



Physicochemical characterization of winter PM₁₀ aerosol impacted by sugarcane burning from São Paulo city, Brazil



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HIGHLIGHTS

- Chemical characterization of winter PM₁₀ during 2012 and 2013 in São Paulo, Brazil.
- Levoglucosan accounted for 2% of the organic carbon (OC) mass.
- Secondary biomass burning markers contributed from 0.28% to 0.35% to the OC mass.
- PM₁₀ is heavily impacted by regional sugarcane burning in winter.
- Levoglucosan/galactosan ratio smaller than 30 indicates sugarcane burning.

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ABSTRACT

Atmospheric particulate matter samples (PM₁₀) were collected at an urban site in São Paulo (SPA) city in winter episodes of 2012 and 2013. Several organic compounds were determined in the samples to characterize the composition of the particulate matter with emphasis on marker compounds for biomass burning. Organic carbon (OC), elemental carbon (EC), monosaccharide anhydrides, monosaccharides, nitroaromatic compounds, isoprene secondary organic aerosol markers, and polyols were measured. The PM₁₀, OC and EC median concentrations were higher for samples collected in 2013 than in 2012, with the contribution of OC to the PM₁₀ mass being 17% and 11% in 2012 and 2013. The three anhydrosugars, levoglucosan, mannosan and galactosan together, accounted, on average, for 2.0 and 2.2% of the OC mass in 2012 and 2013, whereas the nitro-aromatic compounds, including 4-nitrophenol, 4-nitrocatechol, isomeric methyl nitrocatechols and dimethyl catechols, showed the same trend, contributing, on average, for 0.28% and 0.35% to the OC mass in 2012 and 2013, and thus indicating a higher contribution from biomass burning in 2013 compared to 2012. The methyl nitrocatechols were substantially correlated with levoglucosan, consistent with their proposed origin from biomass burning. The results demonstrate that biomass burning compounds are important contributors to the OC mass, especially in winter. Furthermore, it is suggested that a levoglucosan/galactosan ratio smaller than about 30 may be indicative for regional sugarcane burning and not for advected air from sites that are impacted by tropical forest fires.

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1. Introduction

Megacities, like São Paulo, Brazil, are increasingly receiving attention as strong pollution hotspots. Located in South America,

the São Paulo Metropolitan Area has 19 million inhabitants and 7.4 million vehicles. During winter (dry season), the average concentration of inhalable particles (i.e., PM₁₀, particulate matter with aerodynamic diameter $\leq 10 \mu\text{m}$) can be as high as $150 \mu\text{g m}^{-3}$ (Miranda and Andrade, 2005). A major known source of pollutants are vehicular emissions; however, in addition to traffic there are also contributions from biomass burning. Previous studies showed that there is a link between particulate concentrations and adverse health effects, more specifically, respiratory problems (Pires-Neto

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et al., 2006), mainly during episodes of sugarcane burning in surrounding regions of the city (Arbex et al., 2000; Umbuzeiro et al., 2008).

Biomass burning (BB) is often used in agricultural practices, releasing a substantial amount of PM into the atmosphere, which influences cloud formation, the radiation balance, ozone formation, and human health (Urban et al., 2012). Sugarcane cultivation in the State of São Paulo has economic importance as a source of biofuel, whereby leaves are burnt prior to harvesting to remove excess foliage and avoid injuries to workers (Urban et al., 2012). Previous research suggests that sugarcane burning aerosol is mainly composed of particles smaller than 2.5 µm in diameter (PM_{2.5}) (Lara et al., 2005; Hall et al., 2012). In several previous studies on the composition of sugarcane smoke aerosol in Brazil, levoglucosan and related monosaccharide anhydrides were determined (Dos Santos et al., 2002; Urban et al., 2012, 2014, 2016; Souza et al., 2014; Scaramboni et al., 2015), but none of these studies included measurements on nitroaromatic compounds, which in recent years have been shown to be also important constituents of BB aerosol, as indicated below.

This study focuses on the characterization of BB contributions to the PM₁₀ aerosol, thereby using two types of marker compounds, i.e., monosaccharide anhydrides and nitroaromatic compounds. The use of the anhydrosugar levoglucosan (1,6-anhydro-β-D-glucopyranose), formed by pyrolysis of cellulose and hemicelluloses at higher temperatures, as a BB marker was introduced by Simoneit et al. (1999). It is accompanied by other minor stereoisomeric monosaccharide anhydrides, with mannosan (1,6-anhydro-β-D-mannopyranose) and galactosan (1,6-anhydro-β-D-galactopyranose) being the most important ones (Simoneit et al., 1999; Nolte et al., 2001). Levoglucosan as BB marker has generally been preferred over water-soluble potassium, since studies indicated that potassium has other substantial sources, such as its use as fertilizer (Wang et al., 2009; Gianoni et al., 2012). While the monosaccharide anhydrides are of primary origin, nitroaromatic compounds have both a primary and secondary origin (Iinuma et al., 2010), and have more recently received attention as BB secondary organic aerosol (SOA) markers (Kitanovski et al., 2012a; Kahnt et al., 2013; Chow et al., 2016). They comprise a group of aromatic compounds with abundant ones being 4-nitrophenol, 4-nitrocatechol, and isomeric methyl and dimethyl nitrocatechols, formed by further oxidation of cresols and other aromatics emitted during the fires (Iinuma et al., 2010; Borrás and Tortajada-Genaro, 2012). The concentrations of certain nitroaromatic compounds, i.e., 4-nitrocatechol and methyl nitrocatechols, were shown to correlate with those of levoglucosan in PM₁₀ collected from Ljubljana, Slovenia (Kitanovski et al., 2012b) and from Hamme, Belgium (Kahnt et al., 2013), and in PM_{2.5} collected from Hong Kong (Chow et al., 2016), consistent with their common BB origin. Other important features of nitroaromatic compounds such as 4-nitrocatechol and isomeric methyl nitrocatechols present in BB aerosol are their absorption in the UV/Vis range (Claeys et al., 2012), thereby contributing to the direct effect of aerosols on the solar radiation balance, as well as their possible adverse health effects (Harrison et al., 2005).

Aerosol samples were collected in São Paulo city (SPA) during two intensive winter campaigns (2012 and 2013). In order to characterize contributions due to sugarcane burning to the PM₁₀ mass, measurements were made of organic carbon (OC), elemental carbon (EC), and monosaccharide anhydrides and nitroaromatic compounds. To our knowledge, concentration data about nitroaromatic compounds are not yet available for South American sites. In addition, measurements were also made of biogenic constituents which contribute to the natural background, such as isoprene-related SOA markers and markers for biological particles, namely,

fungus spores, microorganisms, and pollen. The isoprene-related SOA markers comprised 2-methyltetrols [2-methylthreitol (2MT) and 2-methylerythritol (2ME)], 2-methylglyceric acid (2MG), and C₅-alkene triols (Claeys et al., 2004a, 2004b; Wang et al., 2005; Surratt et al., 2006), whereas the monosaccharides, fructose and glucose, are related with microorganism and plant emissions (Caseiro et al., 2007), and the polyols, arabitol and mannitol, are markers for fungal spores (Bauer et al., 2008). Of these, the monosaccharides could also be emitted into the atmosphere upon sugarcane burning (Scaramboni et al., 2015). Furthermore, in order to evaluate whether anhydrosugar ratios (i.e., levoglucosan/mannosan and levoglucosan/galactosan ratios) can provide some information on the type of biofuel, aerosol samples were also collected in Piracicaba, in the vicinity of São Paulo, during the 2014 sugarcane cultivation period, and analyzed for monosaccharide anhydrides, considering that hemicelluloses from sugarcane residue have a relatively high galactose (monosaccharide precursor of galactosan) content (Peng et al., 2009). It is known that the levoglucosan/mannosan ratio can give some indication about the type of biofuel used in BB. Distinctly different ratios have been reported for softwood (range 3.6–6.7) and hardwood (range 13–24) burning (Fine et al., 2004; Schmidl et al., 2008), while rice straw burning results in typical high ratios (range 40–42), due to the relatively low mannose (monosaccharide precursor of mannosan) content in the hemicelluloses (Sheesley et al., 2003; Engling et al., 2009). The anhydrosugar ratios obtained for the samples collected in SPA were compared with those for Piracicaba in the area of sugarcane cultivation and other Brazilian sites in Rondônia which are impacted by forest fires where burning of tropical hardwood takes place in the dry season.

2. Experimental

2.1. Aerosol collection

PM₁₀ filter samples were collected in São Paulo (SPA, 23°33′34″S and 46°44′01″W) during 2012 and 2013 winter periods. The sampling site was located at the top of a building at the University of São Paulo, approximately 2 km away from a major highway with dense vehicular traffic. Another measurement site was in Piracicaba city (PRB, 22°42′20″S and 47°38′27″W), an urban area about 200 km away from SPA, where the principal activities are agricultural (sugarcane, coffee). Biomass burning smoke at this site is often observed and transported to other regions (Vasconcellos et al., 2007; Souza et al., 2014). PM₁₀ samples were collected with a high-volume sampler at a flow rate of 1.13 m³ min⁻¹ for 24 h. The quartz fiber filters were pre-heated at 800 °C for 8 h before sampling. Samplings in SPA were carried out between 8 and 23 August 2012 (n = 16) and between 30 July and 9 August 2013 (n = 11), and in Piracicaba between 29 September and 2 October 2014 (n = 4) at the end of the burning season. After sampling the filters were kept at 5 °C in a refrigerator until analysis. During the 2012 and 2013 sampling periods, about 46,000 km² of sugarcane plantation was burned in São Paulo State (Scaramboni et al., 2015), where 2553 fire hotspots were observed in 2012, and 1329 in 2013 (INPE, 2014).

2.2. PM mass measurement and analysis for carbonaceous components

The PM₁₀ mass concentration was determined by dual weighing of the filters, before and after sampling. The samples and the field blanks were weighed and the PM₁₀ mass data for the samples were corrected for the net masses obtained from the field blanks. One punch (1.5 cm²) of the filter was used for the determination of OC, EC and total carbon (TC) by a thermal-optical method using the

NIOSH temperature protocol (Maenhaut et al., 2012), whereby light transmission (TOT) and reflectance (TOR) were simultaneously monitored. The TOT data were retained for further analysis. The data for the actual samples were corrected for the data obtained for the field blanks. The field blank values were around $0.6 \mu\text{g m}^{-3}$ for OC, $0.7 \mu\text{g m}^{-3}$ for TC, and $0.05 \mu\text{g m}^{-3}$ for EC.

2.3. Analysis for monosaccharide anhydrides and other polar marker compounds

A 2.0 cm^2 filter punch of each sample and field blank were extracted three times with 10 mL of methanol under ultrasonic agitation for 5 min. The combined extracts were concentrated using rotary evaporation to about 1 mL, the resulting solution was filtered through a Teflon syringe filter with a pore diameter of $0.45 \mu\text{m}$ (Grace Davison Discovery Sciences, Deerfield, IL, USA), and the filtrate was dried under a nitrogen flow. The analyses were performed by gas chromatography/mass spectrometry (GC/MS) in the electron ionization mode with prior trimethylsilylation, following the method described in Maenhaut et al. (2016). The internal recovery standard used was methyl-*O*- β -xylanopyranoside (mXP; Sigma-Aldrich, St. Louis, MI, USA). The GC temperature program was as follows: initial temperature of $100 \text{ }^\circ\text{C}$, which was maintained during 2 min, followed by a gradient of $5 \text{ }^\circ\text{C min}^{-1}$ to $180 \text{ }^\circ\text{C}$, then followed by a gradient of $20 \text{ }^\circ\text{C min}^{-1}$ to $310 \text{ }^\circ\text{C}$, after which this last temperature was maintained during 2 min. The total GC/MS analysis time was 26.5 min. For the quantification of the monosaccharide anhydrides, calibration curves of 10 points were made. For levoglucosan, the blank-free detection limit for the analysis of the filters was 0.02 ng m^{-3} .

2.4. Analysis for nitroaromatic compounds

Nitroaromatic compounds were determined with liquid chromatography/mass spectrometry in the negative electrospray ionization mode [LC/(–)ESI-MS], thereby following the method reported in Kahnt et al. (2013) with minor modifications of the LC gradient program. The following nitroaromatic compounds were measured: 4-nitrophenol (4NP), 4-nitrocatechol (4NC), three isomeric methyl nitrocatechols (MNCs) [i.e., 3-methyl-5-nitrocatechol (3M5NC), 3-methyl-4-nitrocatechol (3M4NC), 4-methyl-5-nitrocatechol (4M5NC)] and four dimethyl nitrocatechols (DMNCs) with unknown isomeric composition. 3-nitrophenol (3NP; Sigma-Aldrich) was used as internal recovery standard; authentic standards used for calibration were 4NP (Sigma-Aldrich), 4NC (Sigma-Aldrich), and 4M5NC (Santa Cruz Biotechnology Inc., CA, USA). The latter compound served as surrogate standard for the isomeric MNCs and DMNCs. As to the identification of 3M4NC as the minor isomeric methyl nitrocatechol, it is noted that this compound was previously attributed to 3-methyl-6-nitrocatechol (Kitanovski et al., 2012a) but recently was structurally revised (Frka et al., 2016).

The LC/MS analysis was performed with a Surveyor Plus System (pump and auto-sampler) (Thermo Scientific, San Jose, USA) connected to a linear ion-trap mass spectrometer (LXQ, Thermo Scientific). The chromatographic column employed was a Hypersil Gold column ($2.1 \times 150 \text{ mm}$; $3 \mu\text{m}$) (Thermo Scientific). The mobile phases consisted of a 50 mM ammonium formate buffer pH 3 (A) and acetonitrile (B). The buffer was prepared by dissolving ammonium formate (>99%, MS grade, Sigma-Aldrich) in Milli-Q water and adding formic acid (pro analysis 98–100%, Merck KGaA, Darmstadt, Germany) until the pH value was 3. The following 65 min program was applied during the LC analysis: eluent B was kept at 3% for 5 min, then increased to 95% in 15 min, kept at 95% for 25 min, decreased back to 3% in 10 min, and conditioned at 3% for

10 min for the following analysis. Samples were injected with an injection volume $10 \mu\text{L}$ and the analysis was carried out at a flow rate of 0.2 mL min^{-1} . Additional details about the LC/MS analysis of the targeted nitroaromatic compounds can be found in Kahnt et al. (2013).

3. Results and discussion

3.1. PM_{10} , organic, elemental and total carbon concentrations

The sugarcane cultivation period in the state of São Paulo occurs from May till November. It is coincident with the dry season in southern Brazil and the peak of the burning season is observed with minimum precipitation. The mean and median concentrations and interquartile ranges for the PM_{10} mass, OC, EC and TC in SPA are given in Table 1. The PM_{10} median concentration was more than twice higher in 2013 ($89 \mu\text{g m}^{-3}$) than in 2012 ($39 \mu\text{g m}^{-3}$). One of the possible reasons for this increase is the higher sugarcane burning in 2013, although the production of sugarcane in 2013 (329.923 thousand tons) was less than 10% higher than in 2012 (304.230 thousand tons) (UNICA, 2014). Another reason for the difference in the PM_{10} concentrations could be the vehicle fleet, although this only increased with about 3% in 2013 (7.1 million of vehicles) compared with 2012 (6.9 million of vehicles) (CETESB, 2013). It is worth mentioning that the value recommended by the World Health Organization for daily exposure to PM_{10} ($50 \mu\text{g m}^{-3}$) was exceeded for three samples in 2012 and for nine samples in 2013. In previous work performed for South American cities (Vasconcellos et al., 2011), average PM_{10} concentrations in winter samples were $64 \mu\text{g m}^{-3}$ in SPA, $47 \mu\text{g m}^{-3}$ in Bogotá (Colombia), and $61 \mu\text{g m}^{-3}$ in Buenos Aires (Argentina). During winter the regional meteorology facilitates the formation of a stable atmosphere, temperature inversion, and a low mixed boundary layer, which is unfavorable for the dispersion of pollutants and results in accumulation of pollution species in the boundary layer. Another factor which could partly explain the higher median PM_{10} concentration in 2013 compared to 2012 could be the average temperature ($17.8 \text{ }^\circ\text{C}$ in 2012 versus $16.5 \text{ }^\circ\text{C}$ in 2013), considering that a higher temperature favors the partial evaporation of organic compounds in particulate matter (Schwarz et al., 2008).

The median OC concentration in the PM_{10} samples from SPA was higher in 2013 ($10.4 \mu\text{g m}^{-3}$) than in 2012 ($7.0 \mu\text{g m}^{-3}$), whereas the median EC concentration showed the same trend ($5.1 \mu\text{g m}^{-3}$ in 2013 versus $2.2 \mu\text{g m}^{-3}$ in 2012). OC accounted, on average, for 19% and 13% of the PM_{10} mass in 2012 and 2013, respectively. OC/EC ratios ranged from 1.9 to 4.8 for the 2012 samples and from 1.5 to 4.3 for the 2013 samples. These values may be compared to the average OC/EC ratio of 1.59 ± 0.09 , obtained for sixteen samples collected in a road tunnel in São Paulo (Jânio Quadros Tunnel) (Brito et al., 2013), indicating that OC also has contributions other than from traffic. The median EC concentrations may also be compared with other studies done at Piracicaba, a sugarcane burning site, where the mean EC concentration ($1.7 \mu\text{g m}^{-3}$) was much lower (Souza et al., 2014), suggesting that EC in SPA is mostly impacted by traffic.

3.2. Monosaccharide anhydride concentrations

Table 1 presents the median and mean concentrations of the monosaccharide anhydrides for PM_{10} samples collected in SPA, whereas their time series are displayed in Fig. 1, together with those of OC and of the nitroaromatic markers. Quite high concentrations of levoglucosan were determined with the median concentration estimated at 400 ng m^{-3} in 2013 and at 260 ng m^{-3} in 2012, corresponding to 1.81% and 1.93% of the OC mass, respectively. These

Table 1
Concentration data of the samples collected in SPA for PM₁₀, TC, OC, EC, and organic compounds.

	2012 (n = 16)			2012 Mean % of OC	2013 (n = 11)			2013 Mean % of OC
	Conc., ng m ⁻³ (* μg m ⁻³)				Conc., ng m ⁻³ (* μg m ⁻³)			
	Median	Mean	Range		Median	Mean	Range	
PM ₁₀ *	39	40	28–68		89	94	43–148	
OC*	7.0	7.9	4.6–18.3		10.4	11.3	7.1–18.4	
EC*	2.2	2.5	0.96–5.6		5.1	5.3	2.2–10.2	
TC*	8.9	10.4	5.6–24		15.1	16.6	9.5–29	
L	260	330	129–820	1.81	400	510	250–980	1.93
M	19.0	27	8.6–80	0.137	29.1	40	16.0–89	0.148
G	13.1	17.5	4.9–56	0.092	16.7	21	8.1–40	0.080
Σanhydrosugars	290	380	142–930	2.0	460	570	270–1100	2.2
L/M	14.2	14.0	9.6–18.8		12.8	13.9	10.7–23	
L/G	21	22	9.6–31		24	26	18.2–49	
fructose	27	33	14.2–105	0.174	23	23	13.2–33	0.084
glucose	33	42	16.6–176	0.21	31	32	19.3–44	0.117
2MG	8.6	9.7	4.5–21	0.050	15.8	13.8	6.4–17.9	0.052
2MT	2.0	2.5	1.02–5.3	0.150	1.93	2.3	1.00–4.8	0.105
2ME	4.9	6.1	2.3–12.3	0.037	5.2	5.5	2.2–10.5	0.026
alk1	0.156	0.20	0.081–0.46	0.0013	0.84	0.85	0.30–1.40	0.0044
alk2	0.50	0.64	0.30–1.42	0.0044	1.82	2.0	0.67–3.4	0.0106
alk3	0.37	0.50	0.185–1.11	0.0032	2.1	2.4	0.80–4.2	0.0123
Σisoprene SOA	16.1	19.6	11.7–36	0.111	28	27	16.3–40	0.115
arabitol	9.3	10.0	5.0–19.3	0.061	11.6	10.7	3.7–15.3	0.044
mannitol	11.3	12.5	7.9–22	0.070	14.8	14.4	5.3–21	0.053
4NP	1.57	1.75	0.77–3.8	0.0118	2.1	2.2	0.98–3.2	0.0105
4NC	13.6	16.9	4.8–51	0.094	32	33	15.6–68	0.133
ΣMNC	14.1	16.3	4.4–46	0.102	20	28	10.7–65	0.117
ΣDMNC	8.4	11.5	3.3–45	0.069	14.1	22	7.7–56	0.093
Σnitroaromatics	39	46	14.1–144	0.28	68	85	37–192	0.35

Abbreviations: OC, organic carbon; EC, elemental carbon; TC, total carbon; L, levoglucosan; M, mannosan; G, galactosan; 2MG, 2-methylglyceric acid; 2MT, 2-methylthreitol; 2ME, 2-methylerythritol; alk1, alk2 and alk3, three C₅-alkene triols; SOA, secondary organic aerosol; 4NP, 4-nitrophenol; 4NC, 4-nitrocatechol; ΣMNC, sum of three isomeric methyl nitrocatechols; ΣDMNC, sum of four dimethyl nitrocatechols.*means that the concentration of PM₁₀, OC, EC and TC (that contain *), are in microgram per cubic meter (the other species are in nanogram per cubic meter)

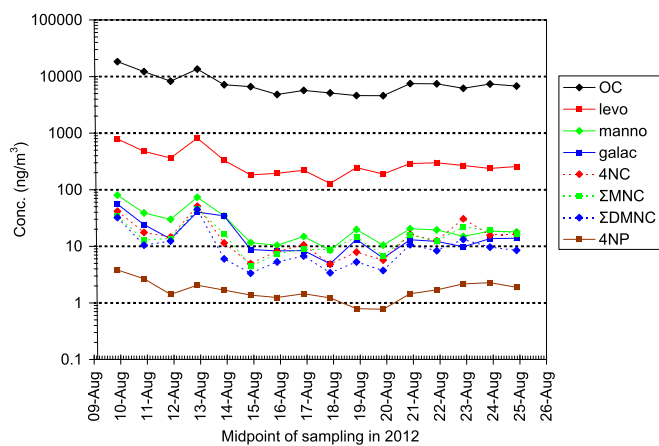


Fig. 1. Time series of OC, monosaccharides and nitroaromatic compounds for the 2012 winter campaign.

results demonstrate that the PM₁₀ was somewhat more impacted by BB in 2013 than in 2012. It can be noted from Table 1 that the concentrations of mannosan and galactosan are much lower than those of levoglucosan. This is as expected because mannosan and galactosan result from the pyrolysis of hemicelluloses, which are lower in mass than cellulose present in sugarcane residue (Dawson and Boopathy, 2007). Levoglucosan exhibited values to over 800 ng m⁻³ in both years. It is also relevant here to examine the levoglucosan/mannosan (L/M) and mannosan/galactosan (M/G) ratios and to evaluate whether they can give some indication about the biofuel. The anhydrosugar ratio data are summarized in Table 2 and compared with literature data from previous Brazilian studies

on sugarcane burning and with data obtained for the dry season in Rondônia, Brazil, where tropical hardwood is burned for land clearing purposes. Also literature data from sites in other countries are included in Table 2. The L/M ratios for SPA were on average 14.0 and 13.9 in 2012 and 2013, while the L/G ratios were on average 22 and 26. The average L/M ratio for Piracicaba was 18.1, while the average L/G ratio was 28. Our L/G and L/M ratios are roughly in line with those obtained in previous Brazilian studies on sugarcane burning. No conclusions can be drawn about the diagnostic value of the L/M ratio to gain information about the biofuel for Brazil, as the average values are close to those obtained for the pasture site in Rondônia (17.3, 19.5, 24, and 14.2), but the average L/G values for SPA and Piracicaba appear to be lower than for Rondônia (64, 44, 52, and 37). This suggests that a L/G ratio smaller than about 30 may be indicative for regional sugarcane burning and not for advected air from sites that are impacted by tropical forest fires. It is noted that low L/G ratios (between 10 and 20) were also obtained for sites in Europe, where wood burning (usually a mixture of softwood and hardwood) is the main source of BB aerosol. It is clear, though, that the L/G ratios for European wood burning are substantially lower than the L/G ratios for Amazonian forest fires.

Levoglucosan median concentrations presented a different profile than previous studies in urban areas, but were substantially lower than in studies performed in Rondônia where deforestation and agricultural burning takes place during the dry season. The levoglucosan concentrations were higher in this study than in samples collected at a site in the Atlantic Forest, 11.0 ng m⁻³ (Vasconcellos et al., 2010), at an urban site Piracicaba, 66 ng m⁻³ (Souza et al., 2014) and at an urban site in Rio de Janeiro State, ranging from 0.15 to 1.65 ng m⁻³ (Dos Santos et al., 2002). They were also higher than in samples collected at a rural site in Rio de Janeiro State, where extensive sugarcane burning occurs in mid-

Table 2
Comparison of anhydrosugar ratios from different Brazilian sites and from selected sites in other countries. Abbreviations: G, galactosan; L, levoglucosan; M, mannosan.

Location (year)	Biomass type burned	Sample type	Mean ratio (range)		Reference
			L/M	L/G	
SPA (2012)	Sugarcane	PM ₁₀	14.0 (9.6–18.8)	22 (14.2–30.6)	this study
SPA (2013)	Sugarcane	PM ₁₀	13.9 (10.7–23)	26 (18.2–49)	this study
Piracicaba (2014)	Sugarcane	PM ₁₀	18.1 (15.3–22)	28 (25–33)	this study
São Paulo State (2010–2012)	Sugarcane	Total	9 ± 5	10.5	Urban et al. (2014)
SPA, winter (2008)	Sugarcane	PM _{2.5}	12.9	17.8	Souza et al. (2014)
Piracicaba, spring (2008)	Sugarcane	PM _{2.5}	33	18.3	Souza et al. (2014)
Rondonia (1999) ^a	Wood	PM ₁₀	17.3	64	Zdráhal et al. (2002)
Rondonia, forest (1999) ^a	Wood	PM _{2.5}	19.5	44	Graham et al. (2002)
Rondonia, forest (1999) ^a	Wood	PM _{2.5}	24	52	Graham et al. (2002)
Rondonia, pasture (2002) ^a	Wood	PM _{2.5}	14.2	37	Claeys et al. (2010)
Czech Republic, winter (2009)	Wood	PM _{2.5}	5.0	10.5	Křůmal et al. (2010)
Flanders, Belgium (2010–2011)	Wood	PM ₁₀	6.6	16.7	Maenhaut et al. (2012)
Northern Italy (2011–2014)	Wood	PM _{2.5}	6.6	13.4	Pietrogrande et al. (2015)
Selangor, Malaysia (2011–2012)	Peatland	PM _{2.5}	18.2	72	Fujii et al. (2015)
Taiwan, winter (2006)	Rice	PM ₁₀	14.5	20	Engling et al. (2013)
Taiwan, summer (2007)	Rice	PM ₁₀	113	104	Engling et al. (2013)
Brisbane, Australia, day (2011) ^b	Various	PM ₁₀	28	53	He et al. (2016)
Brisbane, Australia, night (2011) ^b	Various	PM ₁₀	34	75	He et al. (2016)

^a Dry season.

^b Burning season.

winter, ranging from 0.19 to 28 ng m⁻³ (Dos Santos et al., 2002). Similar levoglucosan concentrations as our data for SPA were obtained for total aerosol from a rural area near Ourinhos, São Paulo State, where the data ranged from 25 to 1190 ng m⁻³ (Urban et al., 2012), whereas over a 21-month period in an agro-industrial region in São Paulo State, an average levoglucosan concentration of 116 ng m⁻³ was obtained (Urban et al., 2014). The levoglucosan concentrations for SPA in this study were higher than those found for Piracicaba at the end of the 2014 sugarcane harvest where precipitation likely had removed pollutants from the atmosphere; the levoglucosan levels at Piracicaba ranged from 47 ng m⁻³ to 130 ng m⁻³. Samples collected from Rondônia, at a tropical pasture site during two different campaigns, exhibited levoglucosan concentrations from 1180 to 7000 ng m⁻³ [1999 dry season; median, 2050 ng m⁻³ (Graham et al., 2002)] and from 126 to 7500 ng m⁻³ [2002 dry season; median, 1380 ng m⁻³ (Claeys et al., 2010)].

3.3. Nitroaromatic compound concentrations

Table 1 presents the median and mean concentrations of the nitroaromatic compounds for PM₁₀ samples collected in SPA,

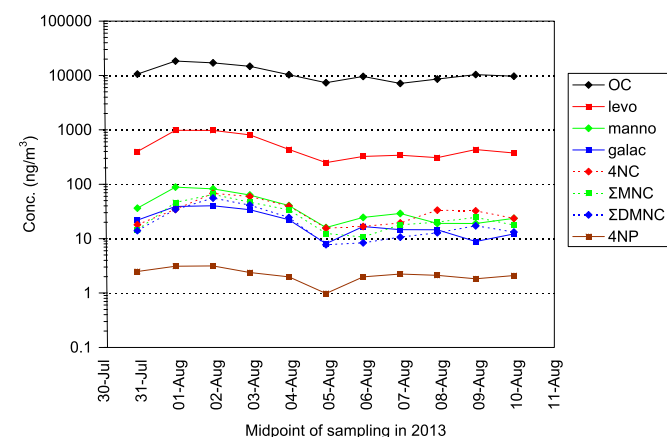


Fig. 2. Time series of OC, monosaccharides and nitroaromatic compounds for the 2013 winter campaign.

whereas their time series are displayed in Figs. 1 and 2, together with those of OC and the anhydrosugars. Relatively high concentrations of 4NC and the sum of MNCs were determined with median concentrations estimated at 13.6 ng m⁻³ and 14.1 ng m⁻³ in 2012 and at 32 ng m⁻³ and 20 ng m⁻³ in 2013. All together the nitroaromatic compounds contributed to 0.28% and 0.35% of the OC mass. These results support that the PM₁₀ was more impacted by BB in 2013 than in 2012.

It is only possible to compare the nitroaromatic compound concentration data determined for SPA samples with a few studies performed at European sites that are impacted by domestic wood burning during winter. Samples collected from a rural village in Germany in the autumn-winter of 2007–2008 showed an average concentration of 5.2 ng m⁻³ for the sum of the MNCs, which is lower than the average values of 16.3 ng m⁻³ and 28 ng m⁻³ found for the 2012 and 2013 samples from SPA (Linuma et al., 2010). PM₁₀ samples collected from an urban background location during a 2011 winter episode in Ljubljana, Slovenia, exhibited mean concentrations for 4NC and the sum of the MNCs of 76 ng m⁻³ and 70 ng m⁻³, representing 0.39% and 0.36% of the OC mass (Kitanovski et al., 2012b). PM₁₀ samples collected from Hamme, a rural site in Belgium, during 2010–2011 winter, showed mean concentrations for 4NC and the sum of the MNCs of 14.2 ng m⁻³ and 19.5 ng m⁻³, representing 0.22% and 0.30% of the OC mass (Kahnt et al., 2013). The percentage contributions obtained for the winter samples from Belgium and Slovenia are higher than the values of 0.094 and 0.102% and of 0.133 and 0.117% found for the 2012 and 2013 SPA samples in the present study, suggesting that sugarcane burning results in a relatively lower SOA formation from emitted aromatic compounds.

3.4. Isoprene SOA marker, polyol, and monosaccharide concentrations

Table 1 presents the median and mean concentrations of the selected isoprene SOA marker compounds, polyols, and monosaccharide compounds. All together the isoprene SOA marker compounds contributed to 0.11% and 0.12% of the OC in 2012 and 2013, which is lower than the percentages obtained for the anhydrosugars (i.e., 2.0% and 2.2%). It is worth noting that the median

concentration of 2MG is higher (8.6 ng m^{-3} and 15.8 ng m^{-3} in 2012 and 2013) than the medians obtained for the other major isoprene SOA markers, i.e., 2MT (2.0 ng m^{-3} and 1.93 ng m^{-3}) and 2ME (4.9 ng m^{-3} and 5.2 ng m^{-3}). This could be explained by the fact that 2MG is preferentially formed under polluted conditions in the presence of NO_x , while 2MT and 2ME are formed under clean (low- NO_x) conditions (Surratt et al., 2006). Also, the C_5 -alkene triols showed very low concentrations, as could be expected since they are preferentially formed under clean (low- NO_x) conditions (Surratt et al., 2006). The values obtained for the 2-methyltetrols 2MT and 2ME can be compared with values obtained for Rondônia at a pasture site during a 2002 winter episode, where the median concentrations of 2MT and 2ME were estimated at 51 ng m^{-3} and 145 ng m^{-3} (Claeys et al., 2010). One of the possible reasons for the higher values in Rondônia are the higher isoprene emissions from tropical rainforest vegetation.

The monosaccharides fructose and glucose showed median concentrations of 27 ng m^{-3} and 33 ng m^{-3} in 2012 and of 23 ng m^{-3} and 31 ng m^{-3} in 2013, representing 0.17% and 0.21% of the OC in 2012 and 0.084% and 0.12% of the OC in 2013. A straightforward explanation for the higher contributions in 2012 could not be found. The polyols arabitol and mannitol exhibited median concentrations of 9.3 ng m^{-3} and 11.3 ng m^{-3} in 2012 and of 11.6 ng m^{-3} and 14.8 ng m^{-3} in 2013, corresponding to 0.061% and 0.070% of the OC in 2012 and to 0.044% and 0.053% in 2013. The arabitol and mannitol concentrations may be compared with those reported in a previous study for PM_{10} samples from two sites in Vienna, Austria, where the concentrations were estimated at 22 ng m^{-3} and 34 ng m^{-3} in 2004 for an urban fringe site and at 28 ng m^{-3} and 42 ng m^{-3} in 2005 for an urban traffic site (Bauer et al., 2008).

3.5. Time series and correlation analysis

It can be seen from Figs. 1 and 2 that the time series of OC, the anhydrosugars and the nitroaromatic compounds closely follow each other. The correlation coefficients between all these variables were mostly between 0.7 and 1.0 in both campaigns; only a few of the correlations among the nitroaromatic compounds were somewhat lower, but still around 0.6. Figs. 3 and 4 show the time series for the monosaccharides glucose and fructose, the polyols mannitol and arabitol, and the isoprene SOA markers. Glucose and fructose, which are both related with microorganism and plant emissions, closely follow each other and were very highly correlated ($r > 0.9$) with each other in both years. Similar very high correlations (all $r > 0.9$) were observed between the polyols

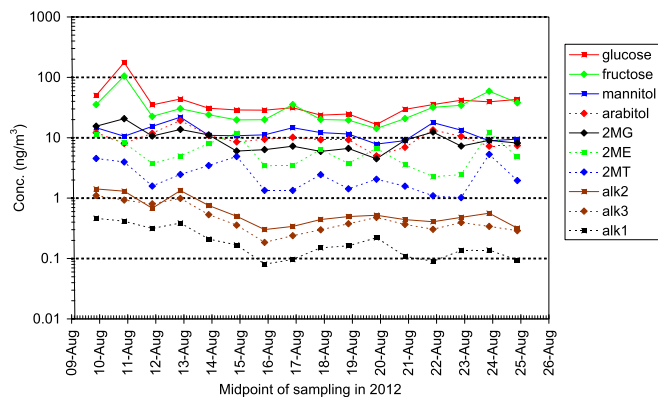


Fig. 3. Time series of the monosaccharides glucose and fructose, the polyols mannitol and arabitol, and the isoprene SOA markers for the 2012 winter campaign.

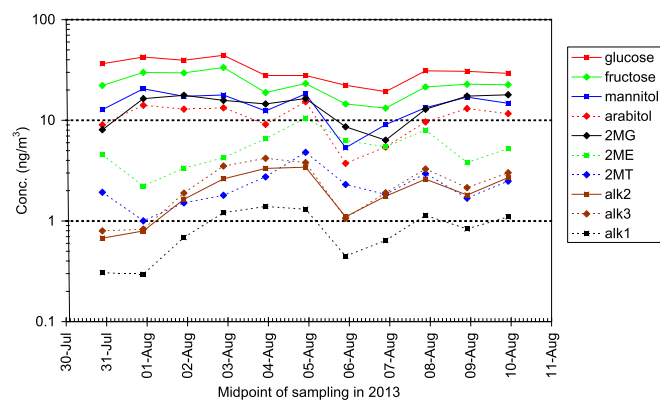


Fig. 4. Time series of the monosaccharides glucose and fructose, the polyols mannitol and arabitol, and the isoprene SOA markers for the 2013 winter campaign.

mannitol and arabitol, as could be expected because of their common origin (fungal spores), between 2MT and 2ME, and among the three alkenetriols (alk2, alk3, and alk1). The correlations between 2MG and the other compounds were less consistent; in 2012, 2MG was highly correlated (all $r > 0.7$) with the two monosaccharides and the three alkenetriols, but in 2013, those correlations were only in the range 0.4–0.7.

4. Conclusions

It is shown in this study that winter PM_{10} aerosol from São Paulo city is severely impacted by regional sugarcane burning, as is evidenced by the high concentrations of anhydrosugars and nitroaromatic compounds. The PM_{10} , OC and EC concentrations were higher in 2013 than in 2012, and could be partly explained by more extensive sugarcane burning and a larger vehicle fleet in 2013 compared to 2012 in the state of São Paulo. The PM_{10} concentrations were below Brazilian legislation but much higher than those recommended by the World Health Organization. Levoglucosan, the major anhydrosugar and a primary marker for biomass burning formed by pyrolysis of cellulose and hemicelluloses, showed median concentrations of 260 ng m^{-3} and 400 ng m^{-3} in 2012 and 2013, which is much higher than the values reported for other Brazilian urban sites in previous studies. Examination of anhydrosugar ratios revealed that a levoglucosan/galactosan ratio lower than about 30 may be characteristic of sugarcane burning. The major nitroaromatic marker compounds, 4-nitrocatechol and the isomeric methyl nitrocatechols, secondary products formed by oxidation of cresols emitted during biomass burning, presented substantial concentrations (medians of 13.6 ng m^{-3} and 14.1 ng m^{-3} in 2012 and of 32 ng m^{-3} and 20 ng m^{-3} in 2013), which correlated well with those of levoglucosan, consistent with their biomass burning origin. Furthermore, other measured organic compounds including isoprene SOA markers, monosaccharides (fructose and glucose) and polyols (arabitol and mannitol) showed substantial concentrations, contributing to the OC mass with 0.63% in 2012 and with 0.42% in 2013. As to the isoprene SOA marker compounds, the concentrations of 2-methylglyceric acid were higher than those of the 2-methyltetrols, consistent with its formation under polluted urban conditions.

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