of development of chronic diseases and cancer for the population of Manaus.

Keywords: Air quality; BTEX; Manaus; The Amazon Tall Tower Observatory (ATTO); Amazon Forest; Green Ocean Amazon Experiment (GoAmazon); Health risk.

1 Introduction

The industrial and urban development, the growth of the automotive fleet, the current patterns of consumption, deforestation, agriculture and fertilizer use and the recurrent forest burning are some of the factors that have, as main consequence, the increase of atmospheric pollutant emissions. The scientific literature agrees that this air pollution is a significant threat to the health of world population, especially in developing countries (WHO, 2006; Bruce et al., 2000; Pope et al., 2004; Urdea et al., 2006; Freitas et al, 2013; Watson, 2014; Kessler, 2014; Fowler et al. 2013), where regulations and inspections in general are less stringent. In the recent decades, a strong correlation indicates the association between high level of air pollution and its effects on human health, such as mortality rates, hospitalization for respiratory problems and cardiovascular diseases, worsening of asthma attacks, adverse effects on the functioning of the lungs, low weight newborn, high infant and perinatal mortality, tuberculosis, cataract, nasopharyngeal, larynx and lung cancer (Bruce et al., 2000; Pope et al., 2004; Pope et al., 2002; Delfino et al., 2003; Valavanidis et al., 2008; Watson, 2014; Kessler, 2014).

Among the main substances studied in the investigation and regulation of air pollutants, volatile organic compounds (VOCs) (Miranda & Tomaz, 2008) contribute significantly with a variety of species and products proven to be toxic to human health and thus representing an important substance group due to their occurrence and concentrations in the indoor and outdoor environment (Delfino et al., 2003). On a global scale, biogenic VOC emissions by vegetation containing highly reactive compounds are dominating the budget of VOC emission and such biogenic sources may aggravate the situation of cities surrounded by large forested areas, such as Manaus (Simpson et al., 1999; Glasius et al., 2000; Fehsenfeld et al., 1992; König et al, 1995; Guenther et al. 1995; Kesselmeier & Staudt, 1999; Kiendler-Scharr et al., 2009).

On a local, urban scale, however, anthropogenic VOCs may become dominant. Among the anthropogenic VOCs, the monoaromatic hydrocarbons benzene, toluene, ethylbenzene, meta, ortho and para-xylene (the so-called BTEX group) are some of the most important in air quality analysis studies due to their high levels of toxicity (Irwin, 1997; Baimatova et al., 2015). Tiredness, headaches, dizziness, weakness, drowsiness, eye and skin irritation are some of the symptoms related to exposure to BTEX, especially when it is combined to inadequate conditions of temperature and humidity (Avigo et al., 2008; Bolden et al., 2015). High concentrations may cause damage to the central nervous system and respiratory, gastrointestinal and reproductive systems (Trigueros et al., 2010). Furthermore, IARC classifies benzene as carcinogenic to humans and ethylbenzene as possibly carcinogenic to humans (EPA, 2010; IARC, 2015).

The BTEX compounds are emitted mostly from anthropogenic sources, with gasoline and diesel powered automobiles contributing with most of these emissions (Bolden et al., 2015). They can also be emitted by biomass burning (Warneke et al., 2011; Karl et al., 2007; Romagnoli et al., 2014). However, some studies present strong evidence that toluene can also be emitted by plants in forest regions (Heiden et al., 1999; Custódio et al., 2010; Misztal et al., 2015). However, due to its persistence in the atmosphere for several hours, BTEX can be carried over long distances, up to tens of kilometers, which may result in the presence of

these pollutants in forest environments (Custódio et al., 2010; Yu et al., 2008).

Besides the mentioned hazards that BTEX present to human health, these compounds are also precursors of other important atmospheric pollutants, namely tropospheric ozone and secondary organic aerosols (SOAs) (Atkinson, 2000). VOCs in general, especially biogenic ones but also including BTEX, participate in photochemical reactions having important contribution in the generation of tropospheric ozone (Edwards et al., 2014). Among BTEX, xylenes are the most important contributors to reactivity (Na et al., 2005). Regarding the formation of SOA, aromatic hydrocarbons play a significant, and possibly dominant, role in its formation in urban areas, being the class of compounds that can also be responsible for producing the majority of the SOA formed during the atmospheric oxidation of whole gasoline vapor (Odum et al., 1997; Atkinson, 2000). The assessment of SOA and the interaction of biogenic and anthropogenic VOCs in the Amazonian atmosphere are subjects of great interest, since these particles interact with clouds and can change precipitation rates, affecting the rainfall pattern of the region (Walsh, 2013).

Moreover, air pollution may also adversely affect vegetation, causing damage to the leaves and plant metabolism as a whole and reducing the resistance against pests and diseases. Considering the global importance of Amazon rainforest natural ecosystems, this aspect becomes relevant, as the forest is of vital importance for the maintenance of rainfall regionally and in the rest of the country, and the devastation of the forest is already interfering with the region's climate (Watts, 2014).

The studied area represents a unique interface between a large city with more than 2 million inhabitants, Manaus, and the biggest tropical forest in the world. The continuously growing automobile fleet, the industrial district with over 600 industries and the large presence of thermoelectric plants figure as great concerns to the air quality of Manaus (MANAUS, 2002), and consequently to the pristine environment around it.

In view of the urban and industrial pollution potential in the interface between Manaus (urban area), Manacapuru (semi-urban area) and ATTO (pristine rainforest area), an initial inventory of air pollutants in the region is of value to evaluate the impact on population and on the environment. Therefore, the present study was elaborated expecting to provide valuable information regarding the natural and urban environments in the region and also on the health of its inhabitants.

This research aims to quantify and compare the concentration of monoaromatic pollutants, BTEX, through monthly sampling over a year in forest (ATTO), urban (city of Manaus) and semi-urban (Manacapuru) areas, as well as to provide a first estimate of the risk that the concentrations found may represent to the population of Manaus. To the authors' knowledge, this is the first attempt to provide quantitative information on the presence of BTEX compounds in the atmosphere of Manaus.

2 Materials and Methods

2.1 Sampling sites

Samples of VOCs were taken at three different sites in Manaus (T1) (Amazon Research Institute - INPA, T1_{INPA}; Mindu Municipal Park, T1_{MP}; and Bilhares Park, T1_{BP}), two different sites at ATTO (T0) (tower top and base, respectively T0_{top} and T0_{base}) and one site at Manacapuru (T3). The selected sampling sites are shown in Figure 1 and details are provided below.

Figure 1 - Sampling sites selected for the present study shown in a satellite picture Google Earth Inc., 2015. Furthermore a zoom of the three sites distributed within Manaus, Google Earth, 2015. At last there is a wind rose of the Manaus area.

Due to the high incident energy levels all year long, the average air temperature in the amazon region is among 24-26°C, presenting small variation during the year. The region also presents high relative humidity and average annual precipitation, of approximately 2,300mm. The wet season comprises the period between November and March, while the so-called dry period happens between May and September. April and October are considered the transition months. The climate in the region is defined as Ami Tropical Monsoon, according to Köppen classification (Fisch et al., 1998; Silva, 2001).

Manaus is the capital of Amazonas state, in northern Brazil, with an estimated population of 2,020,301 habitants (IBGE, 2014), figuring as the 7th most populous city in Brazil (IBGE, 2014). The coordinates of Manaus city are 03° 08' 30" S and 60° 00' 00" W, being at 21 m above sea level. In order to represent Manaus city as a whole and due to logistical amenities, three sites were selected: the Large Scale Biosphere-Atmosphere Experiment at Amazon (LBA) headquarters, located in the Research Institute of Amazon – INPA (T1_{INPA}), Municipal Mindu Park (located in the center-south Manaus, one of the biggest and most visited parks in the state of Amazonas, T1_{MP}) and Ponte dos Bilhares park (also in the center-south Manaus, one of the smallest green areas inside the urban environment, T1_{BP}).

Based on a partnership between Brazil and Germany, an Amazonian Tall Tower Observatory (ATTO) was developed in the course of the last 5 years. It is situated 150 km NE of Manaus and consists of flux towers (80 m) and one very tall tower (325 m), the latter one erected but waiting to be instrumented in 2015/2016, aiming to monitor the air with a footprint of the order of 1000 km, thus representing regional processes (Tollefson, 2010;

Andreae et al., 2015). The area chosen represents a forest area which is regarded as remote, considering that the predominant wind direction in the region is from northeast to southwest most time of the year. The sampling at ATTO took place at the base and at the top of an 80 m walk-up tower (INSTANT tower). For more information and coordinates of the towers see Andreae et al. (2015).

The GoAmazon2014/15 project, on the other hand, is an initiative of the Climate and Environmental Sciences Division – CESD of the U.S. Department of Energy – DOE, which aims to enhance the understanding on how earth-atmosphere processes can affect the tropical hydrology and climate (U.S. DOE, 2011). The project comprises several sampling sites in order to study the influence of the Manaus plume on the regional atmospheric properties of the Amazonian ecosystem. One of them, the T3 site, is located at the Farm Exata S/A in Manacapuru, AM. This site is a pasture area which is partially influenced by the Manaus plume, since the predominant wind direction in the region is from Manaus to the site where the T3 site of the GoAmazon2014/15 project is located. The T3 coordinates are 03°12'47.82" S / 60°35'55.32" O (Ishida, 2012).

2.2 Sampling procedures

Passive sampling of benzene, toluene, ethylbenzene, ortho, meta, and para-xylenes was divided into two campaigns. The first one happened in 6 consecutive weeks between March 31st and April 14th 2012 (corresponding to the region's wet season), at T1_{INPA}, T0_{top} and T0_{base} (amounting 6 samples for each sampling site).

For the second campaign, sampling took place at all 6 sites (T0_{base}, T0_{top}, T1_{INPA}, T1_{MP}, T1_{BP} and T3). Due to unforeseen logistics and resources limitations, the sampling occurred only in the last week of each month, from August 25th 2012 to June 1st 2013 (amounting 10 samples for each sampling site). This campaign comprises both wet and dry seasons.

The selected VOCs were sampled by means of radial diffusion passive samplers (Radiello®, Fondazione Salvatore Maugeri, Padova, Italy). These samplers comprise a compound-specific adsorbing cartridge, surrounded by a cylindrical microporous diffusive body, mounted on a supporting plate. For BTEX compounds, the adsorbing cartridge is comprised of 530 ± 30 mg of activated charcoal with particle size of 35 – 50 mesh.

2.2 Analytical procedures

Laboratory procedures were performed in the Federal University of Paraná, Brazil. Samples extraction was accomplished using chemical desorption with 2 ml of carbon disulfide (CS₂), during 1 hour. Extracts were analyzed with a Perkin Elmer 680 SQ T® gas chromatograph equipped with a Mass Spectrometry Detector (MS). Analyte separation was achieved with the use of an intermediate polar phase capillary column, model RESTEK-624 MS (30 m x 0.32 mm x 1.8 µm). The carrier gas used was helium and the injection volume was 1 µL, in splitless mode. 2000 ppm BTEX standards from Supelco (Pennsylvania, USA) were used to perform the samples quantification. Blanks adsorbing cartridges were analyzed to detect possible contaminants and verification standards were used to confirm the analyses stability. All analyses were made in single ion mode (SIM).

More information on the sampling and analysis technique can be found in Cocheo et al. (2009).

2.3 Meteorological conditions

Precipitation and temperature data were provided by the Brazilian National Institute of Spatial Research (INPE), by the meteorological station of the Brazilian National Institute of Meteorology (INMET) and by the State University of Amazonas (UEA), which were used in the calculation of compounds concentration and to define the wet and dry seasons. The wind direction data was provided by UEA and by the research team from ATTO.

2.4 Statistical analysis

As a first step, a Pearson correlation test was carried out to study the relationship between the assessed compounds. Toluene/benzene ratio for each sample was also calculated, in order to evaluate possible BTEX sources. Then, box plots comparing dataset in relation to sampling site (city/forest/Manacapuru) and to sampling season (dry/wet) were constructed. In order to validate the visual comparison accomplished by the box plots, some statistical tests were performed. Analysis of variance (ANOVA), normal probability plot of residuals, and Bartlett's test of homogeneity of variances were applied to the dataset. The statistical analyses were performed using R software (R Core Team, Vienna, Austria). A preliminary analysis showed that the residuals have a normal distribution and a parametric behavior. However, Bartlett's test presented p-values which indicate a lack of homogeneity of sample variances. Therefore, Dunnett's modified Tukey-Kramer pairwise multiple comparison test (DTK test) was performed, a method which modifies the classic Tukey test, in order to handle vectorized observation and factor data for unequal sample sizes and when population variance homogeneity cannot be assumed (Dunnet, 1980). DTK test was also performed using R software.

2.5 Risk Assessment

Risk probability values were obtained through the Risk Model, available at the Risk Assessment Information System (RAIS) website (available at <http://rais.ornl.gov/>). These values represent a dimensionless probability of an individual to develop cancer or other chronic disease besides cancer in the course of a lifetime. RAIS uses the health risk models from US EPA and the toxicity data base from different institutes and organization to express the risk. The risk values were calculated under the following assumptions: exposure duration of 25 years (assuming that a resident lives 25 years at the same place, in average), lifetime of 73.5 years (Brazilian average lifetime expectancy), exposure frequency of 350 days in a year and exposure time of 15 hours per day.

It should be noticed that, regarding the risk of developing a chronic disease which is not cancer in the course of a lifetime, the results should be read in a non-linear way (and not probabilistic). It should be considered that risk values above 1 mean that there is real risk of chronic diseases occurrence, whereas values below 1 indicate negligible risk. The higher the value, the higher risk, but the ratio, as mentioned, is not linear. The cancer development risk, on the other hand, should be read as a probability value (more information on the model available at http://rais.ornl.gov/tools/rais_chemical_risk_guide.html).

3. Results and discussion

In this section, results obtained after sample analysis and data treatment are presented and discussed. First, the meteorological conditions for the sampling period are presented. Then, a general view of the compounds concentration at the assessed sites is shown. Following, the dataset is statistically analyzed, through box plots and DTK test, first comparing the three different areas of study (urban, semi-urban and forest), and then comparing dry and wet seasons. Lastly, the risk probability values obtained through the RAIS website are presented and discussed for urban results.

3.1 Meteorological conditions

Observing the precipitation data provided by INPE, UEA and INMET, the wet and dry periods for the present study were defined. The wet season comprises the period between March/2012 and May/2012, restarting in November/2012 and ending in May/2013. The dry season starts in the end of May/2012 and extends itself until October/2012.

The wind direction data provided by the UEA and by the research team from ATTO were used to construct wind roses for the different sites, in order to verify the preferential wind direction (shown in Figure 1).

3.2 Concentration of selected VOCs

Table 1 presents BTEX concentration medians for each sampling site.

Table 1 – Median, maximum and minimum concentrations of BTEX at the selected sampling sites for both campaigns: Urban (T1_{MP}, T1_{BP} and T1_{INPA}); forest (T0_{top} and T0_{base}) and semi-urban (T3).

Median (min. – max.) concentration ($\mu\text{g m}^{-3}$)

	T1 _{MP}	T1 _{BP}	T1 _{INPA}	T0 _{top}	T0 _{base}	T3	Quantification limit ($\mu\text{g m}^{-3}$)*
Benzene	0.457 (0.237-19.6)	1.615 (1.28-1.78)	1.19 (0.543-2.10)	0.068 (0.018-0.313)	0.030 (0.020-0.146)	0.104 (0.036-0.948)	0.013
Toluene	3.07 (0.700-832)	6.12 (4.43-8.43)	6.36 (4.67-9.94)	0.133 (0.016-4.93)	0.281 (0.011-4.45)	0.226 (0.091-2.75)	0.014
Ethylbenzene	0.372 (0.165-447)	0.684 (0.524-1.44)	1.34 (0.483-3.66)	0.132 (0.047-0.401)	0.166 (0.097-0.206)	0.061 (0.018-1.10)	0.015
M,P-Xylene	0.729 (0.355-614)	2.39 (1.09-6.17)	2.63 (0.947-7.93)	0.340 (0.036-0.634)	0.293 (0.191-0.375)	0.096 (0.051-3.31)	0.014
O-Xylene	0.232 (0.112-516)	0.526 (0.350-0.809)	0.563 (0.281-1.76)	0.088 (0.015-0.144)	0.054 (0.027-0.103)	0.029 (0.019-1.34)	0.015

*Quantification limits for the analytical method, calculated assuming a mean temperature of 25°C and a sampling period of 10080 minutes (7 days).

Observing the concentrations obtained for the studied gases, it can be noticed that, for nearly all the sampling sites, the levels of o-xylene are the lowest amongst all the five pollutants, whereas toluene presented the highest values. Their respective mean concentrations differ by an order of magnitude. Low xylenes concentrations are usual in

atmospheric measurements, possibly due to their low production and/or faster reactivity in the atmosphere.

At the city of Manaus, it is possible to affirm that Mindu Park is the least polluted site regarding the median values, for all the studied pollutants. The other two sites assessed at the city presents higher levels than Mindu Park (outliers ignored), but similar between themselves. This might be due to the fact that Mindu Park has the largest green area amongst these three site (42 ha, against INPA's 13 ha and Bilhares Park's 6 ha).

The BTEX levels at the pristine rainforest and Manacapuru are generally very low comparing with the other sampling sites, mainly for ethylbenzene and xylenes, which were below the detection limit in several samples. Again, toluene appears as the most abundant VOC. Even though this toluene could have been brought from transport of air masses, a possible biogenic source from vegetation cannot be excluded (Misztal et al., 2015).

Figure 2 displays graphically the data set obtained by the present study. The outliers were not excluded when constructing these graphs.

Among the outliers observed in the data set, three of them specially attract attention due to their elevated BTEX concentrations. The first one corresponds to the last sample collected at T1_{MP} (during week 16). This sample showed extremely high concentrations of all five pollutants (19.6 $\mu\text{g m}^{-3}$ of benzene, 832 $\mu\text{g m}^{-3}$ of toluene, 447 $\mu\text{g m}^{-3}$ of ethylbenzene, 614 $\mu\text{g m}^{-3}$ of p,m-xylene and 516 $\mu\text{g m}^{-3}$ of o-xylene). The second outlier corresponds to the sample collected also at T1_{MP} during week 8, which exhibited relatively high concentrations, around an order of magnitude higher than all the other measures of the same pollutants (6.23 $\mu\text{g m}^{-3}$ of benzene, 10.5 $\mu\text{g m}^{-3}$ of toluene, 6.73 $\mu\text{g m}^{-3}$ of ethylbenzene, 12.5 $\mu\text{g m}^{-3}$ of p,m-xylene and 5.80 $\mu\text{g m}^{-3}$ of o-xylene). The third one corresponds to the sample collected at T3 also in week 16, which presented concentrations up to an order of magnitude higher than the other measurements made at the same site (0.948 $\mu\text{g m}^{-3}$ of benzene, 2.75 $\mu\text{g m}^{-3}$ of toluene, 1.02 $\mu\text{g m}^{-3}$ of ethylbenzene, 3.31 $\mu\text{g m}^{-3}$ of p,m-xylene and 1.34 $\mu\text{g m}^{-3}$ of o-xylene). The three striking measurements were performed during dry season. There are a few possible punctual sources which could explain this outliers, such as a massive biomass burning event or an unusually high automobile traffic. Therefore, it would be interesting to continue studying these sites in order to determine whether this situation is recurrent or if these outliers were just a punctual occurrence, a sampling/transportation issue or even a strong local source.

Except for the outliers already mentioned, all the other samples are below the limit of 5 $\mu\text{g m}^{-3}$ determined by the air quality directive of EU for benzene (2008/EC/50). According to the World Health Organization (WHO, 1996), however, benzene, which is carcinogenic for humans, has no recommended safe exposition. Regarding toluene, only the highest outliers are above the WHO guideline (260 $\mu\text{g m}^{-3}$, weekly mean) (WHO, 1996).

Figure 2 - Concentration of BTEX compounds at each site in each sampling week

3.2 City vs. forest results

Figure 3 displays a box plot graphic comparing the measurements performed in the different types of environment (urban - Manaus, semi-urban – Manacapuru - and forest - ATTO), considering all seasons.

Figure 3 - Box plot comparing BTEX concentration in the different sites.

*Outliers were excluded from the box plot charts in order not to hinder the data visualization.

For all five pollutants, the difference between the pollution levels found in Manaus city and in the non-urban environments is clear, which was confirmed by the DTK test. As expected, the VOCs concentration is significantly higher in the atmosphere of Manaus than in the forest and in Manacapuru. This behavior is easily explained, since the main source of these compounds to the atmosphere is the automobile's traffic.

The Pearson correlation test indicates very strong correlation between all compounds in the urban environment (0.9546-0.9999) and an also strong correlation in Manacapuru (0.9212-0.9986), but weaker correlations were calculated for the forest environment (0.2567-0.9795). Strong correlations suggest a predominant common emission source, such as vehicular traffic in aromatic VOCs case (Fanizza et al., 2014). Considering that Manaus is a large urbanized capital and that the GoAmazon 2014/5 site is located near to the main access road to Manacapuru, the common emission source indicated by the high correlation coefficients in both sites might suggest a prevailing influence of vehicular emissions (even though less impacting in the latter environment than in Manaus, as shown by their average concentrations). On the other hand, the weak correlation coefficients at the forest environment indicate diffuse spatial and temporal sources of BTEX, rather than a common one.

The ratio of toluene to benzene (T/B) is another tool commonly used to identify the VOC emission sources. Toluene has a shorter lifetime in the atmosphere than benzene. Hence, if a sample is taken close to a source, T/B ratios should be high, even if

concentrations are low. T/B ratios ranging from 2 to 5 were found in the atmosphere of several urban areas characterized by vehicular emissions around the world, reflecting the T/B ratio found in gasoline and auto exhaust (3-4) (Brocco et al., 1997; Gee & Sollars, 1998; Monod et al., 2001, Fanizza et al., 2014). The T/B ratio found in Manacapuru (2.53 average, range: 0.72-5.04) reinforces the hypothesis of predominant vehicular source, whereas Manaus presented somewhat higher values (5.23 average, range: 1.69-10.24). This enrichment of toluene in Manaus' atmosphere is more likely due to the combination of mobile (vehicular) and punctual (industrial) sources of pollution, known to coexist in the capital. Concerning the forest environment, though, high T/B ratios were found (8.61 average, range: 0.433-39.38). However, the values found at the tower top were in general lower than the ones found at its base. Besides that, the concentration of BTEX measured in the 1st campaign was considerably higher than in the 2nd one. These results, combined with the weak correlation between the compounds at the site, suggest the presence of an unknown source of toluene near the tower base in the 1st campaign, which was minimized or absent in the 2nd one. This unknown source could plausibly be an emission from vegetation (Misztal et al., 2015) and soils (Asensio et al., 2007).

Many studies already investigated the BTEX concentrations in other urban centers. Table 2 summarizes some of them.

Table 2 - Other BTEX assessments found in the literature.

Reference	Site	Concentration ($\mu\text{g m}^{-3}$)				
		Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Present research	Amazon (Urban)	0.237 – 19.3	0.700 – 832	0.165 – 447	0.355 – 614	0.112 – 516
	Amazon (Forest)	0.018 – 0.313	0.011 – 4.93	0.047 – 0.401	0.036 - 0.634	0.015 – 0.144
	Amazon (Semi-urban)	0.036 – 0.948	0.091 – 2.75	0.018 – 1.02	0.051 – 3.31	0.019 – 1.34
Dutta et al. (2009)	Kolkata, India	24.97 - 78.18	27.65 - 103.31	4.50 - 36.25	11.17 - 35.85	8.06 - 22.60
Stranger et al. (2008)	Antwerp, Belgium	1.8	4.3	0.6	2.1	0.6
Geiss et al. (2011)	11 European cities	3.2	2.0	2.2	5.7	2.0
Rad et al. (2014)	Ahvaz, Iran	1.8	5.2	0.5	1.1	8.6
Tunsaringkarn et al. (2014)	Bangkok, Thailand	15.1	51.2	23.0	5.8	14.7
Song et al. (2012)	Pinus forest (Spain)	0.6	0.6	0.07	0.2	0.04
Custódio et al. (2010)	Atlantic forest (Rio de Janeiro, Brazil)	<4 (sum of all five BTEX)				
Yu et al. (2008)	Forest (China)	6.29 (sum of all five BTEX)				

Stranger et al. (2008) assessed the air quality in 27 primary schools in Antwerp, Belgium, measuring, amongst several other pollutants, BTEX compounds. The mean concentrations in ambient air obtained in their study are similar to the ones measured in Bilhares Park and INPA. Dutta et al. (2009), on the other hand, found much higher mean concentrations when analyzing three different sites in Kolkata, India.

However, examining the maximum concentrations obtained by the present study, the data reported by Dutta et al. (2009) did not reach values as high as the maximum previously mentioned, occurred in the last sampling week of the present study (except for benzene, which was found by Dutta et al. (2009) in higher levels than $20 \mu\text{g m}^{-3}$).

Geiss et al. (2011) obtained slightly higher mean outdoor concentrations of BTEX than the present study, during their statistical assessment of a database containing information from 2003 to 2008 about 11 European cities. The mean concentration of toluene obtained in the AIRMEX project, however, was slightly lower than the present study.

In Bangkok, Thailand, Tunsaringkarn et al. (2014) detected high concentrations of BTEX, which seems to indicate that Bangkok, similarly to Kolkata, is more polluted than Manaus, regarding BTEX compounds.

Another recent study, performed in Ahvaz, Iran, by Rad et al. (2014), obtained results closer to the ones obtained in the present study, even though the values of o-xylene reported by them are considerably higher.

Though in reduced number, it is possible to find some studies which report the concentration of BTEX compounds in forest environments. One of them was conducted by Custódio et al. (2010), in the remnant of Atlantic forest located in the Tijuca Forest Park, in Rio de Janeiro, Brazil. This study obtained low concentrations of BTEX inside the forest environment. Other studies follow the same trend, showing that BTEX levels in forest environments are generally low. For example, the assessment performed by Kesselmeier et al. (2000) in the Amazon forest, at Balbina, Brazil, obtained very low concentrations of benzene and toluene, supporting the argument that monoaromatic VOCs emissions are predominantly anthropogenic.

Yu et al. (2008) evaluated the air quality inside the Prince Hill Forest Park, in southern China, finding a slightly higher total concentration than the observed in the present study, but it can still be considered low. Besides, Yu et al. (2008) concluded, in their study, that the BTEX sources in the assessed area are mainly anthropogenic. A study performed by Song et al. (2012) in a pine forest located in southwest Spain also came to the same conclusion.

Concerning the T/B ratio, Custódio et al. (2010) found lower values in the forest environment than in the city, which they attributed to the faster photochemical oxidation of toluene and considered an indication of low impact of the urban area on the forest.

3.3 Wet season vs. dry season results

Figure 4 presents box plot graphics comparing the measurements performed during wet and dry season, at urban and forest environments (the semi-urban environment presented too low amount of data for dry season in order to make a satisfying comparison).

Figure 4 - Box plot comparing BTEX concentration in wet and dry season, for urban ($T1_{MP}$, $T1_{BP}$ and $T1_{INPA}$) and forest ($T0_{top}$ and $T0_{base}$) environments separately.

Figure 4 indicates that the concentration values measured in wet and dry seasons are close to one another at both the studied sites. The DTK test confirmed that the difference in BTEX mean concentration is not significant ($p > 0.05$) when comparing wet and dry seasons at the same site.

Usually in atmospheric pollution studies it is considered that precipitation scavenges air pollutants from the atmosphere, in a process commonly known as rain washout. However, rain washout dominates the atmospheric removal of polar chemicals while non-polar chemicals, such as BTEX, are removed mainly through degradation or particle-associated dry deposition (Götz et al., 2008). Therefore, it should be expected that the occurrence of precipitation does not affect the presence of BTEX in the atmosphere. In addition, the BTEX source (vehicular emission) is not related to the season, being continuous over the year.

However, it was expected that the pollution levels in the atmosphere of both sites would decrease in the wet season, considering the higher occurrence of forest fires in the dry season and their contributions by pyrogenic volatiles (Andreae & Merlet, 2001). Furthermore, aromatic compounds might be degraded and incorporated into aerosols from the formation of the urban plume by wet route, meaning that BTEX can be indirectly incorporated into the wet phase (Volkamer et al., 2001).

It is then advised to further assess these sites in order to define which role the forest fires play as a considerable source of BTEX to the Amazonian atmosphere.

3.4 Risk Assessment

Table 3 displays the values of risk probability calculated by means of the Risk Model of the Risk Assessment Information System – RAIS for the sampling sites located in the urban area.

Table 3 - Risk values for the VOCs concentration at the urban area.

Polutant	Mindu Park		Bilhães Park		INPA	
	IAAR* (chronic) (x 10 ⁻³)	IAAR (carcinogenic) (x 10 ⁻⁶)	IAAR* (chronic) (x 10 ⁻³)	IAAR (carcinogenic) (x 10 ⁻⁶)	IAAR* (chronic) (x 10 ⁻³)	IAAR (carcinogenic) (x 10 ⁻⁶)
Benzene	13.4	1.07	49.9	3.97	37.7	3.01
Ethylbenzene	0.326	0.278	0.828	0.705	1.13	0.963
Toluene	0.685	-	1.24	-	1.23	-
p-Xylene	8.32	-	20.2	-	22.8	-
m-Xylene	8.32	-	20.2	-	22.8	-
o-Xylene	2.19	-	5.09	-	5.36	-
Total risk	33.3	1.35	97.5	4.68	91.1	3.97

*Inhalation Ambient Air Risk

It is important to notice that some of the risk probability values were not calculated due to the unavailability of toxicity data for some compounds.

Observing the values from Table 3, it is not possible to affirm that the concentrations obtained in the present study have an influence on the development of chronic diseases which are not cancer.

The concentration values measured in the present study may induce cancer development in 1.35 people in a million during the course of a lifetime at Mindu Park, in 4.68 people in a million at Bilhães Park and 3.97 people in a million at INPA. According to the Guidance on Risk Assessment for Air Contaminant Emission, a cancer development risk lower or equal to one person in a million (1×10^{-6}) can be considered negligible. However, values higher than one person in ten thousand (1×10^{-4}) are considered unacceptable (NJDEP, 2009). This means that, even though the total risk of cancer development obtained in the present study is not considered inadmissible, it is also not negligible, meaning that there should be a bigger concern regarding Manaus' air quality.

4. Conclusions

Results indicated that there is an increase in the pollutants concentration with increasing proximity to urban areas, which was expected, since the studied pollutants are

emitted mainly by anthropogenic sources, such as vehicles emission. Correlation test and toluene/benzene ratio suggest that BTEX pollution in Manaus derive equally from automobile traffic and industrial emissions. Also, these tests indicated that the GoAmazon 2014/5 site is influenced by vehicles emissions, even though in a lesser degree than Manaus. Even though the BTEX concentration in the forest environment was very low, there is evidence of the presence a toluene source near the tower base, more evident in the first campaign during the wet season.

However, there was no significant difference between the pollution levels measured during the dry and the wet season at both urban and non-urban sites, differently from what was expected. It was expected that the concentrations measured during the dry season were higher than the ones measured during the wet season, considering the increase in forest burnings in the dry season.

Besides that, it was observed that the air quality in Manaus is apparently less deteriorated by monoaromatic organic compounds than in other large cities, even though the risk assessment performed in the present study indicated that the possibility of cancer development influenced by air pollution is not negligible for Manaus' pollution levels. Therefore, it is possible to conclude that, even though it is surrounded by the greatest rainforest in the world, Manaus is also subject to issues similar to the ones faced by other capitals in Brazil and in the world.

The main goal of the present research is to serve as a first diagnosis on atmospheric pollution for the region, which lacks studies regarding Manaus urban area. Considering Manaus' continuously growing automobile fleet, industrial district and presence of thermoelectric plants (MANAUS, 2002), the systematic assessment of the air quality in the surrounding area is imperative. The measurements taken in the forest testify how human activity has been already deteriorating the air quality in the Amazon region, which must be taken into account when developing public policies for atmospheric pollution control.

5. Acknowledgements

This work was financially supported by the National Council for Scientific and Technological Development (CNPq). We also thank the support of the Fundação de Amparo à Pesquisa do Estado do Amazonas (FAPEAM) and the Financiadora de Estudos e Projetos (FINEP).

We thank the Atmospheric Radiation Measurement (ARM) Climate Research Facility and the U.S. Department of Energy Office of Science user facility sponsored by the Office of Biological and Environmental Research. We also acknowledge the support from the Central Office of the Large Scale Biosphere Atmosphere Experiment in Amazônia (LBA), the Instituto Nacional de Pesquisas da Amazônia (INPA) and the Universidade do Estado do Amazonas (UEA).

We also thank the Max Planck Society and INPA for continuous support. We acknowledge the support by the German Federal Ministry of Education and Research (BMBFcontract 01LB1001A) and the Brazilian Ministério da Ciência, Tecnologia e Inovação (MCTI/FINEP contract 01.11.01248.00) as well as the UEA, FAPEAM, LBA/INPA and SDS/CEUC/RDS-Uatumã. We would like to especially thank all the people involved in the logistical support of the ATTO project, in particular Reiner Ditz and Hermes Braga Xavier. We acknowledge the Micrometeorological group of the INPA/LBA for their collaboration concerning the meteorological parameters, with special thanks to Marta Sá, Antonio Huxley and Leonardo Oliveira.

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