

Size-segregated aerosol chemical composition from an agro-industrial region of São Paulo state, Brazil

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Received: 7 June 2016 / Accepted: 7 October 2016 / Published online: 21 October 2016
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Abstract The main objective of this research included a detailed inorganic and organic characterisation of atmospheric aerosols, to understand the changes in their composition as a result of the implementation of the Sugar and Ethanol Industry Green Protocol, in the southeastern region of Brazil. A set of 10 samples segregated into PM_{2.5}, PM_{2.5–10} and PM_{>10} fractions were collected in May and July of 2014, covering the beginning of the sugarcane harvest period. The analytical methods included gravimetric determination, water-soluble ions by ion chromatography, major elements by inductively coupled plasma mass spectrometry, carbonaceous content by a thermal-optical system and organic speciation by gas chromatography–mass spectrometry. A substantially higher mean concentration ($57 \pm 36 \mu\text{g m}^{-3}$) was obtained for PM_{2.5} in comparison with PM_{2.5–10} ($15 \pm 6.2 \mu\text{g m}^{-3}$) and PM_{>10} ($8.5 \pm 13 \mu\text{g m}^{-3}$). The carbonaceous content represented, on average, approximately 18 and 21 % of the particulate matter of the PM_{2.5} and PM_{2.5–10} fractions, respectively. On average, water-soluble ions accounted for 12 and 7.7 % of the

PM_{2.5} and PM_{2.5–10} mass, respectively. With the implementation of the Green Protocol, a decrease of biomass burning ion tracers would be expected, however, this trend was not observed. With regard to major elements, aerosols from both fractions were dominated by K, Ca, Na and Al. Concentrations of the major elements were lower than those observed in earlier studies. Organic compounds were present at higher levels in the fine than in the coarse fraction. *n*-Alkanes, *n*-alkanoic acids and polycyclic aromatic hydrocarbons related to biomass combustion showed lower concentrations than previously reported.

Keywords Water-soluble ions · Major elements · Organic speciation · São Paulo state · Brazil

Introduction

The central region of São Paulo state is occupied by a large area for sugarcane cultivation. This study was carried out in Araraquara, a city located in the main region of this crop production. Araraquara's economy is based on trade, services, industry and agriculture by this order of importance. The main industrial and agricultural activities include ethanol/sugar production, cattle farming and sugarcane cultivation (SEBRAESP 2016).

The sugarcane crop expansion in São Paulo state, as in other Brazilian regions, result from the increasing demand for ethanol as a fuel source. The total sugarcane area increased in the period 2010–2015 from 5,071,205 to 5,728,285 ha in the São Paulo state (UNICA 2016). However, the common practice of pre-harvest burning of sugarcane straw emits huge amounts of particulate material, greenhouse gases and tropospheric ozone precursors to the atmosphere. According to Lara et al. (2005), 20 t of sugarcane straw are burned per hectare, contributing to a global emission of 0.48 Tg of carbon

Electronic supplementary material The online version of this article (doi:10.1007/s11869-016-0441-0) contains supplementary material, which is available to authorized users.

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per year. Soot, which remains suspended in the air, is considered one of the causes of the high incidence of respiratory diseases in Brazil (Arbex et al. 2000). In 2002, the São Paulo state government regulated the gradual elimination of sugarcane burning: until 2021 in mechanisable areas and in non-mechanisable areas by 2031 (State Decree n° 47700/2003; State Law n° 11241/2002). Therefore, manual harvesting work shall continue, at least, until these dates. In order to anticipate the end of the pre-harvest burnings to 2014, the São Paulo state Secretary of Environment (SMA) and the Sugarcane Industry Union (UNICA) signed in June 2007 the Sugar and Ethanol Industry Green Protocol to promote sustainable production practices for sugarcane in the state. At the time of this study, the pre-harvest field burning accounted for approximately 11 % of the total sugarcane areas in the Araraquara region, whilst in 2010 a percentage of 43 % had been registered (UNICA 2016).

Previous air quality studies indicated higher concentrations of both gases (e.g. nitrogen oxides, NO_x) (Allen et al. 2011; Machado et al. 2008) and aerosol constituents, such as SO_4^{2-} , NO_3^- , Cl^- , Na^+ , K^+ , NH_4^+ , Mg^{2+} and Ca^{2+} (Allen et al. 2004), during the harvest than in the non-harvest period. Although the few studies available in the region have shown that agro-industrial activities lead to important emissions of organic compounds to the lower troposphere, such as polycyclic aromatic hydrocarbons (PAH) (Andrade et al. 2010), water-soluble organic carbon (WSOC) (Souza 2011) and sugars (Scaramboni et al. 2015; Urban et al. 2014, 2016). The researches devoted to the organic speciation are still very scarce. The organic contribution was estimated to be about 62 % of the aerosol emitted during sugarcane burning (Allen et al. 2010).

In this transition period, the particulate matter (PM) sources are expected to experience some changes. A reduction of sugarcane burning, and an increase of mechanised cutting and road transport, may lead to a decrease in concentrations of tracers from biomass combustion, and to an enhancement of both mineral dust resuspension and vehicular emissions.

The present research aimed to (i) accomplish a detailed chemical characterisation of size segregated inorganic and organic compounds during the harvest period, (ii) understand the changes in the aerosol composition due to the implementation of the Sugar and Ethanol Industry Green Protocol and (iii) understand the influence of changes in anthropogenic activities on the atmospheric particulate matter in the south-eastern region of Brazil.

Materials and methods

Sampling details

Araraquara is a city with 226,508 inhabitants located within the sugarcane growing region of São Paulo state (IBGE 2016)

(Fig. 1). A total of 10 samples were collected from May 20 to 25 and from July 14 to 18 of 2014, covering the beginning of the harvest period. Sampling was performed with a high-volume sampler (Model TE-5000, Tisch Environmental, Inc.), operating at a flow rate of $1.12 \text{ m}^3 \text{ min}^{-1}$. The aerosol samples were collected into three size fractions ($\text{PM}_{2.5}$, $\text{PM}_{2.5-10}$ and $\text{PM}_{>10}$) at the São Paulo State University (UNESP) campus ($21^\circ 48' 50'' \text{ S}$, $48^\circ 12' 07'' \text{ W}$), in a suburban area, ~4 km southwest of the Araraquara City. The equipment was installed on the roof of a building, at ~5 m above ground level. Particulate matter was collected on quartz fibre filters (Whatman) for 24-h periods. After collection, filters were stored in a freezer (at -14°C) prior to analysis.

The acquisition of meteorological parameters (temperature, relative humidity, wind direction) was performed continuously by a meteorological station near the sampler. The data were stored using a CR10 datalogger (Campbell Scientific, Inc.) with attached multiplexers.

Analytical methods

The gravimetric determination was performed with a microbalance (Sartorius CP225D) after 24-h equilibration in a room with controlled temperature and relative humidity ($20 \pm 2^\circ \text{C}$, $50 \pm 5\%$). Quartz fibre filters used in this study were placed in an oven at 500°C for 6 h, to remove organic contamination. Filter weight before and after sampling was obtained as the average of several measurements, when observed variations were less than 5 %. The gravimetric measurements included the three size fractions ($\text{PM}_{2.5}$, $\text{PM}_{2.5-10}$ and $\text{PM}_{>10}$), but due to the lower loads of the super-coarse fraction ($\text{PM}_{>10}$), together with the fact that legislation refers to inhalable particles, only the fine ($\text{PM}_{2.5}$) and coarse ($\text{PM}_{2.5-10}$) fractions were subjected to chemical determinations.

The determination of water soluble ions was carried out by ion chromatography (IC). The solution obtained after extraction with 20 ml of ultra-pure deionised water was filtered with PTFE syringe filters with a pore size of $0.45 \mu\text{m}$ (VertiClean™) and subsequently analysed in a Dionex/Thermo Scientific ICS-5000. The filter extracts were analysed for F^- , Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , acetate ion (CH_3COO^-), formate ion (HCO_2^-), oxalate ion ($\text{C}_2\text{O}_4^{2-}$), Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} . Seven-point calibration curves were constructed for each ion (in triplicate), encompassing the following concentrations: 0.2, 0.4, 0.6, 0.8, 1.0, 2.0 and 3.0 mg l^{-1} . The detection limits (of the mass of 8 blank filters) were estimated to be $0.17 \mu\text{g ml}^{-1}$ for Na^+ , $0.01 \mu\text{g ml}^{-1}$ for NH_4^+ , $0.17 \mu\text{g ml}^{-1}$ for K^+ , $0.01 \mu\text{g ml}^{-1}$ for Mg^{2+} , $0.07 \mu\text{g ml}^{-1}$ for Ca^{2+} , $0.003 \mu\text{g ml}^{-1}$ for Cl^- , $0.03 \mu\text{g ml}^{-1}$ for NO_3^- , $0.33 \mu\text{g ml}^{-1}$ for PO_4^{3-} , $0.11 \mu\text{g ml}^{-1}$ for SO_4^{2-} and $0.13 \mu\text{g ml}^{-1}$ for $\text{C}_2\text{O}_4^{2-}$. The quality of the measurements was judged by calculating the balance of negative and positive ions. In the $\text{PM}_{2.5}$ fraction, the ion balance was close to

Fig. 1 Location map of Araraquara City, São Paulo state



neutral. The $PM_{2.5-10}$ fraction showed a deficit of anions. This deficit is probably due to unaccounted carbonates from soil resuspension.

Elements in particulate matter were determined by inductively coupled plasma mass spectrometry (ICP-MS) equipped with collision cell technology (CCT) (Xseries II-Thermo Scientific), after digestion with diluted acid solution (HNO_3 , 1 %). This solution was used to characterise the composition of the aerosol which is prone to solubilisation in the environment. The filters remained for 5 h in a mechanical shaker (115 rpm) at room temperature, for a better removal of elements to the solution. Before ICP-MS analysis, the samples were filtered with PTFE syringe filters with a pore size of $0.45 \mu m$ (VertiClean™). Although this analytical technique allows the determination of 57 different elements, in this study, only major elements were quantified. The detection limits (of the mass of 8 blank filters) were estimated to be 0.4 ng ml^{-1} for Al, 9.0 ng ml^{-1} for Ca, 0.05 ng ml^{-1} for Cu, 29 ng ml^{-1} for Fe, 47 ng ml^{-1} for K, 0.2 ng ml^{-1} for Mg, 0.03 ng ml^{-1} for Mn, 2.0 ng ml^{-1} for Na, 0.002 ng ml^{-1} for Pb, 0.01 ng ml^{-1} for Rb, 0.009 ng ml^{-1} for Sr, 0.08 ng ml^{-1} for Ti and 0.004 ng ml^{-1} for Zn. For quality control, all analyses

were performed in triplicate (IC) and duplicate (ICP-MS). The blank values for ions and elements were subtracted from the sample results.

For the determination of the carbonaceous content, small discs with 9-mm diameter were punched out of the quartz fibre filters. The carbonaceous content (organic carbon (OC), elemental carbon (EC)) of particulate matter was measured with a homemade thermal-optical transmission system, based on the thermal desorption/oxidation of particulate carbon to CO_2 , which was subsequently analysed in a non-dispersive infrared (NDIR) CO_2 analyser, following a protocol similar to EUSAAR (European Supersites for Atmospheric Aerosol Research). This technique is described in detail in Pio et al. (2011). Controlled heating in anoxic conditions was performed to separate OC into two fractions of increasing volatility. The first fraction corresponds to the volatilisation at $T < 200 \text{ }^\circ C$ of lower molecular weight organics (OC_1). The second fraction is related to decomposition and oxidation of higher molecular weight species at temperatures ranging from 200 to $600 \text{ }^\circ C$ (OC_2). The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon (PC) produced in the previous heating steps. Separation

between OC and EC was achieved by initially heating the filter punches under an inert atmosphere to evaporate first the OC fraction. The remaining fraction is sequentially evaporated/burnt under a gas flow containing O₂. This last carbon fraction contains initial EC plus OC that has pyrolysed during heating under an inert atmosphere. The interference between PC and EC can be controlled by continuous evaluation of the blackening of filter using a laser beam and a photodetector measuring the filter light transmittance. This methodology was tested with the NIST (National Institute of Standards and Technology) filter standard and in an intercomparison experiment with real aerosol samples (Schmid et al. 2001), delivering OC/EC ratios between those obtained by the NIOSH (National Institute for Occupational Safety and Health) and the IMPROVE (Interagency Monitoring of Protected Visual Environments) protocols, but closer to the latter. The procedure was also compared with the EUSAAR II protocol through the analysis of samples of different types and origins (Almeida 2009).

The samples were subjected to detailed organic analysis by gas chromatography–mass spectrometry (GC–MS). Based on the previously determined OC content, two to three consecutive filters were pooled, resulting in four sets of samples for each PM fraction (ARF1 to ARF4—PM_{2.5} fraction, ARG1 to ARG4—PM_{2.5–10} fraction). The combined portions of the filters were consecutively extracted with dichloromethane and methanol (Fisher Scientific). Both extracts were then combined, vacuum concentrated and dried under a gentle nitrogen stream. The total organic extract (TOE) was subsequently separated into five different organic fractions by flash chromatography with activated silica gel and different solvents of increasing polarity. The TOE was transferred to the top of a glass column (30 × 0.7 cm) pre-packed with 1.5 g of silica gel (pore size 60 Å, 230–400 mesh, Merck Grade 9385), previously activated at 150 °C for 3 h. Each TOE was successively washed with different mixtures of solvents and added to the silica column. The following solvents were used to elute the different compound classes: (1) 22.50 ml *n*-hexane (fraction 1, aliphatics), (2) 22.50 ml toluene–*n*-hexane (8.40:14.10) [fraction 2, polycyclic aromatic hydrocarbons (PAHs)], (3) 22.50 ml *n*-hexane–dichloromethane (11.25:11.25) (fraction 3, carbonyl compounds), (4) 30.00 ml ethyl acetate–*n*-hexane (12.00:18.00) (fraction 4, *n*-alkanols, sterols and other hydroxyl compounds) and (5) 30.00 ml solution of pure formic acid in methanol (4 %, v/v) (fraction 5, acids and sugars). To speed up the process, all the solvents were eluted using a gentle nitrogen stream. After elution, all the extracts were vacuum concentrated and evaporated to approximately 1 ml using a rotary evaporator and then dried under a gentle ultrapure nitrogen flow. The detailed description of the methodology for the organic compound extraction can be found in Alves et al. (2011). The fractionated extracts were analysed with a Gas Chromatography model 6890 coupled to a

quadrupole Mass Spectrometry Detector 5973 from Hewlett Packard and with a GC–MS from Shimadzu, model QP5050A, with automatic injection. Before injection, the compounds with hydroxylic groups were converted for 3 h at 70 °C into the corresponding trimethylsilyl derivatives by addition of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA): trimethylchlorosilane (TMCS) 99:1 (Supelco). The GC–MS calibration was performed with injection of about 110 standards in different concentration ranges and relative response factors calculated for each compound and for each organic class. For those with no authentic standards available, relative response factors were calculated as an average of the relative response factors from the overall homologous series or from compounds with similar chemical structure and retention time. Standards and samples were both co-injected with one internal standard: tetracosane-d50 (Sigma Aldrich). Compound identification was based on comparison of resulting spectra with mass spectra libraries (Wiley 275 and NIST MS Search 2.0), co-injection with authentic standards and analysis of fragmentation patterns. The quantitative analysis was performed by both single ion monitoring (SIM) and total ion chromatogram (TIC) methods, in two separate GC runs. The blank filters were analysed in the same way as for the samples and the data obtained were subtracted from the samples in order to obtain blank-corrected results.

The Spearman's correlation coefficient (r_s) was used to measure the strength and direction of the relationship between the different variables (Sachs 1984). Tables with complete data are attached as supplementary material (Tables 1S, 2S, 3S and 4S).

Results and discussion

Meteorological conditions, air mass trajectories and biomass burning frequency

During the sampling period, mean temperatures ranged from 16 to 23 °C. The highest precipitation volume occurred on May 22, reaching 17 mm. During the rest of the campaign, precipitation mean values of 2 mm were registered. Backward trajectory analysis was carried out by applying the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by NOAA's Air Resources Laboratory (Draxler et al. 1997, 1998), which uses meteorological files from GDAS (Global Data Analysis System). Five days (120 h) backward trajectories ending at the sampling place were calculated using the vertical velocity option.

In São Paulo state, sugarcane harvest happens between May and November, coinciding with the low rain precipitation period. The peak of the burning season (August) coexists with the least amount of precipitation in the region (INPE 2016). Therefore, samples collected in this study represent the beginning of the dry season/harvest period.

Figure 2 shows the paths of air masses over two different periods of the sampling campaign. In May, the Araraquara region was mostly affected by air masses with continental origin that have passed through several northern and central states of Brazil and near the border with Bolivia, before arriving at the study site (Fig. 2a). In July (Fig. 2b), the region of Araraquara was mostly affected by two backward trajectories (500 and 1500 m) containing Atlantic components. However, these air masses approached from southeast, crossing southern regions of Brazil. Araraquara was also affected by a higher altitude backward trajectory (3000 m) with continental origin and with a path very similar to the one observed in May.

The monthly distribution of fires in São Paulo state between January and December 2014 is shown in Fig. 3, together with data from the municipality of Araraquara (INPE 2016).

In Araraquara, the number of fires increased from 2 in May, at the start of the sampling period, to 24 in July. The maximum was reached in August with 213 fires, followed by a decline until December. The monthly frequency of fires recorded by INPE (2016) for São Paulo state followed a similar trend as that obtained for the municipality of Araraquara.

Particulate matter and carbonaceous content

The PM concentrations varied between 11 and 114 $\mu\text{g m}^{-3}$, between 8.2 and 28 $\mu\text{g m}^{-3}$ and between 0.75 and 45 $\mu\text{g m}^{-3}$ for the $\text{PM}_{2.5}$, $\text{PM}_{2.5-10}$ and $\text{PM}_{>10}$ fractions, respectively. A

substantially higher mean concentration was obtained for $\text{PM}_{2.5}$ in comparison with $\text{PM}_{2.5-10}$ and $\text{PM}_{>10}$ (Table 1). The daily mean concentrations of $\text{PM}_{2.5}$ ($57 \pm 36 \mu\text{g m}^{-3}$) and PM_{10} ($\text{PM}_{2.5} + \text{PM}_{2.5-10}$) ($73 \pm 42 \mu\text{g m}^{-3}$) exceeded, by 128 and 46 %, respectively, the values considered as standards by the World Health Organisation (WHO 2006) (24 h mean $\text{PM}_{2.5} = 25 \mu\text{g m}^{-3}$ and 24 h mean $\text{PM}_{10} = 50 \mu\text{g m}^{-3}$), which is indicative of bad atmospheric quality and a signal of alert to long-term health effects in the study region (Andrade et al. 2012; de Miranda et al. 2012). $\text{PM}_{2.5}$ represented, on average, approximately 75 % of the PM_{10} ($\text{PM}_{2.5} + \text{PM}_{2.5-10}$) mass. The PM_{10} concentrations obtained in this study are of the same order as those measured, over the same time period of the year, in 2002 ($103 \pm 31 \mu\text{g m}^{-3}$) by Andrade et al. (2010) and Godoi et al. (2004) and in 2003 ($67 \pm 16 \mu\text{g m}^{-3}$) by Andrade et al. (2010), but higher than the mean level reported by Oliveira et al. (2013), in 2009 ($26 \mu\text{g m}^{-3}$), for the harvest period. Cançado et al. (2006) and Lara et al. (2005) described $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ concentrations of $23 \pm 15 \mu\text{g m}^{-3}$ and $68 \pm 43 \mu\text{g m}^{-3}$, respectively, for Piracicaba (1997–1998), other sugarcane region. More recently, Vasconcellos et al. (2010) observed a declining trend in PM_{10} concentrations in Piracicaba, with $55 \pm 26 \mu\text{g m}^{-3}$ in 2007 and $47 \pm 30 \mu\text{g m}^{-3}$ in 2008.

The carbonaceous content (TC = OC + EC) represented, on average, approximately 18 and 21 % of the $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ masses, respectively (Table 1). The OC concentrations in

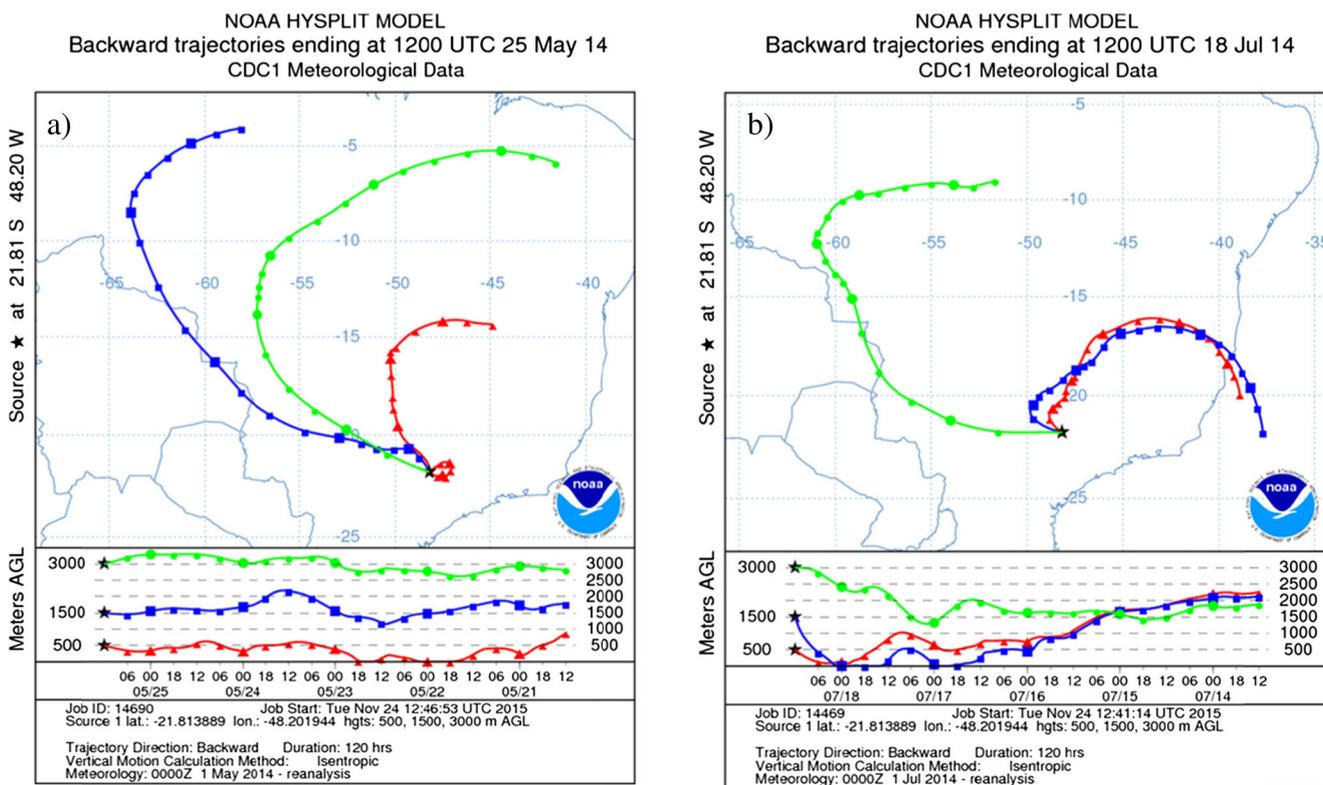


Fig. 2 HYSPLIT model backward trajectories arriving at Araraquara for two different periods of the sampling campaign. a May 2014. b July 2014

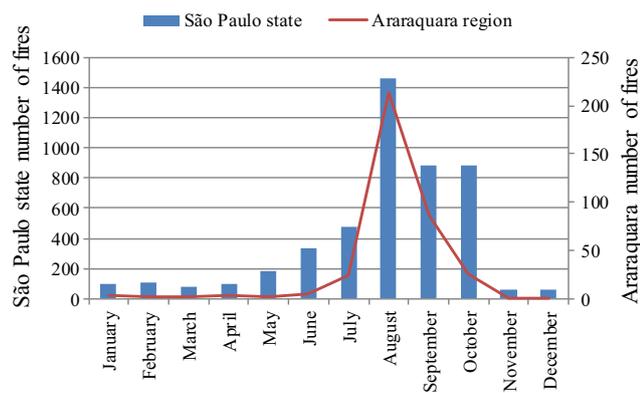


Fig. 3 Fire occurrences by month in São Paulo state and Araraquara municipality, in 2014

PM_{2.5} samples varied between 1.9 and 17 $\mu\text{g m}^{-3}$, whilst EC presented values between 0.60 and 3.3 $\mu\text{g m}^{-3}$. In the PM_{2.5–10} fraction, OC ranged from 1.5 to 3.5 $\mu\text{g m}^{-3}$. EC varied from undetectable levels to 0.42 $\mu\text{g m}^{-3}$.

The OC-to-EC ratio in PM_{2.5} remained relatively constant throughout the campaign, whilst variable values were obtained for the coarse mode (Table 1). It has been reported that organic-to-elemental C ratios (OC/EC) measured in deciduous tree smoke samples range from 9 to 43 (average = 24), whereas in grass smoke samples range from 19 to 44 (average = 31) (Oros et al. 2006; Oros and Simoneit 2001). Comparatively, the ratios obtained in the present study are much lower (4.1 ± 1.1), especially in the PM_{2.5} fraction. This fact may be related to the decrease of the sugarcane pre-harvest burning and, on the other hand, to an increase of petroleum derived combustion emissions from mechanical harvesting processes, consequence of the Sugar and Ethanol Industry Green Protocol implementation. Moreover, it should bear in mind that sugar cane burning is characterised by very intense flaming conditions, which lead to higher EC emissions (Hall et al. 2012). High OC–EC correlations ($r_s = 0.879$) in the PM_{2.5} fraction indicates that the relative rates of EC and OC would be proportional to each other and that both carbonaceous species would have common sources and transport processes. In the PM_{2.5–10} fraction, a weak correlation between OC and EC ($r_s = 0.563$) was obtained, indicating the contribution of different sources (e.g. soil resuspension). These observations make sense if we consider that the majority of particles resulting from biomass burning were reported to be less than 2.5 μm in diameter (Ferge et al. 2005; Hedberg et al. 2002).

Average concentrations of PM, OC, EC and TC and some ratios are shown in Table 1.

Inorganic speciation

Water-soluble ions accounted for about 3.4 to 26 % of the PM_{2.5} concentrations, averaging 12 %. In the PM_{2.5–10} fraction, they represented about 1.8 to 15 % (average 7.7 %). The

average concentrations and standard deviations of water-soluble ions in the PM_{2.5} and PM_{2.5–10} size fractions are presented in Table 2 and are compared with some other studies made in Araraquara, during the harvest period. Tables with complete data are attached as supplementary material (Tables 5S, 6S).

In this study, NO_3^- , SO_4^{2-} , K^+ and NH_4^+ were the ionic species with the highest concentrations in PM_{2.5}. It has been reported previously that nitrate, sulphate and ammonium are important secondary aerosol components in the region, being involved in nucleation and growth processes of particles (Allen et al. 2004; Caetano-Silva et al. 2013). On average, 87 % of the K^+ mass was concentrated in fine particles. The samples collected in July (1070 ng m^{-3}) presented approximately twice the K^+ concentration of the samples collected in May (536 ng m^{-3}) (Tables 5S and 6S). According to INPE (2016), the number of fires increased from 2 to 24 between May and July 2014 in the region of Araraquara and from 181 to 481 in the São Paulo state. Moreover, K^+ showed a good correlation with SO_4^{2-} , also associated with biomass burning ($r_s = 0.891$). The K^+ /OC ratio was also taken into account. In the literature, average K^+ /OC in PM_{2.5} samples from rice straw burning (field and chamber burn) around 0.22 ± 0.12 have been reported, whereas in samples from fresh sugarcane leaves (field burn), the same ratio was around 0.45 ± 0.16 (Lin et al. 2010). Comparatively, lower values (0.11 ± 0.04) were obtained in this study. The emission factors of particulate compounds from burning of a given type of biomass typically vary with combustion conditions (Andreae and Merlet 2001). Likewise, K^+ and OC emissions are affected by the fire temperature and the combustion stage (i.e. smouldering and flaming phases) (e.g. Echalar et al. 1995; Khalil and Rasmussen 2003). The presence of K^+ confirms that a significant part of these particles originated from biomass burning. The ammonium concentrations observed in the PM_{2.5} fraction can be explained, at least in part, by the production of NH_3 from the bacterial metabolism in the remaining plant debris from the mechanical harvesting process and/or fertilisers added to the soil. Moreover, the NH_3 can be also emitted during biomass burning processes (Machado et al. 2008). The dominant ions in coarse particles were NO_3^- , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} ,

Table 1 Size segregated PM, OC, EC and TC concentrations (average \pm standard deviation, $\mu\text{g m}^{-3}$) and some ratios

	PM _{2.5}	PM _{2.5–10}	PM ₁₀	PM _{2.5} /PM ₁₀ (%)
PM	57 \pm 36	15 \pm 6.2	8.5 \pm 13	75 \pm 10
OC	7.3 \pm 5.3	2.4 \pm 0.61		
EC	1.7 \pm 0.93	0.17 \pm 0.18		
TC	8.9 \pm 6.1	2.6 \pm 0.73		
OC/EC	4.1 \pm 1.1	23 \pm 37		
TC/PM (%)	18	21		

Table 2 Average concentrations and standard deviations (ng m^{-3}) for water-soluble ions in fine and coarse particles

	This study		Paterlini 2007			Vasconcellos et al. 2007	Allen et al. 2004	
	PM _{2.5}	PM _{2.5–10}	PM _{<2.5}	PM _{>2.5}	PM ₁₀	PM ₁₀	PM _{<3.5}	PM _{3.5–10}
Na ⁺	97 ± 86	120 ± 112	80	163	238	340 ± 80	99	136
NH ₄ ⁺	401 ± 216	22 ± 18	656	179	1076	800 ± 470	278	37
K ⁺	803 ± 522	123 ± 54	607	698	1242	1590 ± 430	694	399
Mg ²⁺	n.d.	88 ± 47	27	130	98	260 ± 40	45	173
Ca ²⁺	285 ± 185	150 ± 77	155	834	472	730 ± 100	197	657
HCO ₂ ⁻	52 ± 62	17 ± 13					127	74
Cl ⁻	138 ± 84	93 ± 103	46	129	113	200 ± 90	114	222
NO ₃ ⁻	1602 ± 500	485 ± 342	635	1278	1895	1950 ± 420	605	532
SO ₄ ²⁻	1466 ± 518	143 ± 96	1706	1160	2713	4120 ± 1140	1358	569
C ₂ O ₄ ²⁻	61 ± 46	11 ± 5	181	8.7	368		270	353
PO ₄ ³⁻	117 ± 102	n.d.	43	19	50	210 ± 60		

n.d. not detected

Na⁺ and K⁺. Nitrate and chloride ions prevailed at significant concentrations in both size fractions. This is due to the fact NO₃⁻ and Cl⁻ in the vapour phase (HNO₃ and HCl) can be either absorbed into the coarse aerosol fraction with basic properties and may also participate in the nucleation process with ammonia vapours in the fine fraction. It would be expected that the Ca²⁺ concentration was greater in the PM_{2.5–10} fraction, but as can be seen in Tables 5S and 6S, this is not the case. There may be another Ca²⁺ source that justifies a higher concentration in the fine fraction. Reid et al. (2005) argued that approximately 10 % of fine-mode mass of fresh smoke is composed of trace inorganic species, most notably potassium, chlorine and calcium, which are likely present in the particle core. It has also been shown that calcium has an important function in stiffening the cell walls of a plant. It is volatilised during combustion and then condenses as submicron particles (Johansson 2002). Ca²⁺ and Mg²⁺ in coarse mode particles have a likely common origin in resuspended surface soil dust (Allen et al. 2004). These species can be resuspended by the wind or by fire-induced atmospheric turbulence and due to its size does not travel long distances, having a greater effect at local level (Allen et al. 2010). Magnesium is usually associated with calcium and sodium, and is considered a macro-soil constituent. In this study, Mg²⁺ was only present in the coarse fraction, presenting a good correlation with Ca²⁺ ($r_s = 0.928$) and with Na⁺ ($r_s = 0.798$). Taking into account the backward trajectories (Fig. 2), a marine influence would be expected, especially in the samples collected in July. This observation was confirmed by the Na⁺ and Cl⁻ higher average concentrations observed in July compared to May (Tables 5S and 6S).

To compare actual results with those of other studies, it must be taken into account that different sampling techniques and analytical methods can lead to some disparities. Upon comparing the results obtained years apart (Table 2), it can

be seen that the qualitative composition of the aerosol has not changed much. In the case of PM_{2.5}, the quantitative composition was also very similar over the years. For coarse aerosols, a slight decrease in concentrations of ions emitted from biomass burning was observed. With the implementation of the Sugar and Ethanol Industry Green Protocol and the consequent reduction of pre-harvest burnings, a decrease in concentrations of ions from biomass burning would be expected. However, this trend is not observed (Table 2), due to the fact that the sugarcane straw harvested by mechanical processes is subsequently used as energy source of ethanol-producing plants. The ability of a dust collector to remove coarse particles from the exhaust flue gas is limited.

Regarding major elements, aerosols from both particulate size fractions were dominated by K, Ca, Na and Al. Major elements, in their oxidised form, represented, on average, approximately 5.4 % of the PM₁₀ (PM_{2.5} + PM_{2.5–10}) mass, taking into account that a partial extraction was made with diluted acid. The results of this study are compared with those of some other studies made in Araraquara, during the harvest period in Table 3. Once again, different sampling techniques and analytical methods can lead to some disparities between studies. Tables with complete data are attached as supplementary material (Tables 7S and 8S).

In this study, good correlations ($r_s > 0.733$) were found between Ca, Fe and Al in both particle size fractions. These constituents exist essentially as elements of the earth's crust. Other crustal element, Ti, presented good correlations ($r_s > 0.891$), in the fine fraction, with Al and Fe. The soil contribution is estimated by summing all elements predominantly associated with crust minerals, assuming that they are present as oxides. FeO and Fe₂O₃ are assumed equally abundant. An overall factor of 1.16 is used on all stoichiometric ratios to account for minor soil constituents like Na₂O, MgO,

Table 3 Average concentrations and standard deviations of major elements (ng m⁻³)

	This study		Oliveira et al. ^a	Oliveira et al. 2013		Silva et al. 2015	Vasconcellos et al. 2007
	PM _{2.5}	PM _{2.5-10}	TSP	PM _{<2}	PM ₂₋₁₀	PM _{2.5}	PM ₁₀
Al	145 ± 101	61 ± 39		22	125 ± 78	258	2830 ± 530
Ba	7.8 ± 4.5	4.4 ± 2.1					
Ca	447 ± 314	135 ± 124	1631 ± 1078	18	58 ± 33	148	
Cu	11 ± 2	2.7 ± 1.0		0.62	0.65 ± 0.26	10	140 ± 70
Fe	103 ± 70	46 ± 27	343 ± 219	16	114 ± 76	328	2830 ± 620
K	742 ± 382	133 ± 78	1501 ± 1118	113	54 ± 26	1460	
Mg	91 ± 55	53 ± 37	352 ± 219	2.6	22 ± 11		
Mn	13 ± 10	6.0 ± 3.9	44 ± 32	0.79	2.4 ± 1.2	13	40 ± 10
Na	156 ± 52	180 ± 100		11	21 ± 19		
Ni	0.29 ± 0.13	0.07 ± 0.03	0.92 ± 0.45			1.2	30 ± 20
Pb	2.7 ± 1.1	0.30 ± 0.20	4.8 ± 2.5	0.71	0.25 ± 0.08	7.7	10 ± 10
Rb	1.5 ± 0.8	0.21 ± 0.12					
Sr	2.5 ± 1.7	1.2 ± 0.75		0.07	0.40 ± 0.19		
Ti	2.4 ± 1.3	1.2 ± 1.0	18 ± 18			47	240 ± 80
Zn	20 ± 8.4	2.9 ± 1.7		3.8	1.7 ± 0.64	33	60 ± 10
Zr	0.17 ± 0.11	0.02 ± 0.02	1.8 ± 0.67	0.03	0.18 ± 0.11		

^a Unpublished data

H₂O and CO₂. The final equation is the following (Appel et al. 2013; Malm et al. 1994):

$$\begin{aligned} \text{Soil dust contribution} = & (2.20 \times \text{Al}) + (2.49 \times \text{Si}) \\ & + (1.63 \times \text{Ca}) + (2.42 \times \text{Fe}) \\ & + (1.94 \times \text{Ti}) \end{aligned} \quad (1)$$

For the PM_{2.5-10} fraction, the soil dust contribution was higher (9.7 %), on average, compared to the one obtained for the PM_{2.5} fraction (6.5 %).

Source apportionment researches have used particle constituents such as potassium as a biomass burning tracer. In this study, a good correlation between the potassium levels determined by ICP-MS and the water-soluble form of the element was found ($r_s = 0.879$). Thus, most of the potassium observed in the emissions of this study is water-soluble, as indicated by a K⁺/K ratio close to the unity in the PM_{2.5} fraction. Watson et al. (2001) reported K⁺/K ratios ranging from 0.1 in geological material profiles to 0.9 in vegetative burning emissions.

Concentrations of major elements found in this study were much lower than those in PM₁₀ samples collected in Araraquara in July 2003 by Vasconcellos et al. (2007), particularly for Fe, Al and Cu. The actual levels were also lower than those found in PM_{2.5} collected in 2009 by Silva et al. (2015), except for Ca, Cu and Mn. Likewise, during the harvest period of 2010/2011, Oliveira et al. (unpublished data) gathered higher values for TSP (Table 3). Concentrations of the present study, for most elements, were also lower than those reported for both fine and coarse particles sampled in

Piracicaba (May–November, 1997), excepting K (602 ± 389 ng m⁻³), Ca (110 ± 108 ng m⁻³) and Cu (6 ± 5 ng m⁻³), in the PM_{2.5} fraction (Lara et al. 2005).

Organic speciation

The organic fraction of the carbonaceous aerosol is formed by a complex mixture of compounds, which can be grouped into different classes. In this study, attention was focused on homologous series of aliphatic compounds (*n*-alkanes, *n*-alkenes, *n*-alkanoic acids, *n*-alkenoic acids, and *n*-alkanedioic acids), polycyclic aromatic hydrocarbons (PAHs), lignin pyrolysis products, other acids and cellulose pyrolysis products (anhydrosugars). There are different types of diagnostic tools that allow identifying and distinguishing biogenic and anthropogenic sources of homologous compounds. The carbon preference index (CPI), the homologue with the highest concentration (C_{\max}), the average chain length (ACL) and chain-length ratios are some examples of these diagnostic tools (Alves 2008; Oros and Simoneit 2001). For *n*-alkanes, CPI is expressed as a sum of the odd carbon number homologues, over a range, divided by a sum of even carbon homologues, over the same range. For *n*-alkanoic acids, CPI is calculated inverting the ratio to have even-to-odd homologues. A table with complete data for the distinct organic classes is attached as supplementary material (Table 9S).

For all the identified and quantified organic compounds, concentrations were significantly higher, on average, for the PM_{2.5} fraction (192 ± 133 ng m⁻³) compared to the PM_{2.5-10}

fraction ($40 \pm 11 \text{ ng m}^{-3}$) (Fig. 4). The results show the role of organic low-volatile gas-phase compounds in nucleation of particles. New particles are formed by condensation of semi-volatile organic compounds, emitted from either biogenic or anthropogenic sources, followed by growth into small particles (Holmes 2007).

The total concentrations of *n*-alkane varied from 9.3 to 59 ng m^{-3} , with an average of 34 ng m^{-3} and from 3.6 to 13 ng m^{-3} , with an average of 7.9 ng m^{-3} in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$, respectively. These levels were significantly lower than those measured in the total aerosol, during the harvest period (2011), in Araraquara ($458\text{--}118,070 \text{ ng m}^{-3}$, average = $37,999 \pm 57,712 \text{ ng m}^{-3}$) by Urban et al. (2016). This significant difference can be explained by the much higher number of fires recorded in the harvest period of 2011 (INPE 2016). The *n*-alkane series comprised members from C_{11} to C_{38} , with an odd carbon number predominance, maximising for the homologues $\geq C_{23}$. The two dominant *n*-alkanes (C_{max}) were C_{29} and C_{31} , for both particle size fractions. The CPI for the whole range of *n*-alkanes was, on average, 2.5 in $\text{PM}_{2.5}$ and 2.8 in $\text{PM}_{2.5-10}$. CPI values near unity have been pointed out as indicative of anthropogenic inputs, such as emissions from incomplete combustion of fossil fuels (Schauer et al. 2002). On the other hand, values near or greater than 3 suggest a predominant origin in vascular plants (Alves 2008; Oros and Simoneit 2001). In the case of grass, and especially sugarcane burning, CPI values were found to be around 2.1 (Oros et al. 2006). CPI values obtained in this

study are in agreement with the results obtained by Oros et al. (2006).

The aliphatic fraction also contained *n*-alkenes, ranging from C_{14} to C_{29} . These homologues presented an even to odd *C* number predominance, maximising at C_{28} and C_{25} in the $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ fractions, respectively. Total concentrations of these unsaturated aliphatics varied from 0.97 to 2.7 ng m^{-3} , with an average of 1.7 ng m^{-3} in $\text{PM}_{2.5}$, and from 0.20 to 1.9 ng m^{-3} , with an average of 0.69 ng m^{-3} in $\text{PM}_{2.5-10}$. *n*-Alkenes are not major components in plant waxes and their origin has been inferred to be from biomass fuel and motor vehicle exhaust emissions (Abas et al. 1995). In this study, *n*-alkenes can be related to vehicle emissions due to the proximity of a highway and secondary roads with heavy traffic.

n-Alkanoic acids were among the most abundant compounds in all samples. These compounds are basic units in waxes and oils from plants. They ranged from C_8 to C_{26} , showed a strong even to odd *C* number predominance and C_{max} at C_{16} and C_{18} in the $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ fractions, respectively. The CPI (whole range) was, on average, 15 in the $\text{PM}_{2.5}$ fraction and 16 in the $\text{PM}_{2.5-10}$ fraction. These data are consistent with the results of an earlier study on molecular tracers in organic aerosols from burning of grasses, in particular sugarcane combustion (Oros et al. 2006). Total concentrations of *n*-alkanoic acids varied from 2.9 to 36 ng m^{-3} , with an average of 16 ng m^{-3} in $\text{PM}_{2.5}$, and from 3.8 to 7.8 ng m^{-3} , with an average of 5.5 ng m^{-3} in $\text{PM}_{2.5-10}$. Once again, these values were significantly lower than those measured, in the total aerosol, during the 2011 harvest period, in Araraquara ($27\text{--}552 \text{ ng m}^{-3}$, average = $285 \pm 191 \text{ ng m}^{-3}$), by Urban et al. (2016). Some unsaturated fatty acids, such as oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) were also detected, but with lower contributions. These compounds are very reactive and, for this reason, are quite unstable and are removed very rapidly from the atmosphere by oxidation reactions with OH and NO_3 radicals (Simoneit et al. 1990). Hence, the presence of these compounds in the aerosol can be regarded as an indicator of the aerosol age. The ratio $C_{18:0}/C_{18:1}$ and $C_{18:0}/C_{18:2}$ presented values, on average, of 80 and 6.8 and of 12 and 16 in the $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ fractions, respectively. These high ratios during the harvest period point out an aged aerosol, i.e. relatively longer residence time since its formation. This trend was also observed during the harvest period (2011), in Araraquara (46–175), in a previous study (Urban et al. 2016). *n*-Alkanedioic acids were also present in these samples. The homologous series ranged from C_4 to C_{10} , maximising at C_4 , in both seasons. Total concentrations varied from 0.76 to 19 ng m^{-3} , with an average of 7.5 ng m^{-3} , in $\text{PM}_{2.5}$, and from 0.11 to 2.1 ng m^{-3} , with an average of 0.9 ng m^{-3} in $\text{PM}_{2.5-10}$. Although some studies have demonstrated that smoke samples from foliar fuels and deciduous trees contained *n*-alkanedioic acids ranging from C_4 to C_{10} (Hays

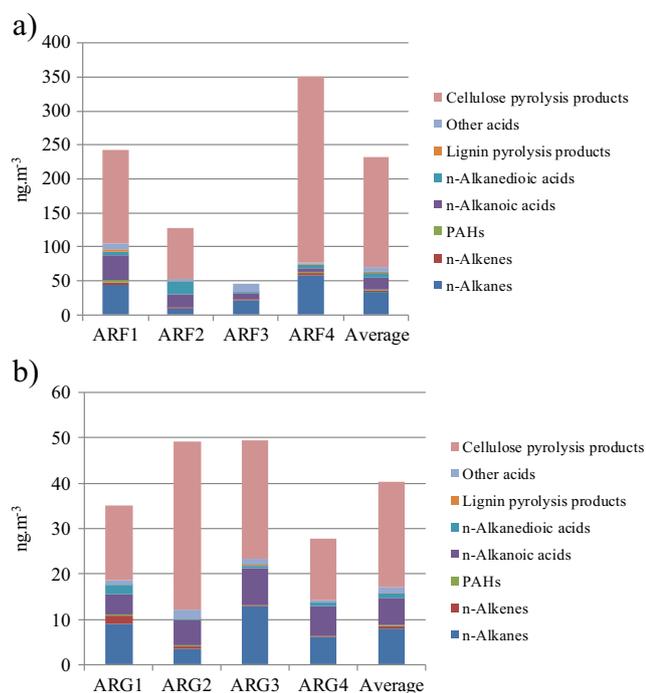


Fig. 4 Relative contributions of each organic class to the total mass of organic compounds. **a** $\text{PM}_{2.5}$. **b** $\text{PM}_{2.5-10}$

et al. 2002) and from C_{16} to C_{22} (Oros and Simoneit 2001), respectively, the *n*-alkanedioic acids have been identified in aerosols from a variety of other sources (Legrand et al. 2007; Oros and Simoneit 2001, and references therein; Wu et al. 2015). Once again, these values were significantly lower than the values obtained for the total aerosol during the harvest period (2011), in Araraquara ($18\text{--}159\text{ ng m}^{-3}$, average = $83 \pm 61\text{ ng m}^{-3}$) by Urban et al. (2016). *n*-Alkanedioic acids from C_4 to C_{10} have also been identified in fine particle emissions from burning foliar fuels (Hays et al. 2002) and in $\text{PM}_{2.5}$ (C_4 to C_7) from cereal straw burning (Zhang et al. 2007). Polycyclic aromatic hydrocarbons (PAHs) are one of the organic compound classes most studied due to its genotoxic, carcinogenic and mutagenic potential (Oros et al. 2006, and references therein). Benzo[a]pyrene is the most studied carcinogen and one of the most potent and it is often used as a toxicological prototype or surrogate for all carcinogenic polyaromatics. PAHs are toxic components of fossil fuels and primary products of incomplete combustion of organic materials (Rogge et al. 1993; Schauer et al. 1996). PAH total concentrations varied from 0.45 to 4.1 ng m^{-3} , with an average of 2.1 ng m^{-3} and from 0.12 to 0.43 ng m^{-3} , with an average of 0.23 ng m^{-3} , in the $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ fractions, respectively. The five most abundant PAHs detected in both particle fractions were benzo[ghi]perylene, indeno[1,2,3-cd]pyrene, pyrene, benzo[b + j]fluoranthene and fluoranthene (Table 4). Concentrations of these PAHs were significantly higher in $\text{PM}_{2.5}$ than in $\text{PM}_{2.5-10}$. Phenanthrene, fluoranthene and pyrene, followed by anthracene and benzo[a]anthracene, were found to be the most abundant PAHs in emissions from burning of grasses (Oros et al. 2006) and *Gramineae* species (Simoneit 2002). In the Araraquara region, the dominant PAHs in TSP during the 2011 harvest period were retene, naphthalene, benzo[a]pyrene, fluorene and chrysene (Urban et al. 2016). Table 4 was created with data from different studies made in the Araraquara region to better understand the variations over time in PAH concentrations. It is necessary to note, once more, that different sampling techniques and analytical methods can lead to some disparities. In other studies, the dominant compounds were benzo[b + k]fluoranthene, fluoranthene, phenanthrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene. PAHs are not exclusive markers of biomass combustion; however, their average concentrations have been declining over time, as can be seen in Table 4. This phenomenon is related to the increased use of mechanised harvesting in the study region, and the consequent phasing out of pre-harvest burnings. This suggests that biomass combustion for power generation emits smaller amounts of PAHs. This fact can also be confirmed by the decrease of the benzo[a]pyrene-equivalent carcinogenic power index (BaPE) (Table 4). This index has been introduced instead of the sole BaP since the latter is easily decomposed in reactive air (Alves 2008). This index aims at parameterising the health risk for

humans related to ambient exposition to carcinogenic PAHs. The cancer risk is significant if values exceed 1.0 ng m^{-3} (WHO 2006).

The major organic components of smoke particles from biomass burning are monosaccharide derivatives (anhydrosugars) from the breakdown of cellulose and hemicellulose, such as levoglucosan, mannosan and galactosan (Oros and Simoneit 2001; Simoneit et al. 1999). As expected, among the three stereoisomers, levoglucosan was the most abundant. Concentrations of these anhydrosugars were significantly higher in $\text{PM}_{2.5}$ ($74\text{--}273\text{ ng m}^{-3}$, average = 162 ng m^{-3}) than in $\text{PM}_{2.5-10}$ ($14\text{--}37\text{ ng m}^{-3}$, average = 23 ng m^{-3}) (Table 9S). Levoglucosan, in particular, varied from concentrations of 58 to 166 ng m^{-3} , with an average of 110 ng m^{-3} , in the $\text{PM}_{2.5}$ fraction and from 12 to 33 ng m^{-3} , with an average of 21 ng m^{-3} , in the $\text{PM}_{2.5-10}$ fraction. These results are in agreement with the data from previous campaigns in the Araraquara region (Urban et al. 2014, 2016), in which higher levoglucosan concentration in $\text{PM}_{2.5-10}$ ($18\text{--}382\text{ ng m}^{-3}$, average = 138 ng m^{-3}) were observed during the 2011 harvest period comparing with the non-harvest period ($12\text{--}176\text{ ng m}^{-3}$, average = 73 ng m^{-3}). Several authors use the levoglucosan-to-mannosan ratio (L/M) to distinguish between hard- and softwood smoke contributions. For instance, Fine et al. (2004) reported ratios around $19\text{--}26$ and 5.4 for hardwood and softwood tree species, respectively. Gonçalves et al. (2010) documented ratios in the range $10.4\text{--}34.9$ for hardwoods, whilst a value of 3.0 was found for softwood. Schmidl et al. (2008) obtained ratios of 3.6 and 14.8 , respectively, for soft- and hardwoods. More recently, Hall et al. (2012) reported a L/M ratio of 10 for sugarcane burnings carried out under controlled laboratory conditions. In TSP samples collected by Urban et al. (2014), the L/M ratio varied from 1 to 22 , with an average of 9 . In this study, the L/M ratio ranged from 3 to 9 , with an average of 6 , in the $\text{PM}_{2.5}$ fraction and from 8 to 11 , with an average of 10 , in the $\text{PM}_{2.5-10}$ fraction. A good linear correlation between levoglucosan and K^+ was observed in this study. The levoglucosan to potassium ratio (L/K^+) was rather constant ($0.06\text{--}0.12$), with an average of 0.1 ± 0.03 , in the $\text{PM}_{2.5}$ fraction. These observations are consistent with what was described by Allen et al. (2004, 2010) and by Urban et al. (2012) for the same region.

A rough estimate of the biomass burning contribution to OC was done as follows:

$$\text{OC}_{\text{biomass burning}} = [\text{levoglucosan}]/49 \quad (2)$$

where 49 is the levoglucosan/OC (mg g^{-1}) ratio obtained by Hall et al. (2002) for sugar cane in a combustion chamber. It was found that, on average, 31 and 18% of OC in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$, respectively, originated from sugarcane burning.

Table 4 Comparison between PAH average concentrations in the Araraquara region of this study and values of previous studies (ng m⁻³)

Compounds	Godoi et al. 2004		Andrade et al. 2010		Magalhães et al. 2007		Silva et al. 2010		Assunção et al. 2014		Souza et al. 2014		This study			
	August 2002	PM ₁₀	August 2002–September 2003	PM ₁₀	July 2003	PM ₁₀	2008	2009	June 2009 to October 2009	TSP	Day	Night	May to June 2010	PM _{2.5}	PM _{2.5-10}	
Naphthalene	0.42 ± 0.27								0.70				0.10 ± 0.05	0.06 ± 0.08	0.002	0.004
Acenaphthylene	0.95 ± 0.62								0.41				0.27 ± 0.07	0.12 ± 0.09	0.011	0.001
Acenaphthene	0.70 ± 0.56								0.03						0.000	
Fluorene	0.42 ± 0.43								0.23				0.04 ± 0.05	0.06 ± 0.13	0.006	0.001
Phenanthrene	2.9 ± 1.2	4.03					0.39	0.12	5.1				0.22 ± 0.08	0.02 ± 0.04	0.121	0.016
Anthracene	0.33 ± 0.13	0.03					0.07	0.09	0.24				0.31 ± 0.43	0.019	0.002	0.030
Fluoranthene	3.3 ± 1.6	3.22					0.18	0.89	4.0				0.38 ± 0.16	2.1 ± 4.3	0.225	0.030
Pyrene	2.5 ± 1.7	0.38					0.38	0.19	3.7				0.26 ± 0.07	0.91 ± 1.89	0.260	0.033
Benzo[a]anthracene		0.15					0.12	0.093	0.24				0.12 ± 0.06	1.6 ± 4.3		
Chrysene	6.6 ± 4.1	0.56					0.29	0.34	0.50				0.15 ± 0.03	0.63 ± 1.0	0.202	0.024
Benzo[b + k]fluoranthene	5.6 ± 3.3	0.52					0.36 ^a	0.18 ^a	0.93				0.26 ± 0.11 ^b	2.9 ± 5.4 ^b	0.254 ^c	0.022 ^c
Benzo[a]pyrene	1.9 ± 1.1	0.46					0.19	0.12	0.34				0.12 ± 0.14	0.29 ± 0.38	0.091	0.007
Benzo[e]pyrene	2.7 ± 1.4	nd					0.27	0.23	nd						0.137	0.011
Indeno[1,2,3-cd]pyrene	8.7 ± 5.6	0.35					2.9	0.32	0.25						0.330	0.030
Dibenzo[a,h]anthracene		1.88					0.16	0.21	0.020						0.029	0.002
Benzo[g,h,i]perylene	8.5 ± 3.8						0.56	0.14	0.69						0.405	0.042
Perylene	3.8 ± 1.5								nd						0.032	0.001
Total	49.3 ± 2.8	12					6.3	3.3	17						1.9	0.20
BaPE index	3.0	0.53					1.40	1.30	0.45				0.15	0.59	0.153	0.013

BaPE–Benzo[a]pyrene-equivalent carcinogenic power = BaPE = BaA × 0.06 + BFs × 0.07 + BaP + DBA × 0.6 + IcdP × 0.08

nd not detected

^a Benzo[k]fluoranthene^b Benzo[b]fluoranthene^c Benzo[b+j+k]fluoranthene

Conclusions

In this study, a detailed chemical characterisation of the atmospheric particulate matter from Araraquara, an agro-industrial region of São Paulo state, was performed. Size segregated samples were collected during the harvest period to understand the impact of implementing the Sugar and Ethanol Industry Green Protocol and the influence of changes in anthropogenic activities on aerosols of the southeastern region of Brazil.

At the beginning of the harvest period (May), the Araraquara region was mostly affected by continental air masses, starting at different northern states of Brazil. By contrast, during the July period, the region was mostly affected by backward trajectories containing Atlantic components, but approaching from the southeast, traversing southern Brazil, before arriving at the study site. The sampling period of this research coincided with the increase of the number of fires, which reached their maximum in August. Significantly higher concentrations of fine than coarse particles were obtained. Aerosol concentrations were of the same order of magnitude as those observed in the few previous studies that have been made in the region. Comparing the water-soluble ion results with other previous studies, some trends were identified. The same predominant ions were observed for both fine and coarse particles, despite presenting different concentrations: NO_3^- , SO_4^{2-} , K^+ and NH_4^+ . With the implementation of the Sugar and Ethanol Industry Green Protocol and the consequent reduction of pre-harvest burnings, the decrease of biomass burning ions, such as K^+ and SO_4^{2-} , would be expected, but this was not observed. Aerosols from both fractions ($\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$) also presented the same predominant major elements: K, Ca, Na and Al. Earth's crust elements, such as Ca, Fe, Al and Ti, showed good correlations among themselves. These elements usually appear associated with episodes of soil resuspension. The carbonaceous content represented, on average, approximately 18 and 21 % of the particulate matter for the $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ fractions, respectively. It was observed that the OC/EC ratio was smaller than the values typically obtained for biomass combustion, in particular grass burning. The abundance order for the major organic groups in samples from the harvest period is as follows: cellulose pyrolysis products >*n*-alkanes >*n*-alkanoic acids, regardless of the analysed particle size fraction. Concentrations and diagnostic tools for *n*-alkanes, *n*-alkanoic acids, *n*-alkanedioic acids and PAHs presented much lower values than those found in previous studies carried out in the same area, with the exception of *n*-alkenes.

Generally, these datasets suggest that the qualitative composition of the aerosol has not changed much over the last few years. In quantitative terms, very slight variations were observed for fine particles over time. However, it seems that concentrations of coarse aerosols and their constituents have

somewhat decreased. These changes may be related to the decrease of the sugarcane pre-harvest burnings, as a consequence of the implementation of the Sugar and Ethanol Industry Green Protocol. Moreover, the sugarcane straw harvested by mechanical processes is subsequently used as energy source of the ethanol-producing plants, releasing into the atmosphere compounds that may coincide with those of pre-harvest burnings. Whilst coarse particles are, in general, efficiently removed from the flue gas by common control devices, the performance for submicron particles may not be so effective.

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