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Observations of particulate matter, NO_2, SO_2, O_3, H_2S and selected VOCs at a semi-urban environment in the Amazon region☆

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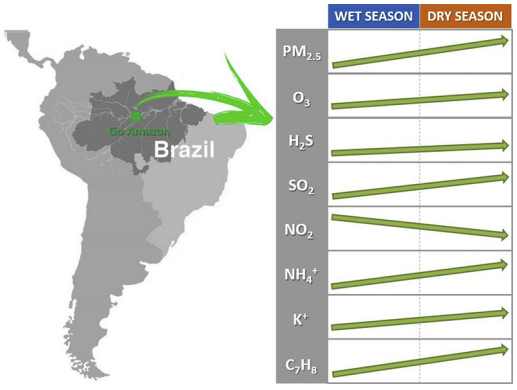
HIGHLIGHTS

- Air quality analysis in transitional site between city-forest at the Amazon region
- Particulate and gaseous pollutants measured in wet and dry seasons
- Several evidences indicate strong influence of biomass burning emissions.
- During dry season, atmospheric pollution in the site rises significantly.

GRAPHICAL ABSTRACT



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ABSTRACT

This research aims to assess air quality in a transitional location between city and forest in the Amazon region. Located downwind of the Manaus metropolitan region, this study is part of the large-scale experiment GoAmazon2014/5. Based on their pollutant potential, inhalable particulate matter ($PM_{2.5}$), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ozone (O_3), hydrogen sulfide (H_2S), benzene, toluene, ethylbenzene and meta-, orto-, para-xylene (BTEX) were selected for analysis. Sampling took place during the wet season (March–April 2014) and dry season (August–October 2014). The number of forest fires in the surroundings was higher during the dry wet season. Results show significant increase during the dry season in mass concentration (wet: <0.01–10 μg m^{-3}; dry: 9.8–69 μg m^{-3}), NH_4^+ soluble content (wet: 13–125 μg m^{-3}; dry: 86–323 μg m^{-3}) and K^+ soluble content (wet: 11–168 μg m^{-3}; dry 60–356 μg m^{-3}) of the $PM_{2.5}$, and O_3 levels (wet: 1.4–14 μg m^{-3}; dry: 1.0–40 μg m^{-3}), indicating influence of biomass burning emissions. BTEX concentrations were

☆ CAPSULE: "*Levels of $PM_{2.5}$, NO_2, SO_2, O_3, H_2S and BTEX were measured at a semi-urban environment in the Amazon region during the wet and dry seasons of 2014, and results indicate a large influence of biomass burning emissions in the region's air quality.*"

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low in both periods, but also increased during the dry season. A weak correlation in the time series of the organic and inorganic gaseous pollutants indicates a combination of different sources in both seasons and NO2 results suggest a spatial heterogeneity in gaseous pollutants levels beyond initial expectations.

1. Introduction

The urban and industrial development, the ever-growing automotive fleet and consumption patterns, the current agricultural methods and use of fertilizers, the high deforestation levels and recurrent forest fires are some of the factors which contribute to the continuous rise in the emission of atmospheric pollutants worldwide. All over the world, scientific literature agrees that the atmospheric pollution represents a significant threat to global public health (WHO, 2006; Bruce et al., 2000; Delfino et al., 2003; Watson, 2014; Kessler, 2014; Dominici et al., 2015; Bourdrel et al., 2017). Atmospheric pollutants also present important effects over the climate, such as interference on the energetic balance, altering the reflection, dispersion and absorption rates of solar radiation by the atmosphere. Several pollutants also act as nuclei of condensation and formation of clouds, potentially leading to rising the precipitation rates at the affected areas (Russo, 2013).

Specifically in forest ecosystems, atmospheric pollution is a concern since it may lead to species elimination, biomass production reduction and a higher incidence of plagues and diseases (Schumacher and Hoppe, 2000). Some relevant compounds from the air quality perspective are also emitted by biogenic sources, which can even possibly aggravate the situation of urban atmospheres in the case of such compounds being transported by the wind (Fehsenfeld et al., 1992; Guenther et al., 1995; König et al., 1995; Kesselmeier and Staudt, 1999).

Amongst the main substances studied in air quality evaluations, are those considered in the present research: particulate matter (PM), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3), hydrogen sulfide (H_2S) and volatile organic compounds (VOCs).

The Amazon basin is one of the areas with the highest animal and vegetal biodiversity in the globe, besides housing one of the largest freshwater reservoirs. The forest in that area is of vital importance to the maintenance of the rainfall regimen in the region and its destruction interferes directly on the microclimate (Martin et al., 2017). The primary known sources of atmospheric pollution, such as industries, vehicles traffic, and biomass burning (forest fires and deforestation), are simultaneously present in the Amazon region (Martin et al., 2017), besides the aforementioned biogenic sources.

Considering the global relevance of the natural Amazon ecosystem, the air quality monitoring in the region and a better understanding of how the different sources (biogenic and anthropogenic) and the meteorological conditions relate to affect it are indispensable. Thus, studies which evaluate the presence of atmospheric pollutants in the Amazon region are valuable both from the environmental and from the social-economic point of view (Martin et al., 2017).

The sampling site selected was the study area of the Green Ocean Amazon (GoAmazon2014/5) project (Martin et al., 2016), which had the goal to quantify and understand the mechanisms affecting the distribution of pollution over the Amazon forest region, especially that originated from anthropogenic sources. The GoAmazon2014/5 project, which ran for a period of 2 years (2014 and 2015) in a site located downwind of the Manaus metropolitan region (an area of lower urban development), sampled several particulate and gaseous substances and compared data obtained during two intensive sampling periods, during the dry and the wet season, with factors such as seasonality and particles transportation (Martin et al., 2017).

The present research is inserted in the GoAmazon2014/5 project, contributing with concentration data of inhalable fine particulate matter with diameter smaller than 2.5 μm ($PM_{2.5}$), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3), hydrogen sulfide (H_2S) and the monoaromatic compounds benzene, toluene, ethylbenzene and xylenes (BTEX). The main goal is to increase the available data on air quality in the Amazon region, since the knowledge about this subject is still superficial.

2. Materials and methods

2.1. Sampling site

The site chosen for the present research was the central study area of the international experiment GoAmazon2014/5 (3°12′47.82″S, 60°35′55.32″W), located downwind of the metropolitan region of Manaus, the capital of the Brazilian state of Amazonas. This location represents a transition area between the urban and forest environments at the Amazon basin, enabling to investigate the extent of the influence of different types of pollution sources, such as the pollution plume originating in Manaus. The chosen site had adequate infrastructure and security for research activities thanks to the GoAmazon2014/5 project, thus being an advantageous location for the fulfillment of the present research. A thorough description of the site and its infrastructure along with details about the GoAmazon2014/5 experiment can be found in Martin et al. (2016).

The sampling of gaseous compounds took place at five points (T3 01, T3 02, T3 03, T3 04 and T3 05), distributed along a 5-km straight line, perpendicular to the Manaus-Manacapuru axis. The central point, T3 03, is located inside the GoAmazon2014/5 installations, and two points were then added to each side. The distance between each pair of consecutive points is 1 km. At each location, gaseous compounds samplers were attached to public lamp posts, heights varying from 1.5 to 2 m, protected from the weather by plastic shelters. All the sampling points are located outdoors, not under trees canopy.

Differently from the gaseous compounds, the samples of $PM_{2.5}$ were taken exclusively at the central point (T3 03), because its sampling procedure requires electrical power. Fig. 1 shows a satellite image of the sampling points location, with particular detail to point T3 03, which shows the surroundings of point T3 03, consisting in the T3 site from the GoAmazon2014/5 project. In the detail-picture, it is possible to see the suite of containers installed by GoAmazon2014/5 researchers, each of them containing different equipment. Point T3 03 specifically was located in the grass area by the right side of the detail-picture.

Gaseous samples were collected weekly in two different periods: the first during the region's wet season, from March 1 to 31, 2014 (called First Intensive Operating Period, IOP1), and the second during the dry season, from August 15 to October 15, 2014 (called Second Intensive Operating Period, IOP2). The $PM_{2.5}$ samples were collected on a daily basis, also divided into two periods in the dry and wet seasons, but with start and end dates slightly different (wet season: March 3 to 21; dry season: September 4 to October 17).

2.2. Sampling procedures

$PM_{2.5}$ was sampled daily on 37 mm diameter Nucleopore® polycarbonate filters (Polezer et al., 2018). The polycarbonate filter was used for sampling because it is an inert material. For the $PM_{2.5}$ sampling, a Harvard impactor was used, connected to a vacuum pump and a flow meter.

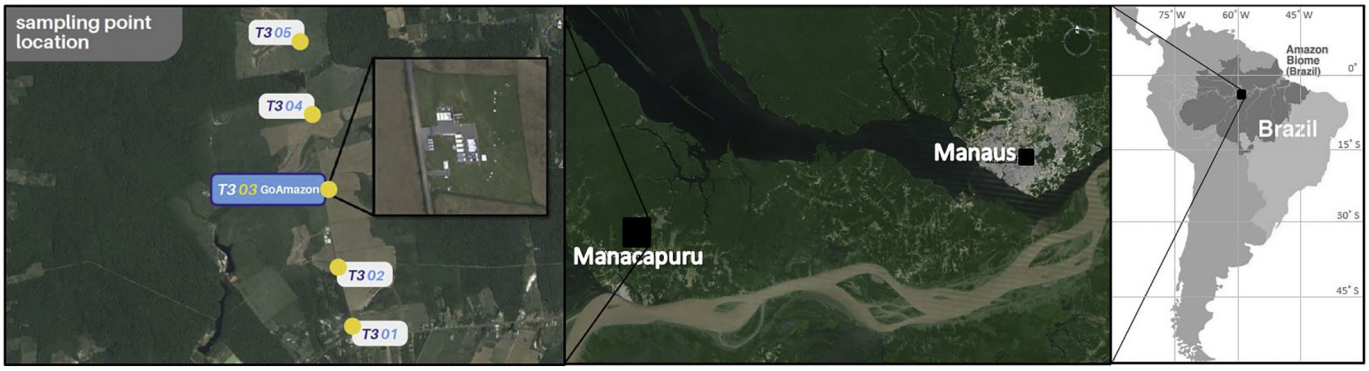

Fig. 1. Sampling site location in the Brazilian Amazon Basin (right panel), downwind Manaus city (center panel), with five selected sampling points in the study area of the GoAmazon2014/5 project, in detail, and referred as T3 03 point (left panel).
Source: GeoEye© Satellite, Google Earth, 2015.

Gaseous pollutants were sampled using Radiello® passive diffuser samplers, manufactured by Fondazione Salvatore Maugeri (Padova, Italy). For NO_2 and SO_2 (co-captured in the same sampler), H_2S and O_3, the samplers consist of chemo-absorber cartridges impregnated with substances suitable to collect each type of gas (Godoi et al., 2013; Godoi et al., 2018). BTEX gases were co-captured by cartridges composed of a cylindrical mesh of stainless steel filled with activated carbon, where VOCs are retained by means of adsorption (Paralovo et al., 2016).

The Radiello samplers are previously validated in laboratory by the manufacturer. Detailed information about the validation and calibration of the sampling technique can be found elsewhere (Swaans et al., 2007; Cocheo et al., 2009; Campos et al., 2010).

2.3. Analytical procedures

All laboratory procedures and analyzes performed in this research were made in Federal University of Paraná (UFPR) laboratories. Different techniques were used to characterize the $PM_{2.5}$ samples: gravimetric mass analysis (Analytical micro scale, model MSA2.7S-000-DF, Sartorius), black carbon (BC) concentration by black carbon transmittance (Sootscan optical transmissometer, model OT 21, Magee Scientific Company) and cations concentration by ion chromatography (Ion Chromatograph, ICS5000 Dionex/Thermo Fisher). The gravimetric calculations were done using the average mass of the blanks as initial mass for all samples. An ANOVA test was carried out in order to statistically compare the average final mass of blanks with the average initial mass of the sampled filters. The result showed that, with 95% confidence, there is no significant difference between those averages (p-value = 0.1), nor between their variances.

The SO_2/NO_2 samples obtained after extraction with ultrapure water were analyzed also by ion chromatography (as NO_2 and SO_2 gases are chemiadsorbed onto the sampler cartridge as the ions SO_4^{2-} and NO_2^-, respectively), using the same equipment used to determine the cation concentration of the $PM_{2.5}$. The capillary system (2 mm) uses ultrapure water and methanesulfonic acid (20 mM) as eluent in a static flow of 0.33 mL min^{-1} with automatic suppression and separation thought the IonPac CG-12 and CS-12, guard and separation columns, respectively.

The BTEX samples, after extraction using CS_2 solvent for desorption, were analyzed in a Perkin Elmer 680 SQ T® gas chromatograph with a flame ionization detector (FID). Concentrations of O_3 and H_2S were determined by UV–Vis spectrophotometry using a Varian spectrophotometer.

Table 1 shows the method limits of detection and quantitation for each of the pollutants analyzed by chromatography and spectrophotometry. Additionally, the expanded uncertainty at the 95% level of confidence (BIPM, 2008) for the sampling, analysis and unit conversion procedures for each substance is also presented.

2.4. Meteorological conditions and forest fires monitoring

Meteorological data (temperature, precipitation, relative humidity, wind speed and direction at surface level) in this research was measured every 60 s by sensors located on the soil surface at the GoAmazon2014/5 sampling site (T3 03) and was consulted online in the ARM website (ARM, 2016). Burning outbreaks were monitored via a fire outbreak monitoring tool provided by the National Institute of Space Research's (INPE's) Burning and Fires Monitoring, available online (INPE, 2016). The images were later juxtaposed to satellite images obtained via GoogleEarth (2016). More detailed information on meteorological conditions and fire outbreaks during IOP1 and IOP2 can be found in Martin et al. (2016).

2.5. Statistical analysis

Spearman's correlation test, adequate when the distribution deviates from normality, was used to evaluate the level of correlation between each pair of pollutants. A positive correlation between two pollutants possibly indicates a common emission source, whereas a negative correlation may suggest that one of the contaminants causes the other one's formation or degradation.

Boxplot charts were also used to evaluate the dataset, as a means of detecting extreme values, i.e. values that do not represent the data group and may affect correlation coefficients and the application of other statistical tests and ultimately compromise the discussion and conclusions of the study (Morettin and Toloi, 2004).

Table 1
Limit of detection (LOD), limit of quantitation (LOQ) and uncertainty for each analyzed substance.

Pollutant	LOD (μg m^{-3})	LOQ (μg m^{-3})	Uncertainty (%)
NO_2	0,0304	0,0608	15.25
SO_2	0,0397	0,0793	8.27
O_3	0,4687	0,9374	12.05
H_2S	0,0002	0,0005	17.44
Benzene	0,0559	0,1117	14.89
Toluene	0,0598	0,1197	16.14
Ethylbenzene	0,0194	0,0388	19.87
m,p-Xylene	0,0259	0,0518	18.16
o-Xylene	0,0064	0,0127	15.76
Li^+	<0,0001	0,0002	6.07
Na^+	0,0128	0,0256	5.39
NH_4^+	0,0067	0,0134	5.14
K^+	0,0038	0,0076	4.25
Mg^{2+}	0,0017	0,0035	9.29
Ca^{2+}	0,0105	0,0210	1.87

To validate the graphical comparison provided by the boxplots, the variance test (ANOVA) was used to compare each two data groups of interest, at a 95% confidence level. As a complement for the variance analysis, a mean comparison test was performed to indicate how the compared groups differ,the DTK test (*Dunnett-Tukey-Kramer* Pairwise Multiple Comparison Test),adequate for use when the variance homogeneity of the population cannot be assumed (Dunnett, 1980).

3. Results and discussion

3.1. Meteorological conditions and forest fires

Precipitation events recorded during both seasons presented similar intensity. However, were more frequent during the wet season. According to data from the INMET A119 automatic station, the cumulative rainfall during IOP1 (03/01/2014 to 04/21/2014) nearby in Manacapuru was 757 mm, while in IOP2 (08/15/2014 to 10/17/2014) was 291 mm (INMET, 2016), confirming that the studied period followed the region previously observed pattern. Some difference between both periods was also observed regarding relative humidity (RH): while night-time maximum RH during both periods was very similar (~90%), daytime RH during IOP1 was higher (89%) compared to that from IOP2 (66%). Further details concerning precipitation over T3 during the GoAmazon2014/5 project can be found in Giangrande et al. (2017).

Another meteorological condition that may influence the measurements is wind. Prevailing direction of wind can often indicate where the transported pollutants come from and may go to, although it is important to notice that surface winds and overhead winds can differ. Driven by the easterlies of the trade winds, the plume from Manaus frequently reaches T3 all year long, potentially carrying urban pollutants into the site. In the wet season, although the pollution outflow from Manaus most frequently continues southwesterly, 40% of the time it is modeled to go westerly towards T3. In the dry season, the plume primarily passes westerly from Manaus, and 60% of the time it is modeled to pass over T3, potentially adding urban pollutants to the already significant pollution from regional- and continental-scale biomass burning (Martin et al., 2017; Artaxo et al., 2002). In fact, modelling demonstrates that anthropogenic emissions influence chemical reactions over the rain forest far downwind of Manaus (Martin et al., 2017). At times, there are also episodic intrusions of background and polluted Atlantic and African air masses deep into the Amazon (Martin et al., 2010).

Wind direction data measured at T3 in the present study was used to construct wind roses. The data showed that surface wind predominant direction was from the east during the first 5 weeks of IOP1 (wet season). In the last two weeks of IOP1 and throughout IOP2, surface wind direction varied considerably. Wind speed data shows that the winds in the period were mostly mild (between 2 and 6 m s^{-1}) and calm (<2 m s^{-1}): in IOP1, 97% of the time wind speeds remained below 6 m s^{-1}; in IOP2, they stayed in that interval 98% of the time. According to Kourtchev et al. (2014), strong winds (above 6 m s^{-1}) are related to longer distances transportation and also to greater dilution of pollutants in the atmosphere, while mild and calm winds may indicate prominence of closer sources.

Fire outbreak spots registered by several satellites in the first and last weeks of IOP1 and IOP2 in the state of Amazonas are shown in Fig. 2. During IOP2, the number of fire outbreaks observed in the state of Amazonas exceeded 1000 in 5 of the 7 sampling weeks, while during IOP1 this number does not reach a 100 in either of the sampling weeks. Besides, the amount of fire outbreaks registered differs only slightly from one week to the next in the same period. Therefore, the magnitude of the difference is observable only between dry and wet seasons as a whole regarding the number of fire events of the region's biomass.

The forest fires may be directly connected to the health of the population living in the Amazon region. According to data provided by the Brazilian Ministry of Health (MS, 2016), the number of hospitalizations due to respiratory issues registered in the public hospitals in Manacapuru rose from 31 in March/2014 to 69, 46 and 45 in August, September and October/2014, respectively. The trend in 2014 was similar in Manaus (702 in March; 1085 in August; 941 in September and 965 in October), as was in the whole Amazonas state (1117 in March; 1647 in August; 1551 in September and 1551 in October). These numbers suggest a possible adverse effect of biomass burning over the Amazon population and should be further studied.

3.2. Fine particulate matter ($PM_{2.5}$)

3.2.1. Mass concentration and BC

The boxplots presented in Fig. 3 allow a direct comparison between both seasons: wet and dry (IOP 1 and 2) regarding mass and BC concentrations. In this Figure, it is possible to observe the clear difference between both periods regarding mass concentration, whereas IOP2 presents higher concentrations than IOP1. The ANOVA test confirmed that there is a significant difference between the average mass concentration in both IOPs (p-value < 0.01). PM removal from the atmosphere happens in both season, but by different mechanisms. Dry season removal mechanisms include: Brownian diffusion for ultrafine (<0.1 μm) PM, consisting in the movement of the particles immersed in air, caused by its collisions with the surrounding molecules; and wind, direct impaction and sedimentation by gravity for fine and coarse PM. The latter depends on the deposition velocity of the particle, which rises proportionally to the particle size (Yang et al., 2014; EPA, 2004). During the wet season, PM removal is mostly due to wet deposition resulting from precipitation events, due to the impact of the droplets against the larger particles or due to the finer particles diffusion into the raindrops, resulting in their carrying and consequent removal (Yang et al., 2014; EPA, 2004).

According to Martin et al. (2010), the atmospheric pollution levels in the Amazon forest during the wet season are close to those observed over remote oceans, making it similar to a pristine atmosphere. During the dry season, however, the Amazon atmosphere becomes highly polluted, mostly because the number of forest fires, both the naturally occurring ones and the purposefully initiated for deforestation, increases significantly.

The values of mass and BC concentration measured in the present study are compared to the ones measured by other researchers in other locations in Table 2.

The mass concentration observed by Artaxo et al. (2013) in the central Amazon forest was low compared to the present research. Similar results for both seasons was also reported by Pauliquevis et al. (2012) in forest environment at Balbina, Amazonas state and by Barbosa (2014) at the ATTO experiment (Amazonian Tall Tower Observatory, detailed in Andreae et al., 2015). At the city of Manaus, however, Barbosa (2014) obtained average values closer to the ones found by the present research, indicating that, with regards to $PM_{2.5}$ mass concentration, T3's atmosphere might be more similar to the atmosphere of the urban environment of Manaus than to the surrounding forest's atmosphere.

Miranda et al. (2012) investigated the air quality in six Brazilian capitals. The average mass concentration of $PM_{2.5}$ measured during the wet season in the present research (1.65 ± 2.04 μg m^{-3}) is below the averages observed in the six capitals (Table 2). However, the dry season average (21.6 ± 14.6 μg m^{-3}) is close to the average mass concentrations observed in São Paulo and Rio de Janeiro, the two biggest cities in Brazil. The average $PM_{2.5}$ of IOP2 is also close to the observed in Santiago, Chile, during the warmer seasons (Villalobos et al., 2015). These comparisons showcase the large influence of the dry season fires for air quality in IOP2 at the site. López et al. (2011), on the other hand, registered higher levels of $PM_{2.5}$ in Córdoba, Argentina, where the average values in both urban and semi-urban sites were close to the maximum registered in Manaus, during IOP2.

Regarding BC concentration, the difference between the measurements made in the present research during dry and wet seasons is

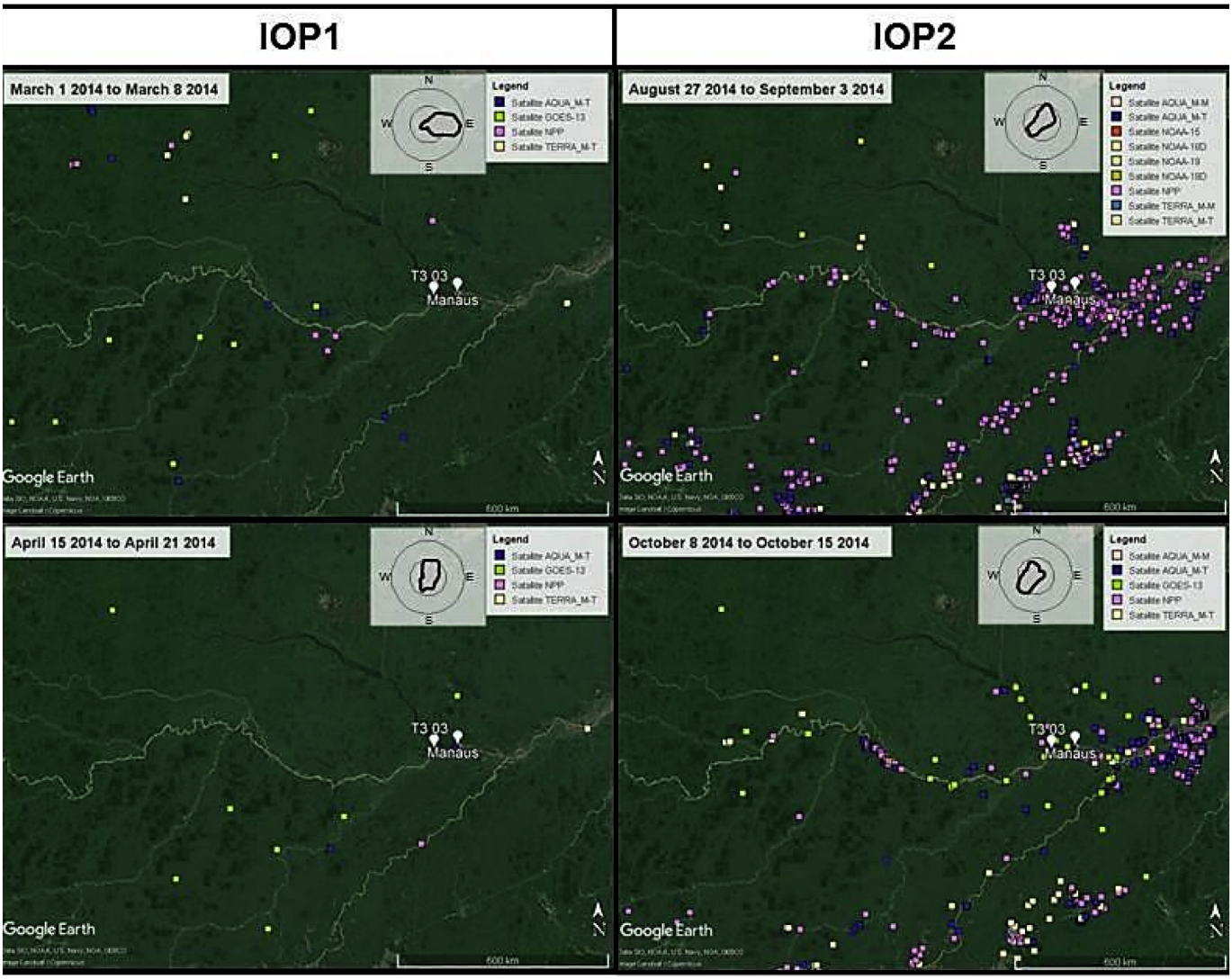

Fig. 2. Forest fires registered by several satellites during the first and last sampling weeks of IOP1 and IOP2. In detail, wind roses represent the predominant average wind direction in each week.

subtle, but ANOVA test indicated that this small difference is in fact significant (p-value = 0.03). The primary anthropogenic BC source is the automobile fleet, which is a factor that does not vary from one season to the other. This is reflected in the less evident difference between the average BC concentrations measured in both seasons. Similar results were reported by Pauliquevis et al. (2012) and Barbosa (2014) at ATTO,

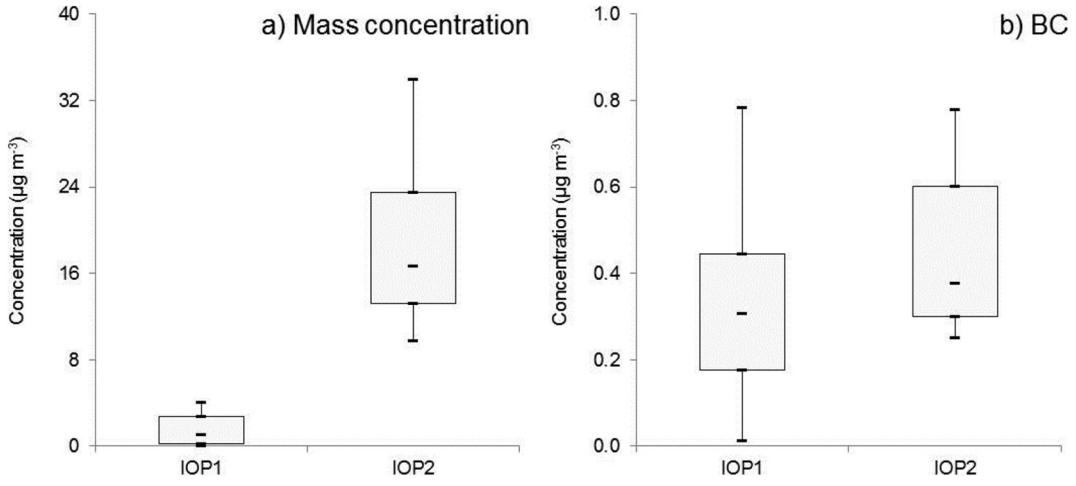

Fig. 3. Boxplots comparing (a) mass concentrations and (b) BC concentrations measured in each season (outliers not displayed in order not to hinder visualization).

Table 2
Similar studies in other locations and their reported $PM_{2.5}$ and BC average concentrations.

Study	Location	Concentration (μg m^{-3})	
		Mass	BC
Present study	T3 (downwind of Manaus)	<0.01–10 (wet) 9.8–69 (dry)	0.013–0.78 (wet) 0.25–1.2 (dry)
Artaxo et al. (2013)	Central Amazon (For.)[a]	1.3 (wet) 3.4 (dry)	2–4
Barbosa (2014)	Manaus	8.8 (wet) 12 (dry)	1.9 (wet) 2.4 (dry)
	Central Amazon – ATTO (For.)	1.6 (wet) 2.4 (dry)	0.25 (wet) 0.080 (dry)
Miranda et al. (2012)	São Paulo Rio de Janeiro Belo Horizonte Curitiba Recife Porto Alegre	28 (annual average) 17(annual average) 15(annual average) 14 (annual average) 7.3 (annual average) 13 (annual average)	11 (annual average) 3.4 (annual average) 4.5 (annual average) 4.4 (annual average) 3.9 (annual average) 1.9 (annual average)
López et al. (2011)	Córdoba, Argentina	71 (urban site) 67 (semi-urban site)	–
Villalobos et al. (2015)	Santiago, Chile	62 (winter) 20 (summer/spring)	–
Pauliquevis et al. (2012)	Balbina, AM (For.)	2.2 (wet) 6.2 (dry)	0.048 (wet) 0.053 (dry)

[a] For.: Forest area.

who measured similar BC average concentrations in both seasons and close to the values obtained in the present research. Artaxo et al. (2013), on the other hand, observed slightly higher BC concentration values compared to the current investigation, but also reported a small difference between seasons.

In Manaus, Barbosa (2014) also measured higher values of BC concentration when compared to T3, but also very similar between both seasons. Miranda et al. (2012), in their turn, observed higher BC levels in all six Brazilian capitals, being Porto Alegre the closest one to IOP2 in that sense.

3.2.2. Soluble cations on $PM_{2.5}$

In Fig. 4 it is possible to observe the soluble cations concentration data organized in a boxplot in order to compare the IOPs. Among the six cations analyzed in the samples, only potassium (K^+), ammonium (NH_4^+) and magnesium (Mg^{2+}) presented average concentrations

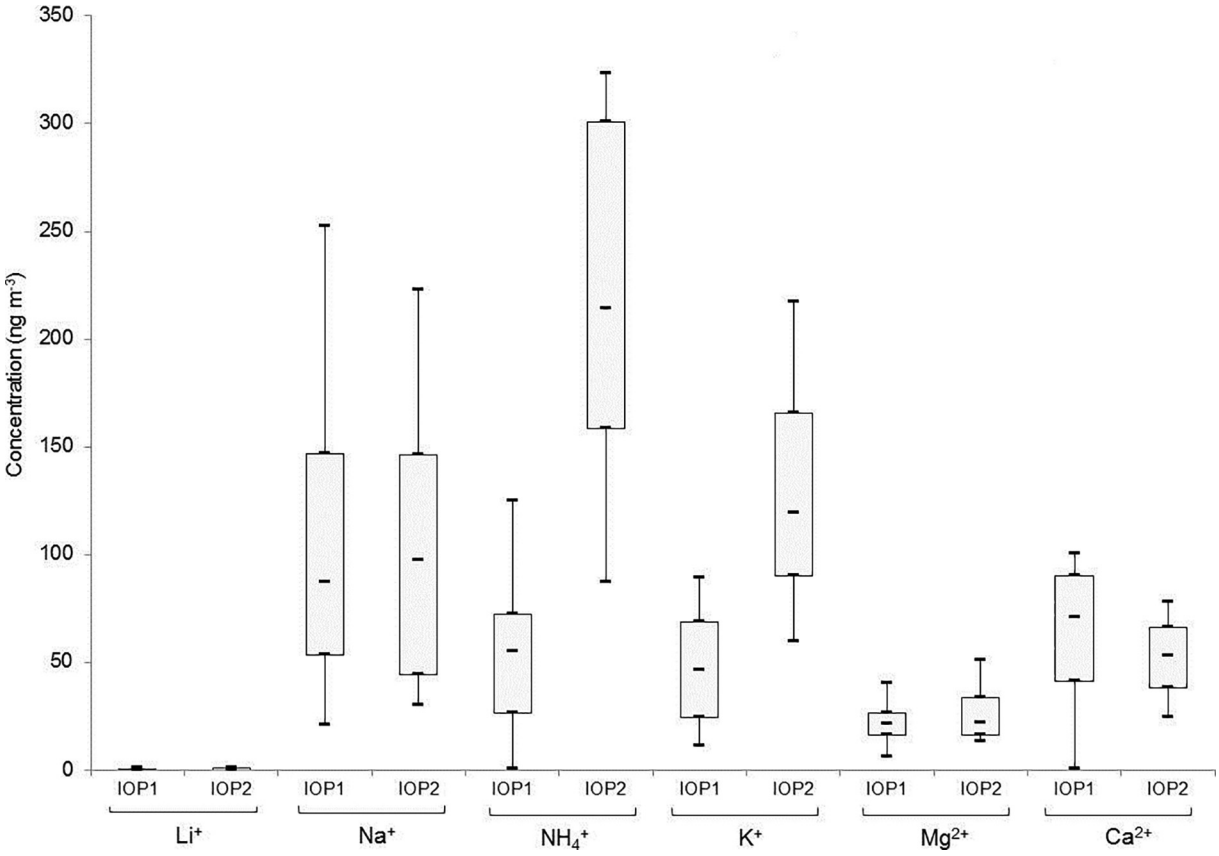

Fig. 4. Boxplot chart comparing soluble ion concentration (ng m^{-3}) in atmospheric $PM_{2.5}$, measured in each season. Minimum and maximum values (outside bars), median value (inside bar) and 1st and 3rd quartiles (box) displayed.

significantly different between the two IOPs (p-values < 0.05), being all three higher during IOP2.

The K^+ ion is often used as a tracer for forest fires and biomass burning (Yamasoe et al., 2000), though K^+-rich particles may also be emitted by the biota in rainforest environments (Pöhlker et al., 2012). The higher levels of K^+ during IOP2, as well as the positive correlation between K^+/BC concentrations (0.7), might be another indication of the biomass burning influence over the air quality in the site.

The ammonium ion most likely indicates the occurrence of secondary aerosols containing ammonium salts, formed primarily from the reaction of ammonia (NH_3) with acidic substances in the atmosphere (da Rocha et al., 2012; Felix and Cardoso, 2004). In addition, O'Brien et al. (2013) suggested that NH_3 may also react with organic components leading to the formation of nitrogen containing compounds. The authors also indicated that up to 50% of observed nitrogen containing organic compounds in their study could have been formed via this reaction. This suggestion is in convergence with the observation of organonitrates in T3 site reported in a parallel study carried out in T3 (Kourtchev et al., 2016), which showed that the number of molecular formulae containing CHON subgroups increased by 20% from IOP1 to IOP2. There is a range of potential sources of NH_3 gas to the atmosphere, including biomass and fossil fuels burning, fertilizers, human and animal waste, etc. (Felix and Cardoso, 2004). Considering that the NH_4^+ concentrations were higher during IOP2, it is possible to conclude that the presence of NH_3 gas at the site is also higher during the dry season, which may be connected to the fact that several known NH_3 sources are more present during the dry season (especially biomass burning), but also to the fact that the main NH_3 removal route from the atmosphere is wet deposition (Felix and Cardoso, 2004).

Regarding magnesium ion, the observed difference between the two IOPs is more subtle, but still significant according to the ANOVA test (p-value < 0.05). According to da Rocha et al. (2012), the presence of magnesium ion in PM might be an indication of sea spray emission influence.

Even though very similar between both IOPs, calcium (Ca^{2+}) and especially sodium (Na^+) were measured at high concentrations at the studied site. The presence of such ions is connected to the influence of sea spray or sea salt (Martin et al., 2010; da Rocha et al., 2012). The high and constant concentrations of Na^+ and Ca^{2+}, along with the aforementioned Mg^{2+} concentrations, suggest the influence of this type of source at the T3 03 site.

Also as a part of the GoAmazon2014/5 experiment, Kourtchev et al. (2016) analyzed the organic fraction of $PM_{2.5}$ aerosol samples collected at T3 during IOPs 1 and 2. The results obtained in that study led to the conclusion that T3 is influenced not only by biogenic emissions from the forest but also by biomass burning and potentially other anthropogenic emissions from the neighboring urban environments. Influence of pollution plumes carried by air masses from Manaus to T3 has been observed by both Martin et al. (2016) and Kourtchev et al. (2016). Although the surface wind data presented in this research is not sufficient to draw any conclusions, it is likely that the samples from the present research were also subjected to urban pollution carried from Manaus by overhead winds, in addition to aforementioned biogenic and biomass burning sources.

3.3. Gaseous pollutants

The levels of gaseous pollutants were compared among the five different sampling points to verify the spatial variability of the studied pollutants concentrations. The average concentrations of all gaseous pollutants show little variation from one point to the other in both IOPs. The DTK test results show that, with 95% of trust, there is not in fact any significant difference among the average concentrations measured at the different points in each period. Therefore, it is possibly more adequate to treat the five points as representative of one single site. Thus, the data set was divided into only two groups for each compound, one corresponding to IOP1 and the other to IOP2, disregarding the different points, as shown by the boxplots in Fig. 5. Then, the difference between the two periods was evaluated statistically using the ANOVA test.

Usually in studies of atmospheric pollution, it is held that precipitation removes gaseous pollutants from the air in a process commonly known as the "washout effect". This process dominates the removal of polar compounds (and particulate matter, as explained in Section 3.2.1), while non-polar compounds are removed by degradation or by processes of dry deposition (Götz et al., 2008). The process of gas removal from the atmosphere, however, is more complex than just the washout effect. This effect, of great environmental importance due to intensifying episodes of acid rain (Yoo et al., 2014), is usually significant for the NO_2 and SO_2 gases, considering their high solubility in water.

In this research, the difference between IOP1 and IOP2 was slight but significant for NO_2 (p-value < 0.05), which appeared in some samples in concentrations up to an order of magnitude higher in IOP1. This behavior in NO_2 concentration, which seems to contradict the washout effect, was also observed by Yoo et al. (2014), who attributed the higher concentrations NO_2 during the wet season to indirect generation of NO_2 by lightning during precipitation. However, this data does not agree with the NO_y measurements reported in the parallel study conducted by Kourtchev et al. (2016), in which IOP2 presented significantly higher levels of NO_y than IOP1. Although the reason for such a discrepancy is not yet clear, two factors may have contributed for it: 1) the fact that the measurements reported by Kourtchev et al. (2016) were all taken exclusively at the point T3 03, considering that T3 03 also presented low NO_2 concentrations during IOP1 and IOP2 in the present study and 2) the fact that point T3 01, right beside the road that connects Manaus to Manacapuru (whereas point T3 03 was 2 km distant from it), presented much higher NO_2 concentrations (during both periods, but especially during IOP1) than the other 4 points, shifting the average value up. This might suggest a relevant spatial heterogeneity for NO_2 levels at the site, in the sense that sources of NO_2 (the regular automobile traffic from the road and possibly lightning, since it is more active during the wet season) might affect more the peripheral sampling points than the central one. Nevertheless, when testing the NO_2 dataset considering just points T3 02 to T3 05, the ANOVA test showed no significant difference (p-value > 0.05) between the IOP1 and IOP2 (Fig. 5a).

For SO_2, the ANOVA test indicated no significant difference between the IOPs (p-value > 0.05), but the highest concentrations were observed in IOP2. This might indicate either a mild washout effect influence over the concentration of this gas in the atmosphere or a more intense SO_2 emission during IOP2.

Ozone concentrations were the highest among the four inorganic gaseous pollutants (Fig. 5a). Tropospheric O_3 is not directly emitted from any source, being a secondary pollutant formed in the atmosphere by a complex set of chemical reactions involving essentially NO_x, VOCs and sunlight (Wark et al., 1998). Thus, extensive forests may also act as an indirect source of O_3 due to the action of sunlight on the hydrocarbons normally released by vegetation, with the availability of NO_x acting as a limiting factor (Bonn et al., 2017). Considering that T3 site is located in a transition environment, between forest and urban environment, these measurements may have been influenced simultaneously by the O_3 generated secondarily from typical anthropogenic and/or urban emissions (i.e. automobiles, closer to T3 by the road connecting Manaus and Manacapuru; industries, not as close to T3; and the air masses coming from Manaus) and from biogenic emissions, including forest fires and the emission of VOCs by the surrounding vegetation.

It is common that tropospheric O_3 concentrations rise during precipitation events, due to the vertical mixture between stratospheric and tropospheric O_3 during convective rains and storms (Martin, 1984; Jain et al., 2005; Wang et al., 2016). In this research, the result of the ANOVA test shows that there is no significant difference between the average concentrations of O_3 in IOP1 and IOP2 (p-value > 0.05). Considering that the more frequent precipitation events during the wet season

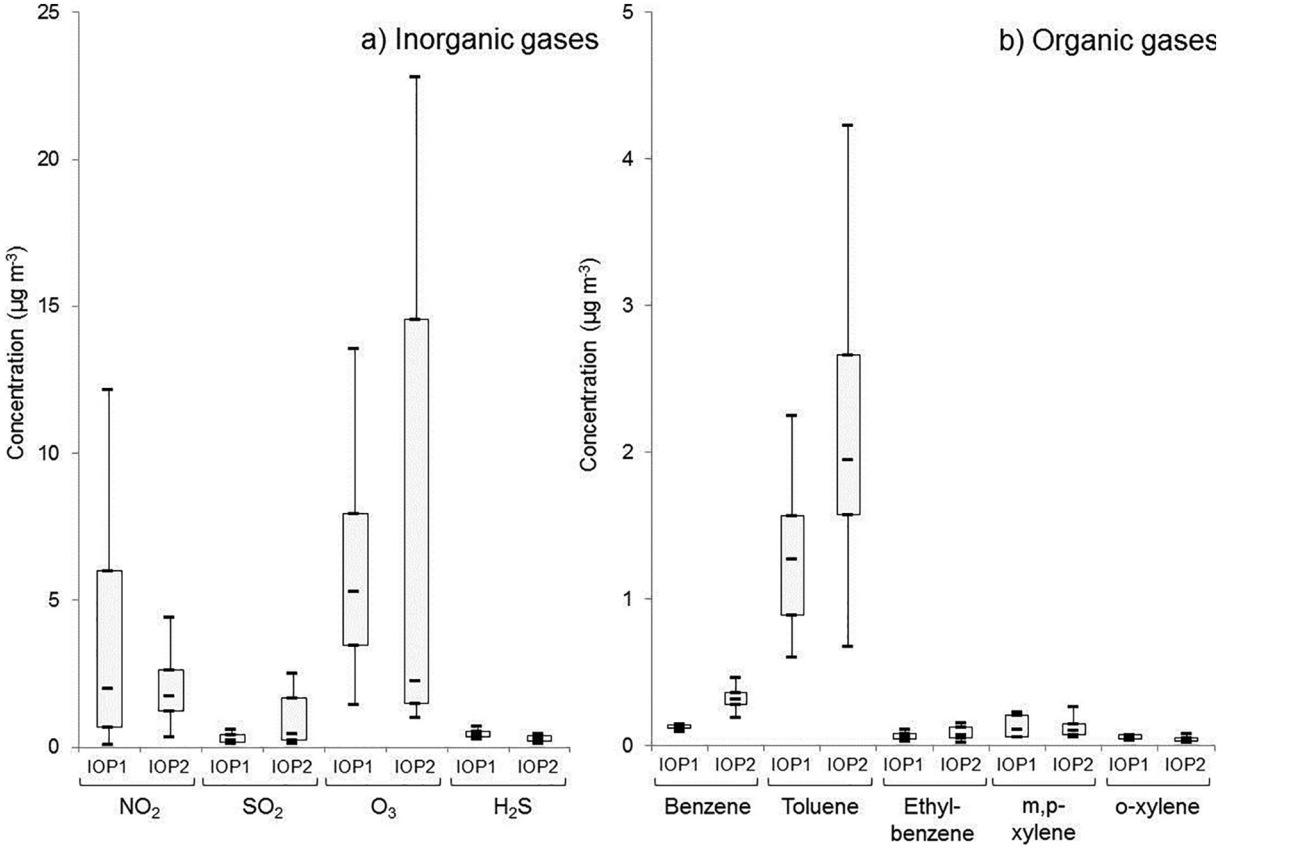

Fig. 5. Boxplots comparing the a) inorganic and b) organic gaseous pollutants concentrations measured in each season; outliers not displayed in order not to hinder visualization.

should naturally raise O_3 concentrations, it can be assumed that, in order for the O_3 levels to remain constant, the total O_3 emission should be higher during the dry season. Thus, these relatively high and constant O_3 concentrations possibly reflect a combination of 4 main factors: 1) biomass burning, which emits large amounts of volatile pyrogenic compounds (Andreae and Merlet, 2001) and is dominant during the dry season; 2) the vertical mixture during precipitation events, dominant during the wet season; 3) the intense and sustained incidence of solar radiation across the region (Martin et al., 2017) and 4) the presence of an extensive forested area nearby, which releases a range of biogenic VOCs regardless of the season.

Table 3 presents a comparison between the average gaseous concentrations observed in this study and concentrations of the same pollutants observed in other sites. A study developed by Campos et al. (2010) measured the concentration of pollutants in the Brazilian cities Curitiba and Salvador and in the atmosphere of a remote rural area in the Amazon forest (where forest was transformed into pasture), located in the state of Rondônia. In Curitiba and Salvador, the minimum concentrations of NO_2, SO_2 and O_3 are about 1 order of magnitude higher than the minimum concentrations in the IOPs, indicating that the pollution in Manacapuru is less constant than in those cities. Dales et al. (2012) observed considerably higher levels of NO_2, SO_2 and O_3 in Santiago, Chile, which is possibly explained by the elevated urbanization of the Chilean capital.

The levels of NO_2 and SO_2 found in the Amazon forest by Campos et al. (2010) were closer to those found in Manacapuru. For O_3, however, they registered considerably higher concentrations. Comparing dry and wet seasons, Campos et al. (2010) recorded higher NO_2 concentrations in the dry season than in the wet season, the opposite of what was observed in Manacapuru. For O_3, the dry season average result was about three times higher than the obtained in wet season. Campos et al. (2010) concluded it was due to the increase of the fires in the region, which may also explain the similar result in Manacapuru.

Adon et al. (2013) evaluated the air quality in the equatorial forest in Cameroon and Congo. Both sites presented averages of NO_2, SO_2 and O_3 close to the values obtained in this research. Bytnerowicz et al. (2005) observed the atmospheric pollution in the temperate forest located in the Retezat Mountains, Romania, obtaining maximum NO_2, SO_2 and O_3 concentrations considerably higher than the maximum observed in this study.

Concentrations of H_2S were the lowest among the inorganic gases (Fig. 5a). H_2S gas is generated biogenically in the absence of O_2. Marshy areas constitute the major part of this type of emission (Kinsela et al., 2011). Soils, both forest and used in agriculture, can also be sources of H_2S, but in general these concentrations are low and restricted to ground level (Kinsela et al., 2011; Andreae et al., 1993). The only anthropogenic source found in the vicinity of the studied site (car traffic) does not emit significant amounts of H_2S. The low H_2S concentrations measured indicate that pollution plumes from other anthropogenic emissions (i.e. from industries, such as the petroleum refinery located in Manaus) do not reach the site or rather do so after undergoing substantial dilution.

The ANOVA test indicated that the average concentration of H_2S in IOP1, although low, is significantly higher than in IOP2 (p-value < 0.01). This behavior in H_2S concentrations indicates a weak influence of the washout effect and possibly some influence of biogenic sources (considering that during events of strong rain the soil becomes less oxygenated, and thus more liable to the action of sulfo-reducer bacteria).

It was observed that this research obtained H_2S concentrations close to those observed by Nunes et al. (2005) in a mangrove region in Bahia (Table 3). Studies performed in urban areas such as Paranoá (DF) and South Korea showed much higher levels of H_2S than was found in Manacapuru (Kim et al., 2013; Silva, 2007). The study by Bingemer et al. (1992), however, obtained lower H_2S concentrations in Congo, both in equatorial forest area and in clearing area. These evidences

Table 3
Similar studies carried out in other locations and their obtained gases concentrations.

Research	Location	Concentrations (μg m^{-3})								
		NO_2	SO_2	O_3	H_2S	Benzene	Toluene	Ethylbenzene	m,p-Xilene	o-Xilene
Present research	T3	0.10–23 (wet) 0.30–6.1 (dry)	0.12–3.7 (wet) 0.14–15 (dry)	1.4–14 (wet) 1.0–40 (dry)	0.27–1.0 (wet) 0.13–0.69 (dry)	0.10–0.15 (wet) 0.20–0.47 (dry)	0.60–2.3 (wet) 0.68–4.2 (dry)	0.03–0.11 (wet) 0.02–0.15 (dry)	0.06–0.23 (wet) 0.06–0.27 (dry)	0.03–0.08 (wet) 0.02–0.12 (dry)
Adon et al. (2013)	Camaroon (F.)[a]	1.8	0.86	10	–	–	–	–	–	–
	Congo (F.)	2.9	1.1	8.6						
Bingemer et al. (1992)	Congo (F.)	–	–	–	0.06	–	–	–	–	–
	Congo (Cl.)				0.03					
Bytnerowicz et al. (2005)	Romania (F.)	30 (máx.)	36 (máx.)	224 (máx.)	–	–	–	–	–	–
Campos et al. (2010)	Curitiba, Br.	6.7–11	1.2–1.9	19–22	–	–	–	–	–	–
	Salvador, Br.	3.6–12	1.8–3.9	17–37						
	Rondônia, Br. (F.)	1.1 (wet) 4.6 (dry)	0.26 (wet) 0.58 (dry)	16 (wet) 51 (dry)						
Custódio et al. (2010)	Rio de Janeiro, Br. (F.)	–	–	–	–	<4				
Dales et al. (2012)	Santiago, Chile	88.25	25.4	136.1	–	–	–	–	–	–
Gee and Sollars (1998)	Caracas, Venezuela	–	–	–	–	14.2	28.9	5	16.4	5.7
	Quito, Ecuador	–	–	–	–	5	15.2	2.2	6.4	2
	Santiago, Chile	–	–	–	–	14.8	29.8	6.5	25.2	8.9
	Sao Paulo, Br.	–	–	–	–	16.7	28.1	6	18.5	6.2
	Bangkok, Thailand	–	–	–	–	18.2	186	36.6	81	28.9
	Manila, Philippines	–	–	–	–	12.6	168	21.9	55.8	16.8
Kim et al. (2013)	South Korea	–	–	–	5–60	–	–	–	–	–
Nunes et al. (2005)	Bahia, Br. (Ma.)	–	–	–	0.28	–	–	–	–	–
Paralovo et al. (2016)	Manaus	–	–	–	–	0.237–19.3	0.700–832	0.165–447	0.355–614	0.112–516
	Amazon (F.)					0.018–0.313	0.011–4.93	0.047–0.401	0.036–0.634	0.015–0.144
	Manacapuru					0.036–0.948	0.091–2.75	0.018–1.02	0.051–3.31	0.019–1.34
Silva (2007)	Paranoá, Br.				1.5–56	–	–	–	–	–
Song et al. (2012)	Spain (F.)	–	–	–	–	0.6	0.6	0.07	0.2	0.04
Yu et al. (2008)	China (F.)	–	–	–	–	6.29				

[a] F.: Forest area; Cl.: Clearing; Ma.: Mangrove area; Wet: Wet season; Dry: Dry season; Br.: Brazil.

suggest that the soil in the T3 area might be as poorly oxygenated as in a mangrove area.

Concentrations of the BTEX compounds (Fig. 5b) were generally low. BTEX are associated primarily with anthropogenic sources, especially vehicular traffic, indicating a low influence of such sources in the site. Among the BTEX compounds, toluene presented the highest concentrations. This may be due to an exclusive source of toluene, possibly the vegetation in the surroundings, considering that previous studies presented evidence that toluene can be emitted by many plants in forest regions (Heiden et al., 1999; Custódio et al., 2010; White et al., 2009; Paralovo et al., 2016).

Although BTEX are non-polar organic substances and therefore not subject to the washout effect, these compounds may be indirectly incorporated into the liquid phase, since aromatic compounds can be degraded and incorporated into the aerosol by the wet route (Volkamer et al., 2001). Results of the ANOVA test indicated that the benzene, toluene, m,p-xylene and o-xylene levels were significantly higher in IOP2 than in IOP1 (p-values < 0.01), indicating that the contribution of volatile pyrogens emitted to the atmosphere during the dry season was important in this research (Andreae and Merlet, 2001).

Comparing the obtained BTEX levels to the literature (Table 3), Paralovo et al. (2016) studied the same region as the current investigation. The BTEX levels reported in the present research are similar to those observed in that study in Manacapuru and in the Amazon forest. On the other hand, in Manaus such levels reached much higher maximum values, showcasing the magnitude of the influence of the urbanization in the area. This can also be observed in a study by Gee and Sollars (1998), which reported mean ambient concentration levels of VOCs for 4 South American and 2 Asian capitals. The BTEX levels observed in that study were much higher than the ones observed in Manacapuru, especially in the Asian cities.

BTEX concentrations in forests are generally quite low and close to what was observed in Manacapuru. Custódio et al. (2010) registered low concentrations of BTEX in the remnant of Atlantic Forest located in Rio de Janeiro, with maximum concentrations not exceeding 4 μg m^{-3}. Yu et al. (2008) obtained a total BTEX average concentration of 6.29 μg m^{-3} in a forest environment in southern China, and concluded that the sources of BTEX at the site studied are mostly anthropogenic. The study by Song et al. (2012) in a pine forest in southwest Spain reached the same conclusion. All these studies indicate that, regarding BTEX compounds, the atmosphere during IOP1 and IOP2 was more like a pristine environment than an urban environment. Studies using PTR-MS also showed low concentrations of these species in the assessed site (Martin et al., 2017).

The Spearman's correlation test was also performed for all gaseous pollutants concentrations in order to indicate whether these pollutants have predominantly common or diffuse sources. The results of the test were on average close to 0 and similar between the IOPs. This indicates that, in general, the gaseous pollutants are independent of each other, i.e. that the pollutants measured come from more than one relevant source at that location. Considering only the BTEX compounds, the opposite result was observed by Paralovo et al. (2016) in the Amazon basin (including the T3 site), with correlations above 0.9. In that study, the high correlations were interpreted as an indicative of the strong influence of automotive sources in the place. In the present research, automotive sources had a less significant influence, possibly indicating a greater combination with biomass burning emissions and biogenic emissions from the surrounding biota, which is more in line with the conclusion reached by Kourtchev et al. (2016) in their parallel study.

4. Conclusion

This research measured the concentrations of several atmospheric pollutants in a transitional area between a forest environment (Amazon forest) and an urban environment (Manaus metropolitan area) at the Amazon basin. Results indicate a substantial rise in the mass concentration of $PM_{2.5}$ during the dry season. Concentration of the soluble cations NH_4^+ and K^+ adsorbed onto $PM_{2.5}$ also were significantly higher during the same season. The levels of BTEX compounds presented similar behavior, being lower during the wet season. Besides that, pollutant O_3 presented high concentrations during both seasons, not differing significantly between them. All these results point to a strong influence of emissions originating from biomass burning, whose occurrence also intensifies significantly during the dry season. Possibly, this type of pollution source was more important during the studied period than other types, such as industry and automobile traffic.

On the other hand, the low correlations among the different gaseous pollutants suggest that these pollutants originate from different sources, especially during the dry season, indicating a mixed influence of several different types of sources, such as biomass burning, biogenic emissions and urban emissions carried in the Manaus plume, rather than one single pollution source at the site. The gaseous concentrations showed no significant difference between the five different sampling points, indicating that they should be considered as representative of the same site. However, the NO_2 results presented an important discrepancy in one of the points, suggesting that the spatial heterogeneity might be relevant, at least for this pollutant, at the studied scale.

Comparing the results obtained by the present research to similar studies carried out in other cities and forests, it was observed that the levels of NO_2, SO_2 and BTEX pollution at the T3 site present lower pollution levels than the typically observed in urban environments in both seasons, and similar to a pristine forest atmosphere. However, regarding particulate matter pollution, T3's atmosphere during the dry season resembles urban atmospheres, being considerably less polluted during the wet season. This can be interpreted as evidence of the strong influence of biomass burning over the Amazon region air quality: during the dry season, when the occurrence of fire outbreaks increases substantially, the levels of pollution in the studied area were close to that observed in large cities.

Continuity of this type of research in the Amazon region is encouraged. Considering the global importance of such biome, it is advisable to accumulate the most information possible about the air quality in that region. It is also desirable to study in greater detail the temporal and spatial variations, performing more precise measurements than the ones from the present research, which will enable the drawing of stronger-based conclusions regarding pollutants sources and transportation in the region.

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