

Chemical composition of aerosol in São Paulo, Brazil: influence of the transport of pollutants

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Abstract São Paulo is a Latin American megacity impacted by heavy traffic emissions and also affected by biomass burning and biogenic emissions. To better understand the sources of pollution during a highly polluted period, PM₁₀ samples were collected in an intensive campaign in 2013. The concentrations of particulate matter, organic carbon (OC), elemental carbon (EC), biomass burning tracers (levoglucosan, mannosan, and galactosan), water-soluble ions, and polycyclic aromatic hydrocarbons (PAHs) were determined to identify the main sources affecting the air quality. The PAHs results were compared to an intensive campaign done in 2012. Backward air masses trajectories were used in other to investigate the influence of remote sources. The average benzo[a]pyrene equivalent index (BaPE) values represented a higher cancer risk in 2013 samples than in 2012; the diagnostic ratios indicated vehicular emissions for both campaigns but fresher particles emission for 2013 campaign. During the 2013 campaign, the samples presented good correlations between OC and EC with monosaccharides, suggesting an influence of biomass burning on the carbonaceous species. Levoglucosan to mannosan ratio indicated the influence of sugarcane burning; the backward air masses trajectories

suggested transport of aerosol from the sugarcane production region in 60 % of the sampling days.

Keywords Atmospheric pollution · Atmospheric particulate matter · Aerosol transport · Organic pollutants · Water-soluble ions · Biomass burning

Introduction

Atmospheric aerosols play an important role in atmospheric chemistry and physics, climate, and public health. These particles are essential participants in ecosystem biogeochemistry, hydrological cycle, and atmospheric circulation as well as in cloud formation mechanisms (Pöschl 2005). Moreover, aerosols can cause respiratory and cardiovascular diseases. These effects depend on particle size, concentration, structure, and chemical composition (Peng et al. 2009; Newby et al. 2014; Kelly and Fussell 2012).

Urban environments, industrial processes, fuel combustion, transportation, and urbanization are major contamination sources. In particular, São Paulo, located in the southeast of Brazil, is a megacity with a population of nearly 20 million people and 8 million vehicles fueled with different fuel types (Brito et al. 2013).

In addition, São Paulo state alone accounts for over 50 % of the total area (96,166 km²) used for sugar cane plantation in Brazil (IBGE 2013). To facilitate manual harvesting, farmers set fire to the outer leaves of the sugarcane, resulting in increasing emissions of pollutants to the atmosphere (da Rocha et al. 2005). Another source of biomass burning in the region is sugar cane bagasse burning, used to generate energy (the solid crushed cane residue), contributing to the emission of gases and particulate matter (Urban et al. 2014).

Back trajectories are useful to examine source-receptor relationships and the timescales of local and long-range transports

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and their influence on aerosol composition, tracing forward from a geographical region to arrive at the measurement sites where the aerosol is studied. In short-range transport, the aerosol is more influenced by primary emissions than in long-range transport, where exchange and mixing processes, physical losses and chemistry can influence more on the analyzed composition at the receptor location (Fleming et al. 2012).

Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) has been used in several studies on air pollution evaluation, connecting the backward trajectories with the aerosol composition (Vieira-Filho et al. 2013). In previous studies in Metropolitan Area of São Paulo (MASP), the wind trajectories and satellite-derived fire counts have been used in order to determine the effect that biomass burning has on ozone concentration (Andrade et al. 2012a) and on particulate matter composition in the winter months (Vasconcellos et al. 2010).

One important fraction of the aerosol is the carbonaceous material (organic and elemental carbon). Organic carbon is a complex mixture of primary and secondary organic compounds; elemental carbon is derived exclusively from the incomplete combustion of fossil fuels and biomass burning and is known as an important contributor to radiative heating of the atmosphere (Cabada et al. 2004; Liu et al. 2013).

In order to identify the sources of atmospheric aerosols, specific chemical compounds can be used as tracers. The monosaccharides levoglucosan, mannosan and galactosan are known to be formed uniquely through the pyrolysis of cellulose and hemicellulose containing materials, thus acting as an effective tracer for biomass burning emission imprints on atmospheric aerosols (Simoneit et al. 1999; Giannoni et al. 2012). Furthermore, water-soluble potassium also has been proposed as a biomass burning tracer, although corrections are needed due to the contributions from other potential sources such as soil and sea-salt (Duan et al. 2004; Zhang et al. 2015).

Other pollutants are important for their impact on health. Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants produced by the combustion of fossil fuels, industrial sources, tobacco smoke, biomass burning, and other emissions. The occurrence of PAHs in ambient air is an increasing concern because of their carcinogenicity and mutagenicity. The US Environmental Protection Agency has listed 16 PAHs as priority control pollutants, due to the health risk posed by exposure, suggesting a continuing need for their control through air quality management (Ravindra et al. 2008; Samanta et al. 2002).

The objectives of this work are to understand the sources affecting the particulate matter composition (OC, EC, levoglucosan, mannosan, galactosan, PAHs and soluble ions) in a highly polluted period, to estimate the potential risks of the exposure to PAHs in the sampling days and to study remote sources of inhalable particulate matter affecting the site in this period, with the analysis of backward air masses trajectories.

Methodology

Sampling

Atmospheric particulate matter was collected at São Paulo site (SPA, 23° 33' 34" S and 46° 44' 01" W), at the rooftop of the building of Institute of Astronomy and Atmospheric Sciences, inside the campus of the University of São Paulo. The location is circa 2 km from a major expressway with heavy traffic and next to a green area; the fleet includes gasoline, diesel, biodiesel and ethanol fueled vehicles. The sampling occurred in winter (dry season), from July 30th to August 10th, 2013. In this heavily polluted period, several fire spots coming from sugarcane areas were observed in the state (INPE 2013).

PM₁₀ aerosol samples were collected in periods of 24 h, with a high-volume air sampler. The flow rate was at 1.13 m³ min⁻¹. Quartz fiber filters (20 cm × 25 cm) were pre-cleaned in an oven for 8 h (800 °C). After the sampling, the filters were wrapped in aluminum foil, stored in a refrigerator and then weighed and extracted.

Meteorological data

The climate of São Paulo is considered as humid subtropical. The winter in the city is characterized by lower temperatures, lower relative humidity and less precipitation, resulting in higher pollutants concentrations (Miranda et al. 2012). The local circulation is associated with the Atlantic Ocean breeze. Polar mass arrivals in the cold fronts often intensify this circulation, coming from southeast. The samplings were carried out after a cold front; most of the days had reduced relative humidity in the afternoons (average minimum relative humidity of 30 %). The average temperature was 18 °C and the average minimum temperatures were in 11 °C. Rains were not registered in the IAG-USP station in the period. Average wind speed ranged between 2.5 and 6.4 km h⁻¹, most the winds came from NW.

Backward air masses trajectories were generated with 96 h from HYSPLIT model (Draxler and Rolph 2003); through READY (Real-time Environmental Applications and Display System) platform from NOAA (National Oceanic and Atmospheric Administration). The height level used was 900 m above ground level (AGL).

Chemical analyses

The filters were weighed before and after sampling. After mass determination, at Finnish Meteorological Institute, the filters were cut with steel punchers (1 cm² pieces) for determination of water-soluble ions. For determination of the soluble ions (Cl⁻, NO₃⁻, SO₄²⁻, oxalate, Na⁺, K⁺, NH₄⁺), the sample aliquots were extracted in 10 mL ultrapure water (18MΩ.cm) and shaken for 10 min. The analyses were done

using two ion chromatographs (ICS 2000 system, Dionex) simultaneously: cation and anions analyses were made using CG12A/CS12A (4 mm i.d. \times 50 + 250 mm length) and AG11/AS11 (4 mm i.d. \times 50 + 250 mm length) columns. Detection limit for the ions were in the range 1.0 and 2.0 ng mL⁻¹.

For monosaccharides determination, one square punch of 1 cm² was cut for the analysis. The samples were extracted with 5 mL of deionized water with an internal standard by 10 min of gentle rotation; methyl- β -D-arabinopyranoside (purity 99 %; Aldrich Chemical Co., WI, USA) was used as internal standard. Concentrations of three monosaccharide anhydrides (levoglucosan, mannosan and galactosan) were measured using a high-performance anion-exchange chromatography analysis coupled with electrospray ionization to a quadrupole mass spectrometer (HPAEC/ESI-MS; Dionex ICS-3000 System and Dionex MSQTM). The complete procedure is described in Saarnio et al. (2010).

At University of São Paulo, a circular punch of the filters was cut and ultrasonically extracted with methylene chloride. The extracts were filtered, concentrated and then passed through a silica-alumina column separation (3.2 g of silica and 1.8 g of alumina). Two fractions were collected, the first containing alkanes (40 mL of hexane) and the second containing PAHs, nitro- and oxy-PAHs (50 mL of hexane + 50 mL of methylene chloride). Then, all samples were analyzed using a gas chromatograph with mass spectrometer detection (GC/MS), for the PAH determination. The MS operated in EI mode (electron impact) and SIM (selected ion monitoring mode) (De Oliveira Alves et al. 2015). The PAH according to their elution order were phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), retene (Ret), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenzo[ah]anthracene (DBA) and benzo[ghi]perylene (BPe).

Two punches of 9 mm diameter (127.23 mm²) were cut for carbonaceous species (OC and EC) determination and the carbonates were removed with HCl fumes. OC and EC were determined by a thermal-optical transmission technique developed at University of Aveiro. The system consists in a quartz tube with two heating zones, a pulsed laser and a nondispersive infrared CO₂ analyzer (NDIR). The punches are placed vertically inside the quartz tube, within the first heating zone. It is then heated to 600 °C in a nitrogen atmosphere for the organic fraction vaporization. EC is determined with a sequential heating at 850 °C in an atmosphere containing 4 % oxygen. A second heating zone is filled with cupric oxide and maintained at 650 °C in a 4 % oxygen atmosphere, to assure the total oxidation of the volatilized carbon to CO₂, which is quantified by the NDIR analyzer. Correction for the pyrolysis contribution to EC from OC is obtained by monitoring the

transmission of light through the filter with the laser beam (Alves et al. 2015).

Statistical analysis

Statistical analyses were performed using SPSS IBM. They were conducted to verify the correlation between all the species (Pearson Correlations). It determines the extent to which values of the variables are linearly correlated. The coefficients (*r*) were considered significant when *p* < 0.05.

Linear regressions were done in OriginLab 8.0, with the adjusted coefficient of determination *R*².

Results and discussions

Aerosol chemical composition

Particulate matter (PM₁₀) average mass concentration at SPA site was over 93 $\mu\text{g m}^{-3}$, ranging from 42 to 147 $\mu\text{g m}^{-3}$ (Table 1). This value was higher than that observed in the 2008 at the same site, during an intensive campaign (64 $\mu\text{g m}^{-3}$) (Vasconcellos et al. 2011). This is almost twice that recommended by the World Health Organization, which is 50 $\mu\text{g m}^{-3}$ (World Health Organization 2006), but is lower than the daily standard for Brazilian cities, 150 $\mu\text{g m}^{-3}$ (CONAMA 2002). Comparing with other Latin American cities, a study throughout 2013 in Santiago (Chile), conducted to average PM₁₀ concentrations above 80 $\mu\text{g m}^{-3}$ in the most polluted months (autumn and winter) in two stations near downtown (Villalobos et al. 2015). A study at a site in the north of Mexico City, during a cold dry period, pointed to PM₁₀ average concentration of 82.1 $\mu\text{g m}^{-3}$ (Valle-Hernández et al. 2010).

The sampling was carried out during the winter, when the sugarcane burning occurs mostly in the northwest of São Paulo state. This pollution is frequently transported to the São Paulo city by air masses (Vasconcellos et al. 2007). In harvest periods, particulate matter concentrations can reach high values at burning sites. Previous studies in a sugarcane farming area (Araraquara, Brazil), pointed to a mass concentration ranging from 41 to 181 $\mu\text{g m}^{-3}$ during harvest season

Table 1 PM₁₀, carbonaceous species and total particulate organic matter (TOM) concentrations observed at SPA site in 2013

($\mu\text{g m}^{-3}$)	Min.	Max.	Mean \pm SD	Mean/PM ₁₀ (%)
PM ₁₀	42	147	93 \pm 37	
OC	6.9	15.8	11.0 \pm 3.4	11.83
EC	3.6	17.6	9.5 \pm 4.9	10.11
TC	10.5	32.7	20.5 \pm 8.0	22.04
TOM	11.0	25.3	17.6 \pm 5.6	18.92

and from 12 to 47 $\mu\text{g m}^{-3}$ during non-harvest season (Andrade et al. 2010). In Vasconcellos et al. (2007), the average concentration for particulate matter in Araraquara was 76 $\mu\text{g m}^{-3}$ in the winter, similar to São Paulo city in this same period (68 $\mu\text{g m}^{-3}$).

Levoglucon concentrations ranged from 179 to 1086 ng m^{-3} (Table 2). The average for this campaign was 474 ng m^{-3} , more than twice of that obtained in 2008 previous winter intensive campaign (201 ng m^{-3}) and much higher than the 2007 summer intensive campaign (39 ng m^{-3}) (Vasconcellos et al. 2010). In that same study, a campaign was done in the Atlantic Forest (winter) and the levoglucon average concentration was 11 ng m^{-3} . Lower levels of levoglucon were also observed in the intensive campaign of 2012 in São Paulo in a recent study not published yet; the higher concentrations in 2013 were attributed to the relatively higher production of sugarcane in 2013 compared to 2012.

Mannosan and galactosan average concentrations were respectively 39 and 31 ng m^{-3} at SPA site. The highest monosaccharide concentrations were observed on August 1st, 2013. Backward trajectories showed air masses reaching the site after passing through the northwest of São Paulo state, and then passing through the ocean and over Minas Gerais state (Fig. 1). Two hundred thirty-six fires were observed in the sampling period, mostly in the northwest of the state, according to the reference monitoring satellite (INPE 2013). The mass trajectory also passes through important highways and urban areas in the state. August was the month with highest amount of fires registered (497) in São Paulo state, in 2013 (INPE 2013). The trajectories passed through the sugarcane production region in 60 % of the sampling days. One of the trajectories also points to transport of biomass burning from

the north of Paraná state in August 3rd (levoglucon concentration was 405 ng m^{-3}) (Fig. 1).

The study done in Santiago, Chile, also in 2013, showed the highest concentrations in the months of June and July, with levoglucon average concentrations of up to 1789 ng m^{-3} in the winter (Villalobos et al. 2015). The higher concentration of this compound was explained by the higher consumption of residential wood for space heating in colder months. A previous study, done between 2010 and 2012, in an agro industrial region in São Paulo state (Araraquara and Ourinhos), pointed to average concentrations of levoglucon, mannosan, and galactosan of respectively 138, 19 and 11 ng m^{-3} for a sugarcane harvest period, while only 73, 11 and 7 ng m^{-3} were obtained for the non-harvest days (Urban et al. 2014).

Regression analyses of the three biomass burning tracers (levoglucon, mannosan, galactosan) are presented on Fig. 2. As expected, levoglucon was highly correlated with mannosan and galactosan ($R^2 = 0.97$ and 0.93) and the Pearson coefficients corroborates the strong associations (Table 3). At this site, sugarcane burning is the main source for levoglucon and its stereoisomers. In some European regions, burning of lignite as domestic fuel can be an additional input of levoglucon (Fabbri et al. 2009). High correlations between the monosaccharides were also observed in other studies; in a monitoring program carried out in seven different sites in Flanders, Belgium (different seasons, in 2010 and 2011), all correlations were higher than 0.95 (Maenhaut et al. 2012); in Daejeon (South Korea) during the rice harvest period (Jung et al. 2014), there were correlations of 0.60 and 0.89 (respectively, for mannosan and galactosan).

Non-sea-salt potassium (Nss- K^+) and levoglucon were strongly correlated with all monosaccharides in the Pearson analysis (Table 3), suggesting that a great part of it may be originated in the biomass burning. Potassium can also be related to soil resuspension and sea-salt spray (Pio et al. 2008). Correlations between monosaccharides and potassium tend to be different depending on the site. A previous study done in the Amazon forest during forest burning, showed high correlation ($R^2 = 0.83$) (Schkolnik et al. 2005), while in an agro-industrial region in São Paulo the correlation was weaker ($R^2 = 0.38$) (Scaramboni et al. 2015); the suspended soil dust and the fertilizers used may have affected the air quality in that site.

The ratio of levoglucon to mannosan (LEV/MAN) close to 12 in this study was compared with other sites (Table 4). Lower LEV/MAN ratios (3–7) are generally related to softwood combustion, while higher (10–83), are related to hardwood and crop residues. In Zhang et al. (2015), this ratio is related to the content of glucose to mannose in the biomass; softwoods contain higher proportion of mannose than hardwoods.

Table 2 Monosaccharides and water soluble ions concentrations observed at São Paulo site in 2013

(ng m^{-3})	Min.	Max.	Mean \pm SD	Mean/ PM_{10} (%)
Monosaccharides				
Levoglucon	179	1086	474 \pm 297	0.51
Mannosan	12	92	39 \pm 27	0.04
Galactosan	13	59	31 \pm 16	0.03
Water soluble ions				
Cl^-	229	1347	668 \pm 425	0.72
NO_3^-	1771	4457	2774 \pm 958	2.98
SO_4^{2-}	2080	9811	4670 \pm 2714	5.02
MSA^-	37	288	98 \pm 69	0.11
Oxalate	366	1090	610 \pm 204	0.66
Na^+	198	1104	412 \pm 247	0.44
NH_4^+	661	3844	1620 \pm 874	1.74
Nss- K^+	494	922	678 \pm 148	0.73

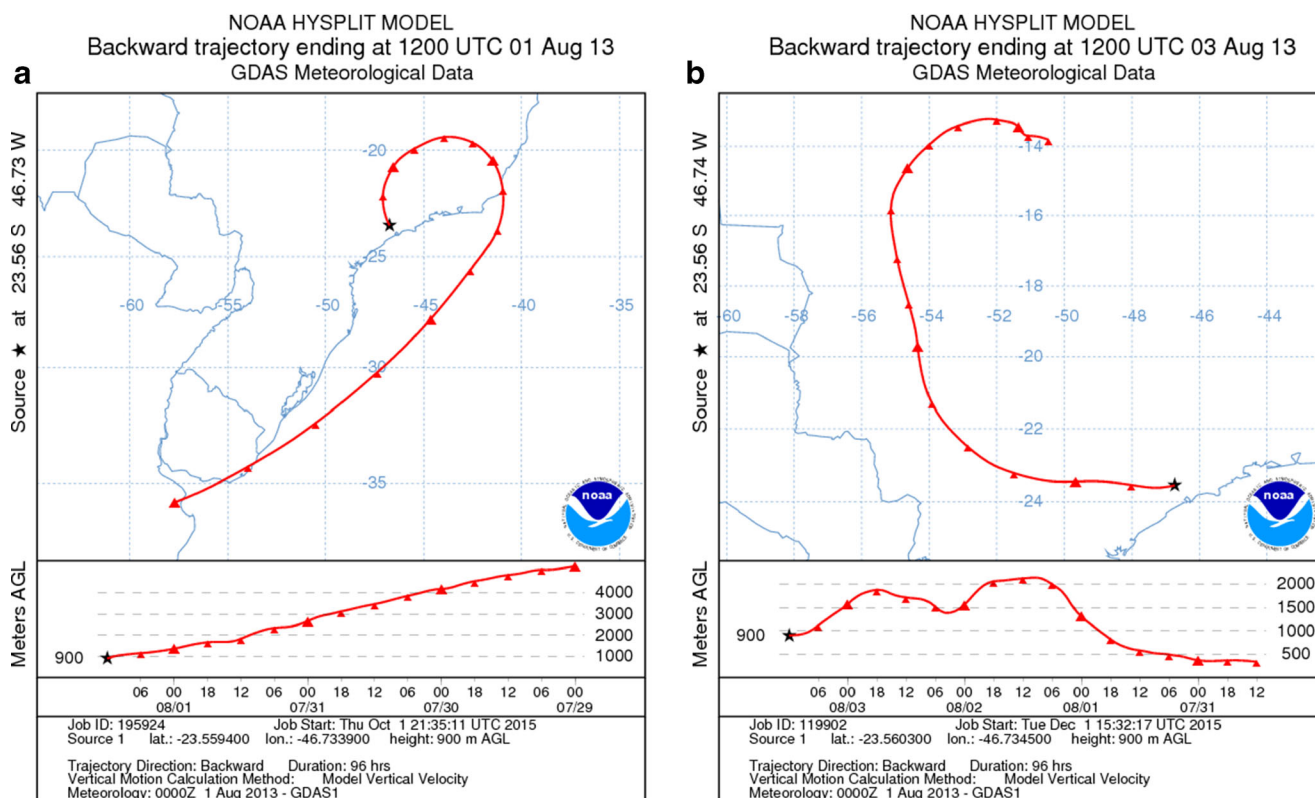


Fig. 1 Backward air mass trajectory calculated on August 1st (a) and 3rd (b), the red line represents the trajectory—NOAA

Studies in ambient influenced by mixed sources of biomass/biofuel burning in the Amazon region in Brazil, in different seasons, showed ratios from 15 to 24 (Decesari et al. 2006; Graham et al. 2002; Engling et al. 2009). In a chamber study with sugarcane combustion, a LEV/MAN ratio

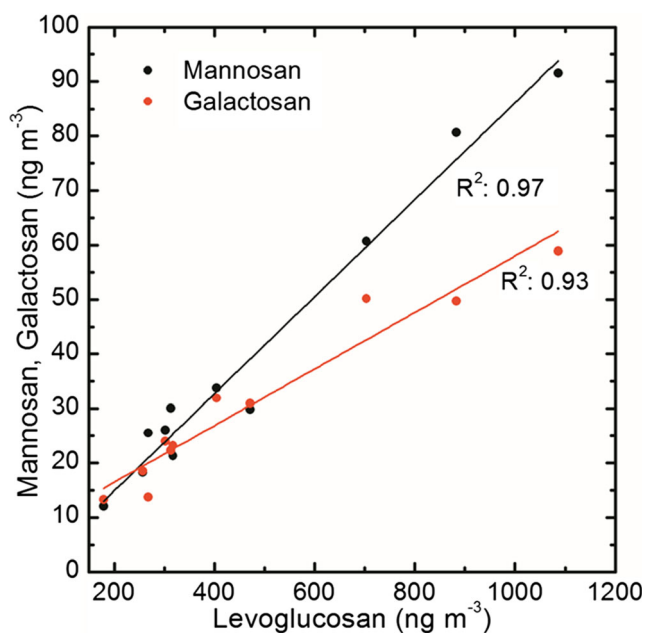


Fig. 2 Linear regression between levoglucosan and mannosan (up); levoglucosan and galactosan (down)

of 10 was obtained (Hall et al. 2012), which is very close to the value retrieved in the present work. A previous study conducted in a sugarcane biomass burning impacted area (Araraquara and Ourinhos) showed a similar mean for this ratio (over 9) (Urban et al. 2014).

The percentage of levoglucosan in the organic carbon content (LEV/OC) was 4.32 % in this study and was also compared with other studies in Table 4. This value was similar to the other studies in biomass burning impacted areas (Jung et al. 2014; Engling et al. 2013). The combustion of different plant tissues (stack and chamber campaigns) showed distinct concentrations of levoglucosan in OC (branches > straw > needles > leaves) (Sullivan et al. 2008). However, at SPA site, there are other sources that can influence the OC content and this ratio, such as the diesel and gasoline combustion emissions and the secondarily formed organic aerosol (Castanho and Artaxo 2001).

The NssK^+/LEV ratio for the campaign was 1.4. In a study carried out in Rondônia state (Brazil) during an intensive biomass burning period, this ratio ranged between 0.3 and 1.2 and was attributed to a combination of smoldering and flaming phases (Kundu et al. 2010). Emission rates of levoglucosan and potassium depended on biomass burning processes. Lower potassium to levoglucosan ratios are obtained from smoldering combustion. Flaming combustion can lead to increased potassium emissions (Lee et al. 2010), while smoldering can increase the levoglucosan emissions (Schkolnik et al. 2005; Jung et al. 2014).

Table 3 Pearson correlation coefficients for 2013 campaign

	Lev	Man	Gal	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	MSA	NssK ⁺	OC
Man	0.99**	–	–	–	–	–	–	–	–
Gal	0.97**	0.95**	–	–	–	–	–	–	–
NO ₃ ⁻	–	–	–	0.86**	–	–	–	–	–
SO ₄ ²⁻	–	–	–	0.70*	0.82**	–	–	–	–
Ox ⁻	–	–	–	–	–	0.50	0.87**	–	–
NH ₄ ⁺	–	–	–	0.68*	0.59	0.79**	–	–	–
NssK ⁺	0.73*	0.74**	0.79**	–	–	–	–	–	–
OC	0.70*	0.75**	0.62*	0.78**	0.71*	–	–	0.48	–
EC	0.78**	0.79**	0.68*	–	–	–	–	0.49	0.84**

*Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed)

The organic and elemental carbon (OC and EC) average concentrations were, respectively, 11.0 and 9.5 $\mu\text{g m}^{-3}$ and the ranges were 6.9–15.8 and 3.6–17.6 $\mu\text{g m}^{-3}$ (Table 1). The OC concentrations were slightly higher than those of EC in this campaign, with an average ratio OC/EC of 1.2; the total carbon accounted for from 11.29 to 35.16 % of the particulate matter concentration. The total particulate organic matter (TOM) concentration was 17.6 $\mu\text{g m}^{-3}$, representing 18.92 % of the PM₁₀; TOM was calculated with an organic matter to organic carbon (OM:OC) ratio of 1.6 (Timonen et al. 2013). In the first 4 days of the campaign, the OC and EC concentrations were higher, coinciding with the lowest values of relative humidity and temperatures.

In Souza et al. (2014), the concentrations for fine particles in São Paulo in the winter campaign (2008) presented a similar range, from 5.5 to 15 $\mu\text{g m}^{-3}$ for OC, but lower for EC, 0.8 to 11 $\mu\text{g m}^{-3}$. The concentrations for Piracicaba, a city with strong influence of biomass burning, in that same season ranged from 2.8 to 6.9 for OC, and from 1.1 to 2.6 $\mu\text{g m}^{-3}$ for EC, with a clear predominance of OC, mainly due to sugar cane fires in that region. In the other study not published yet, OC concentrations levels were lower in the 2012 winter campaign in São Paulo.

Organic carbon was strongly correlated with monosaccharides (Table 3), the Pearson correlation coefficients for

levoglucosan, mannosan, and galactosan were, respectively, 0.70, 0.75, and 0.62. There was only a moderate correlation between OC and Nss-K⁺; this lower correlation may be due to the different sources of potassium, not related to biomass burning. The strong correlations with the monosaccharides suggests that a great fraction of organic carbon may come from air mass transported from biomass burning areas, often observed in this period in São Paulo state. Elemental carbon was also well correlated with the monosaccharides, the Pearson coefficients for levoglucosan, mannosan, and galactosan were, respectively, 0.78, 0.79, and 0.68. These good correlations indicate that the transport of biomass burning can influence the elemental carbon concentrations at this site during this period. Although black carbon has been mainly associated to vehicle emissions at this site in previous studies (Andrade et al. 2012b).

OC and EC presented a strong correlation (0.84). This correlation suggests that major fractions of OC are emitted by a dominant primary source. When there is more than one main primary source, the OC to EC ratio value is not constant and the correlations are weaker (Szidat et al. 2006). São Paulo site is affected mostly by vehicle emissions and biomass burning emissions during this period. OC/EC ratios obtained, together with those of other studies, are shown in Table 4. Ratios ranging from 5 to 15 were indicative of biomass burning;

Table 4 Ratios (LEV/MAN; LEV/OC; OC/EC) between biomass burning tracers for 2013 campaign

Type of biomass	Period	Location	LEV/MAN	LEV/OC	OC/EC	Reference
Rice straw	Winter harvest	Douliou, Taiwan	14.9	3.88 %	7.2	Engling et al. 2013.
Rice straw	Summer harvest	Douliou, Taiwan	60.7	4.68 %	15.7	
Rice straw	Fall	Daejeon, South Korea	6.7	3 %	–	Jung et al. 2014.
Sugarcane	Spring and summer harvest	Araraquara and Ourinhos, Brazil.	9	–	–	Urban et al. 2014
Sugarcane	Non-harvest	Araraquara and Ourinhos, Brazil.	9	–	–	
Sugarcane	Chamber	Florida, USA	10	–	–	Hall et al. 2012
Sugarcane	Winter	São Paulo, Brazil	12.2	4.32 %	2.40	This study

emissions from gasoline or diesel tended to show lower ratios (Nava et al. 2015). The average ratio of OC/EC in this study is close to those of gasoline and diesel emissions. The values for this campaign were close to 1, with exception of three samples (2.1, 1.9, and 2.3 for the days 3rd, 4th, and 5th of August, respectively).

The PAH concentrations were determined for this campaign and compared to those of the 2012 intensive campaign, during which PM₁₀ samples were also collected (Table 5). In the 2013 campaign, the total PAH concentration was 8.7 ng m⁻³, a value that is very similar to that obtained in the previous year (8.2 ng m⁻³). These results were lower than the levels found in 2008 intensive campaign, 25.9 ng m⁻³ and in 2003 intensive campaign, 27.4 ng m⁻³ (Vasconcellos et al. 2011).

The most abundant PAHs were Phe > DBA = Ant for 2012 campaign and BbF > BPe = InP for 2013. Higher levels of Phe were associated with the emission of grasses combustion (Magalhães et al. 2007) and BbF was among the most abundant PAHs in previous studies (Vasconcellos et al. 2010); this PAH was reported as carcinogenic in several studies (Ravindra et al. 2008).

Benzo[a]pyrene-equivalent carcinogenic power (BaPE) is an index that has been introduced for quantifying the aerosol carcinogenicity related to the whole PAH fraction instead of the sole BaP. The maximum value of BaP recommended by WHO is 1 ng m⁻³ due to its high carcinogenic properties. Thus, BaPE values above 1.0 ng m⁻³ represent a significant cancer risk. BaPE is calculated

according to the following equation (Vasconcellos et al. 2011; Yassaa et al. 2001):

$$\text{BaPE} = \text{BaA} \times 0.06 + \text{BbF} \times 0.07 + \text{BkF} \times 0.07 + \text{BaP} \times 1 + \text{DBA} \times 0.6 + \text{InP} \times 0.08 \quad (1)$$

The BaPE values for 2013 and 2012 campaigns ranged, respectively, from 0.4 to 2.8 ng m⁻³ and from 0.4 to 3.4 ng m⁻³. In the 2013 campaign, the average carcinogenic potential was higher (1.4 ng m⁻³) than in 2012 (1.1 ng m⁻³), meaning a higher cancer risk. In the 2008 comparative study, São Paulo, Buenos Aires and Bogota also reached values of BaPE higher than 1 ng m⁻³. In that campaign, one of the samples collected in São Paulo peaked at 12 ng m⁻³ (Vasconcellos et al. 2011). The BaP-TEQ (carcinogenic potential) and BaP-MEQ (mutagenic potential) were assessed as the following equations (Jung et al. 2010):

$$\begin{aligned} (\text{BaP-TEQ})_{\text{88PAHs}} = & [\text{BaA}] \times 0.1 + [\text{Chr}] \times 0.01 \\ & + [\text{BbF}] \times 0.1 + [\text{BkF}] \times 0.1 \\ & + [\text{BaP}] \times 1 + [\text{InP}] \times 0.1 \\ & + [\text{DBA}] \times 0.5 + [\text{BPe}] \times 0.01 \quad (2) \end{aligned}$$

$$\begin{aligned} (\text{BaP-MEQ})_{\text{88PAHs}} = & [\text{BaA}] \times 0.082 + [\text{Chr}] \times 0.017 \\ & + [\text{BbF}] \times 0.25 + [\text{BkF}] \times 0.11 \\ & + [\text{BaP}] \times 1 + [\text{InP}] \times 0.31 \\ & + [\text{DBA}] \times 0.29 + [\text{BPe}] \times 0.19 \quad (3) \end{aligned}$$

Table 5 PAH concentrations and BaPE index for 2012 and 2013 campaigns

PAH (ng m ⁻³)	2013 Mean ± SD	2012 Mean ± SD
Phe	0.2 ± 0.2	1.2 ± 0.8
Ant	0.1 ± 0.1	1.0 ± 0.8
Flu	0.4 ± 0.5	0.2 ± 0.6
Pyr	0.2 ± 0.3	0.3 ± 0.1
Ret	0.1 ± 0.1	0.3 ± 0.1
BaA	0.4 ± 0.4	0.3 ± 0.1
Chr	0.7 ± 0.5	0.3 ± 0.4
BbF	1.6 ± 0.9	0.6 ± 1.0
BkF	0.7 ± 0.5	0.7 ± 1.0
BeP	0.8 ± 0.6	0.6 ± 1.0
BaP	0.8 ± 0.4	0.3 ± 0.3
InP	1.1 ± 0.6	0.7 ± 0.5
DBA	0.6 ± 0.8	1.0 ± 1.1
BPe	1.1 ± 0.6	0.6 ± 0.7
Total	8.7 ± 5.0	8.2 ± 5.0
BaPE	1.4 ± 0.8	1.1 ± 0.9

The lifetime lung cancer risk (LCR) is estimated by multiplying BaP-TEQ and BaP-MEQ by the unit risk (U.R.) on exposure to BaP established by WHO (De Oliveira Alves et al. 2015). The calculated values for LCR-BaP-TEQ and LCR-BaP-MEQ were, respectively, 36.9 × 10⁻⁵ and 17.5 × 10⁻⁵ ng m⁻³ for 2013; 49.2 × 10⁻⁵ and 10.2 × 10⁻⁵ ng m⁻³ for 2012. In both cases, the values exceeded the WHO guideline (8.7 × 10⁻⁵ ng m⁻³) (World Health Organization 2000; Callén et al. 2014).

The higher value of total PAH was observed in the first day of the campaign, when the air mass trajectories crossed a great part of São Paulo metropolitan area, after passing through the ocean (Fig. 3). The higher molecular mass PAHs were more abundant, especially DBA, suggesting a higher contribution of vehicular and stationary emissions. In the first 4 days of the campaign, the PAH concentrations were higher than in the remaining period, following the higher OC concentrations in these days. The samples collected in the weekend (August 3rd and 4th) had lower PAH concentrations, which can be explained by lower traffic in these days.

PAH ratios were calculated for both campaigns (Table 6). The BaP/(BaP + BeP) ratio was close to 0.5 for the 2013

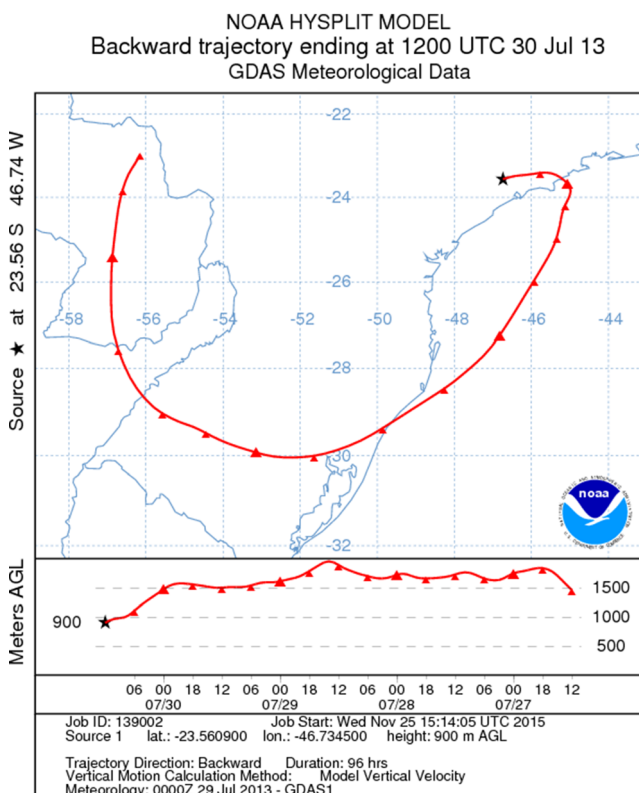


Fig. 3 Backward air mass trajectory calculated on July 30th, the red line represents the trajectory—NOAA

campaign and 0.4 for 2012, indicating local or fresh emission of particulate matter in 2013 and that in 2012 the aerosol may have suffered a greater action of photolysis and/or oxidation, suggesting long-range transport (Oliveira et al. 2011). The ratio Phe/(Phe + Ant) indicated motor oil burning in 2013, as observed in previous studies (Sicre et al. 1987). The ratio Flu/(Flu + Pyr) indicated both motor oil burning and gasoline motor exhaust for the 2012 campaign and wood, grass and coal combustion for 2013 (de La Torre-Roche et al. 2009). BaA/(BaA + Chr) was in the same range for vehicular emissions in 2012 (Miguel et al. 1998).

Table 6 PAH ratios for 2013 and 2012 campaigns

Ratio	2013	2012
Phe/(Phe + Ant)	0.78 ^a	0.54
Flu/(Flu + Pyr)	0.62	0.39 ^{a,b}
BaA/(BaA + Chr)	0.31	0.49 ^c
BaP/(BaP + BeP)	0.49 ^d	0.36

^a Motor oil burning (~0.78)—Sicre et al. 1987

^b Gasoline motor exhaust (0.35–0.51)—Sicre et al. 1987

^c Vehicular emissions (0.47–0.76)—Miguel et al. 1998

^d Fresh emissions (~0.5)—Oliveira et al. 2011

Removing the sample collected in the first day, there was a good correlation between levoglucosan and Flt (0.75), a PAH often attributed to biomass burning (Magalhães et al. 2007). Correlations between levoglucosan and Ret were low for 2013 campaign in SPA site; these correlations were high in a study carried out in the Amazon during a biomass burning period, suggesting a high emission of the compound (De Oliveira Alves et al. 2015).

The most abundant water-soluble ions in this work were SO_4^{2-} , NO_3^- and NH_4^+ , the same as in 2008 previous campaign in São Paulo (Vasconcellos et al. 2011). In that same study, SO_4^{2-} , Ca^{2+} and NO_3^- were the most abundant for Buenos Aires and SO_4^{2-} , Ca^{2+} and Na^+ , for Bogotá. The higher concentrations of sulfate and nitrate in the aerosol may indicate a larger influence of vehicle emissions. This study pointed to a strong correlation between NO_3^- and SO_4^{2-} (0.82) in PM_{10} . Strong correlations of both anions were also observed in Beijing, indicating that both ions were formed via the same in-cloud processes (Li et al. 2012).

Sodium is often attributed to sea-salt aerosol, although in recent studies in São Paulo, it has been observed that the ocean does not play an important role in the occurrence of its excess concentrations, suggesting that it is not exclusively originated from oceanic processes at this site (Vieira-Filho et al. 2013). Potassium is found in particles of biomass burning origin, but is also present in biogenic, marine and mineral dust (Bougiatioti et al. 2013). Non-sea-salt potassium concentrations ranged from 494 to 922 ng m^{-3} , averaging 678 ng m^{-3} (Table 2), which is a similar concentration to that of the 2008 previous São Paulo winter campaign (634 ng m^{-3}). The Cl/Na ratio was considerably lower in some of the days with air mass trajectories showing longer or no transport from the ocean (August 4th, 6th, 8th and 9th). Ratios lower than 1.8 indicate aging of sea-salt aerosol and Cl loss after interaction with acidic species (Zhao and Gao 2008). Figure 4 shows a trajectory of air masses reaching the city less than 12 h after passing through the ocean in July 31st (Cl/Na = 2.9) and a trajectory with no transport from the sea in August 6th (Cl/Na = 1.0).

NH_4^+ showed a strong correlation with SO_4^{2-} (0.79) and moderate with Cl^- (0.68) and NO_3^- (0.59). Ammonium has different sources compared with these other ions, but it reacts with these species, forming salts (Vasconcellos et al. 2011). These correlations suggest that there is formation of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and NH_4Cl salts in the PM_{10} at this site. A previous study showed similar correlations in an industrial city in India (Behera and Sharma 2010). Other studies in urban areas pointed to the formation of ammonium sulfate in the fine particulate matter at urban sites in Shanghai haze days and in Singapore (Du et al. 2011; Karthikeyan and Balasubramanian 2006). There were higher concentrations of NO_3^- and NH_4^+ in the days with lower average temperatures (July 30th, August 1st and 3rd). Lower temperatures seem to increase the formation of NH_4NO_3 in the aerosol, while higher temperatures are

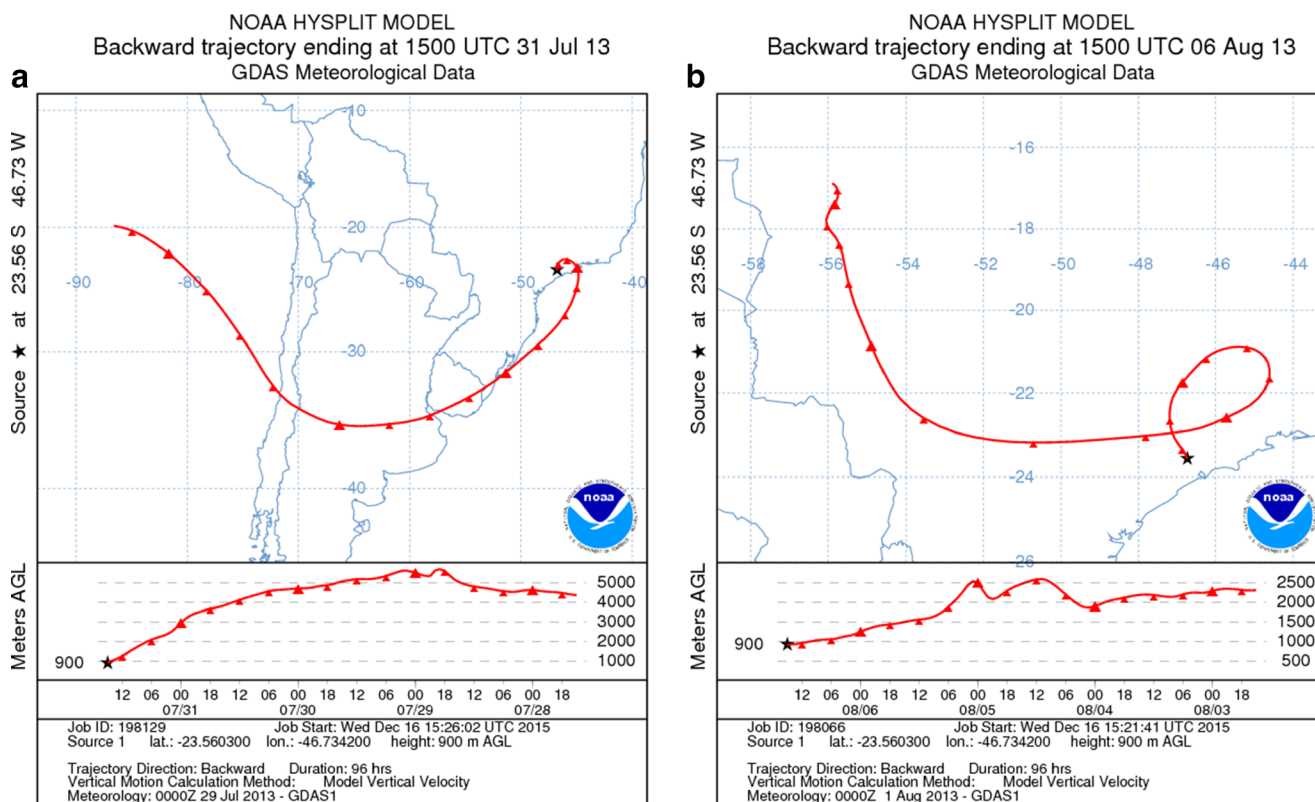


Fig. 4 Backward air mass trajectories calculated on the days July 31st (a) and August 6th (b), the red line represents the trajectory—NOAA

unfavorable to this reaction; this was also observed in a study conducted in a coastal city in China (Zhao et al. 2011).

Methods comparison

Another study involves the 2012 and 2013 winter campaigns. OC, EC, and monosaccharides were determined at University of Antwerp and Ghent University, with different techniques. The carbonaceous species were determined by thermal optical analysis in both studies, but in Ghent the NIOSH protocol was used. The OC concentrations were similar for both, but the EC concentrations determined in Ghent were considerably lower. Despite this difference, the correlations between the two analysis for OC and EC were strong, respectively, 0.82 and 0.93. However, it is noted in previous studies that the NIOSH protocol provides lower EC concentrations than other temperature protocols (Maenhaut et al. 2012).

The monosaccharides determination was carried out with a different technique at Antwerp University, with the extraction of a punch of 1.0 cm² of the filter with methanol, then passing it through a process of trimethylsilylation and finally analyzing it in GC-MS (Maenhaut et al. 2012). The average concentrations for the monosaccharides were similar (512 and 40 ng m⁻³ for levoglucosan and mannosan), but considerably lower for Galactosan (21 ng m⁻³). In a recent intercomparison study of analytical methods used for quantification of monosaccharides, the percentage error (PE) between the results was

wider for galactosan than for levoglucosan and mannosan (Yttri et al. 2015). Both analyses were strongly correlated; the Pearson's coefficients were respectively 0.98, 0.97, and 0.87, for levoglucosan, mannosan, and galactosan.

Conclusions

Three biomass-burning tracers (levoglucosan, mannosan, galactosan), soluble ions, OC, and EC were identified and quantified from aerosol samples collected in SPA during the season (winter 2013). PM₁₀ concentrations samples were above the recommended by WHO in 80 % of the samples. Sulfate, nitrate, and ammonium were the most abundant water-soluble ions. There was a strong correlation between nitrate and sulfate, both dominant species in secondary inorganic aerosol in urban areas.

Based on correlation coefficients between biomass burning tracers and the carbonaceous species, it was suggested that part of the OC and EC in the site were related to biomass burning. Biomass burning tracers were all well correlated and had strong correlations with the non-sea-salt potassium, indicating that part of it may originate from biomass burning. The average Nss-K⁺/LEV ratio suggested mixed smoldering and flaming processes and LEV/MAN influence from sugarcane burning. All samples presented high levels of monosaccharides. The air mass trajectories showed transport of aerosol

from the biomass burning region in 60 % of the sampling days.

The PAH concentrations in 2013 campaign were compared to 2012; the sum of PAHs was similar for both, but the BaPE carcinogenic potential was higher in 2013. Diagnostic ratios indicated vehicular emissions for PAHs at both sites and the emissions in 2013 seemed to be fresher, with lower photolysis or oxidation of BeP.

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