

Polar organic marker compounds in atmospheric aerosols during the LBA-SMOCC 2002 biomass burning experiment in Rondônia, Brazil: sources and source processes, time series, diel variations and size distributions

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Abstract. Measurements of polar organic marker compounds were performed on aerosols that were collected at a pasture site in the Amazon basin (Rondônia, Brazil) using a high-volume dichotomous sampler (HVDS) and a Micro-Orifice Uniform Deposit Impactor (MOUDI) within the framework of the 2002 LBA-SMOCC (Large-Scale Biosphere Atmosphere Experiment in Amazônia – Smoke Aerosols, Clouds, Rainfall, and Climate: Aerosols From Biomass Burning Perturb Global and Regional Climate) campaign. The campaign spanned the late dry season (biomass burning), a transition period, and the onset of the wet season (clean conditions). In the present study a more detailed discussion is presented compared to previous reports on the behavior of selected polar marker compounds, including levoglucosan, malic acid, isoprene secondary organic aerosol (SOA) tracers and tracers for fungal spores. The tracer data are discussed taking into account new insights that recently became available into their stability and/or aerosol formation processes. During all three periods, levoglucosan was the most dominant identified organic species in the

PM_{2.5} size fraction of the HVDS samples. In the dry period levoglucosan reached concentrations of up to 7.5 $\mu\text{g m}^{-3}$ and exhibited diel variations with a nighttime prevalence. It was closely associated with the PM mass in the size-segregated samples and was mainly present in the fine mode, except during the wet period where it peaked in the coarse mode. Isoprene SOA tracers showed an average concentration of 250 ng m^{-3} during the dry period versus 157 ng m^{-3} during the transition period and 52 ng m^{-3} during the wet period. Malic acid and the 2-methyltetrols exhibited a different size distribution pattern, which is consistent with different aerosol formation processes (i.e., gas-to-particle partitioning in the case of malic acid and heterogeneous formation from gas-phase precursors in the case of the 2-methyltetrols). The 2-methyltetrols were mainly associated with the fine mode during all periods, while malic acid was prevalent in the fine mode only during the dry and transition periods, and dominant in the coarse mode during the wet period. The sum of the fungal spore tracers arabinol, mannitol, and erythritol in the PM_{2.5} fraction of the HVDS samples during the dry, transition, and wet periods was, on average, 54 ng m^{-3} , 34 ng m^{-3} , and 27 ng m^{-3} , respectively, and revealed minor day/night variation. The mass size distributions of arabinol and mannitol during all periods showed similar patterns and



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an association with the coarse mode, consistent with their primary origin. The results show that even under the heavy smoke conditions of the dry period a natural background with contributions from bioaerosols and isoprene SOA can be revealed. The enhancement in isoprene SOA in the dry season is mainly attributed to an increased acidity of the aerosols, increased NO_x concentrations and a decreased wet deposition.

1 Introduction

The Amazon basin is a region where widespread biomass burning takes place during the dry season which significantly alters the chemical properties of the tropical pristine background atmosphere. The carbonaceous aerosol over the Amazon basin has been intensively studied during recent years since it contains a large fraction of water-soluble organic carbon (WSOC). The latter fraction is of climatic relevance since it enhances the ability of the aerosol to act as cloud condensation nuclei (e.g., Novakov and Penner, 1993; Novakov and Corrigan, 1996; Mochida and Kawamura, 2004) and may as such affect cloud processes (e.g., Shulman et al., 1996; Facchini et al., 1999; Roberts et al., 2002; Mircea et al., 2005). As to chemical composition studies of the Amazonian carbonaceous aerosol, emphasis has been formerly placed on the measurement and/or characterization of individual compounds that are hygroscopic and/or can serve as tracers for aerosol sources and/or processes, i.e., anhydrosugars, sugars, 2-methyltetrols, polyols, hydroxyacids, dicarboxylic acids, and phenolic acids (Kubátová et al., 2000; Zdráhal et al., 2002; Graham et al., 2002, 2003; Claeys et al., 2004; Falkovich et al., 2005; Schkolnik et al., 2005), as well as of humic-like substances (HULIS) that represent a large fraction of the WSOC (Mayol-Bracero et al., 2002).

The major anhydrosugar detected in the aerosol samples is levoglucosan (1,6-anhydro- β -D-glucopyranose), which is formed through pyrolysis of cellulose, the main building material of wood, at temperatures higher than 300 °C (Shafizadeh, 1982). It is accompanied by minor stereoisomers, including 1,6-anhydro- β -D-glucofuranose, mannosan (1,6-anhydro- β -D-mannopyranose), and galactosan (1,6-anhydro- β -D-galactopyranose), all resulting from the pyrolysis of hemicelluloses present in wood. Levoglucosan is a well-established tracer for pyrolysis of cellulose in biomass smoke (Simoneit et al., 1999; Nolte et al., 2001; Simoneit, 2002) and has been extensively used to monitor biomass smoke in the Amazon basin (Zdráhal et al., 2002; Graham et al., 2002, 2003; Schkolnik et al., 2005) and in other tropical and subtropical areas where biomass burning takes place such as, for example, southern Africa (Gao et al., 2003). Levoglucosan has for a long time thought to be fairly inert; however, recent laboratory studies show that it decays upon a

time scale relevant to particle lifetimes by heterogeneous OH radical-initiated oxidation (Hoffmann et al., 2010; Hennigan et al., 2010). Sugars present in atmospheric aerosol comprise the monosaccharides, glucose and fructose, and the disaccharides, sucrose and trehalose. Glucose, fructose, and sucrose originate from plant material such as pollen, fruits, and their fragments (Bartolozzi et al., 1997; Baker et al., 1998; Pacini, 2000; Yttri et al., 2007), but in addition glucose may also result from cellulose pyrolysis (Shafizadeh, 1982), while trehalose is due to fungal spores (Lewis and Smith, 1967; Bielecki, 1982). The sugar alcohols, arabitol, mannitol, and erythritol, which are denoted by polyols, are marker compounds for fungal spores (Lewis and Smith, 1967; Bielecki, 1982).

The 2-methyltetrols (2-methylthreitol and 2-methylerythritol) and the C₅-alkene triols [2-methyl-1,3,4-trihydroxy-1-butene (*cis* and *trans*) and 3-methyl-2,3,4-trihydroxy-1-butene] have first been identified in Amazonian aerosols (Claeys et al., 2004; Wang et al., 2005) and were, based on their C₅-isoprene skeleton, proposed to be photooxidation products of isoprene. In subsequent laboratory (smog chamber) experiments it was confirmed that the 2-methyltetrols are formed through photooxidation of isoprene under varying NO_x regimes (Edney et al., 2005; Böge et al., 2006; Surratt et al., 2006, 2010; Sato, 2008), while the C₅-alkene triols could only be detected in the absence of NO_x (Surratt et al., 2006, 2010; Kleindienst et al., 2009). Dicarboxylic acids and hydroxycarboxylic acids comprise a very large group of compounds; a major hydroxycarboxylic acid is malic acid, which can be regarded as intermediate in the oxidation of C_n ($n \leq 6$) semivolatile carboxylic acids (which are also oxidation products of unsaturated fatty acids) and is believed to be formed through further photooxidation of succinic acid (Kawamura and Gagosian, 1990; Kawamura and Ikushima, 1993). Dicarboxylic acids are known to have many sources, both anthropogenic and biogenic ones (Rogge et al., 1993; Limbeck and Puxbaum, 1999). A recent study examined the molecular profiles of dicarboxylic acids (C₂-C₁₁) and related compounds (ketocarboxylic acids and dicarbonyls) in PM_{2.5} samples from the intensive biomass burning period of the LBA-SMOCC 2002 campaign and found higher ratios of the latter compounds to biomass burning tracers (i.e., levoglucosan, K⁺) during daytime, suggesting the importance of photochemical production (Kundu et al., 2010).

In the present study, we focus on major polar organic marker compounds and discuss their time series, diel variations, mass size distributions, and aerosol formation processes. The major polar organic marker compounds include: (a) levoglucosan, (b) malic acid, (c) photooxidation products of isoprene, i.e., 2-methyltetrols and C₅-alkene triols, and (d) polyols (arabitol, mannitol, and erythritol). The latter compounds were selected for two reasons: (a) they correspond to major single compounds that can be detected in the fine (PM_{2.5}) size fraction of high-volume dichotomous samples

by gas chromatography/mass spectrometry (GC/MS) with prior trimethylsilylation in the full scan mode, and (b) they provide important information on aerosol sources and source processes. Part of the presented data have been reported by Decesari et al. (2006) on the overall composition of the carbonaceous aerosol in Rondônia during the LBA-SMOCC campaign and its representation through model compounds, and by Fuzzi et al. (2007) on the inorganic and organic composition of the corresponding size-segregated aerosol; these earlier presented data are included here to allow a more detailed and coherent discussion on time series, diel variations, and size distributions of major polar organic marker compounds.

2 Experimental

2.1 Site description

Ground-based measurements were performed as part of the LBA-SMOCC campaign from 9 September till 14 November 2002 (66 days) at a pasture site (Fazenda Nossa Senhora Aparecida, 10°04'44" S, 62°21'27" W, 315 m a.s.l.). This site is located within Rondônia, Brazil, a region where extensive deforestation took place in recent years. The campaign covered a dry period (9 September–8 October), corresponding to the end of the dry season (biomass burning season), a transition period (8–30 October), and a wet period (30 October–14 November), corresponding to the beginning of the wet season. For a more detailed description of the sampling site, see Andreae et al. (2002). For an overview of the meteorological conditions, including temperature, during the campaign, see Fuzzi et al. (2007). The temperature showed little variability during the period considered, with monthly mean values around 25.0 °C, although there was a variation in the daily maximum temperature span: 10.7 °C in September, 9.4 °C in October and 8.0 °C in November. During the dry season, and, to a lesser extent, the transition period, widespread fire activity was observed in Rondônia and Mato Grosso, as well as in other states along the southern and south eastern margin of the Amazon forest. Conversely, biomass burning was substantially reduced at the beginning of November after the onset of persistent wet conditions (Andreae et al., 2004).

2.2 Aerosol sampling

A high-volume dichotomous virtual sampler (HVDS), located 2 m above ground level, was used to collect samples in two size fractions, a fine [$<2.5 \mu\text{m}$ aerodynamic diameter (AD)] and a coarse [$>2.5 \mu\text{m}$ AD] fraction (Solomon et al., 1983). Double Pallflex quartz fiber filters (of 102 mm diameter), which had been pre-fired at 550 °C to remove organic contaminants, were used to collect each of the two size fractions. For collection of size-fractionated aerosol samples, a ten-stage Micro-Orifice Uniform Deposit Impactor (MOUDI), with 50% aerodynamic cutoff diameters for the

pre-impaction stage (stage 0) and 10 regular stages of 18, 9.9, 6.2, 3.1, 1.8, 1.0, 0.603, 0.301, 0.164, 0.094, and 0.053 μm , was employed. Aluminum foils of 37 mm diameter (pre-fired at 550 °C) were used as collection substrates in the MOUDI. Separate day- and nighttime samples were collected during most days of the dry period and part of the transition period. During the rest of the transition period, the collection time was 24 h, whereas during the wet period, day- and nighttime samples were collected for 48 h. A total of 80 HVDS samples and 80 MOUDI sample sets were collected.

PM₂ mass data were derived from the fine ($<2 \mu\text{m}$ AD) size fraction of a Gent PM₁₀ stacked filter unit (SFU) sampler that was operated in parallel. A Pall Teflo filter was used as fine filter in the SFU sampler.

2.3 Aerosol analysis

PM mass data were obtained by weighing the SFU filters and the MOUDI aluminum foils before and after sampling with a microbalance of 1 μg sensitivity. The weighings were done at 20 °C and 50% relative humidity (RH) and the filters were equilibrated at these conditions for 24 h prior to weighing. All filters of the HVDS samples were analyzed for organic carbon (OC) and elemental carbon (EC) by a thermal-optical (TOT) technique (Birch and Cary, 1996) and the fine size fraction filters also for WSOC as described by Viana et al. (2006).

Selected polar organic marker compounds in the front fine filters of all HVDS quartz fiber filter samples and in the aluminum foils of selected MOUDI samples were quantified using GC/MS techniques that incorporated a derivatization step in order to convert carboxylic and hydroxyl groups to trimethylsilylated ester and ether derivatives, respectively. The method was targeted to the quantitation of sugar-like compounds, including anhydrosugars (levoglucosan, mannosan, galactosan, and 1,6-anhydro- β -D-glucofuranose), 2-methyltetrols (2-methylthreitol and 2-methylerythritol), monosaccharides (fructose and glucose), and polyols (erythritol, arabinol, and mannitol). The analytical procedure was adapted from a method previously described and validated for the determination of levoglucosan in urban aerosols (Pashynska et al., 2002). In addition to the above mentioned sugar-like compounds, malic acid was also measured with the same method; however, more accurate data for malic acid were obtained with a method targeted to the analysis of polar hydroxycarboxylic acids, as has been reported in a previous study (Decesari et al., 2006). The malic acid data used in the present study for the fine HVDS samples were, therefore, obtained with the latter method (method 2 of the cited study). In addition, succinic acid data obtained with the latter method were also used for the detailed interpretation of the malic acid data.

A part of the front quartz filter sample (1/16 or 1/32) or of the aluminum foil (1/2 or 1/4) was used for extraction. Before extraction, the recovery standards,

methyl- β -L-xylanopyranoside and deuterated (D_3) malic acid (2,2,3- D_3 -malic acid; Cambridge Isotope Laboratories, Andover, MA, USA) were added. Briefly, the sample work-up procedure consisted of extraction with 3 times 20 mL dichloromethane:methanol (4:1, *v/v*) and derivatization of the residues into trimethylsilylether derivatives with 50 μ L of a 3:5 (*v/v*) mixture of pyridine and *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) containing 1% trimethylchlorosilane (TMCS) (Pierce, Rockford, IL, USA). GC/MS analysis was performed with a TRACE GC2000 gas chromatograph and a Polaris Q ion trap mass spectrometer equipped with a CP Sil 8CB low-bleed capillary column (95% dimethyl-, 5% phenylpolysiloxane, 0.25 μ m film thickness, 30 m \times 0.25 mm i.d.; Chrompack, Middelburg, The Netherlands), which was preceded by a deactivated silica precolumn (2 m \times 0.25 mm i.d.). The following temperature program was applied: the initial temperature was 50 $^{\circ}$ C and kept for 5 min, the temperature was then increased to 200 $^{\circ}$ C at the rate of 3 $^{\circ}$ C min $^{-1}$ and kept at that temperature for a further 2 min and then raised to 310 $^{\circ}$ C at the rate of 30 $^{\circ}$ C min $^{-1}$; the total analysis time was 62 min. For the analysis of the HVDS samples, the GC/MS instrument was operated in the electron ionization and the full scan modes (mass range *m/z* 45–500), and quantification was based on mass chromatographic data (i.e., extracted ion chromatograms), while for the analysis of the MOUDI samples, the instrument was operated in the selected ion monitoring mode (instead of the full scan mode) with an ion dwell time of 25 ms. The selected ions were at *m/z* 204 and 217 for the internal recovery standard (IS), methyl- β -D-xylanopyranoside, and for levoglucosan, *m/z* 219 and 277 for the 2-methyltetrols (2-methylthreitol and 2-methylerythritol), *m/z* 233 and 307 for malic acid, *m/z* 236 and 310 for deuterated (D_3) malic acid, *m/z* 217 and 319 for arabitol and mannitol, and *m/z* 231 for the alkene triol derivatives of isoprene (2-methyl-1,3,4-trihydroxy-1-butene (*cis* and *trans*) and 3-methyl-2,3,4-trihydroxy-1-butene). For derivatization of standard solutions of all saccharidic compounds, the same procedure as that used for the aerosol extracts was applied. The quantification of the monosaccharide anhydrides (levoglucosan, mannosan, and galactosan), the polyols (arabitol, mannitol, and erythritol), the monosaccharides (fructose and glucose), and the 2-methyltetrols was based on an internal standard calibration procedure employing methyl- β -L-xylanopyranoside as internal recovery standard and pure reference compounds, if available. For assessing the amounts of the 2-methyltetrols and C_5 -alkene triols, for which no pure reference compounds were available, the response factor of erythritol was used, while for assessing the amount of malic acid, the response factor of deuterated (D_3) malic acid was used. Duplicate analyses showed that the precision of the determinations was about 10%. All reported concentrations were corrected for procedural blanks.

3 Results and discussion

3.1 GC/MS chromatograms

Figure 1 presents a typical total ion chromatogram (TIC) obtained for a trimethylsilylated extract of a fine daytime HVDS filter sample collected during the transition period (26–27 October). The chromatogram is dominated by levoglucosan and smaller peaks are clearly observed for malic acid, the 2-methyltetrols, the C_5 -alkene triols, and anhydrosugars that are isomeric to levoglucosan (mannosan and 1,6-anhydro- β -D-glucofuranose). It is worth noting that the latter compounds can be detected in the TIC so that more selective detection, i.e., mass chromatographic or selected ion monitoring detection, was not necessary. However, in the present study, mass chromatography using specific ions was utilized to obtain more clear chromatographic peaks for less abundant compounds, i.e., polyols (arabitol, mannitol, and erythritol), and, in most cases, C_5 -alkene triols (2-methyl-1,3,4-trihydroxy-1-butene (*cis* and *trans*) and 3-methyl-2,3,4-trihydroxy-1-butene), while selected ion monitoring was performed for the analysis of aluminum foils collected with the MOUDI, where the amounts found on the different stages are much lower than on the HVDS filter samples.

3.2 Time series, diurnal variations and size distributions

3.2.1 PM, OC, EC, and levoglucosan

Table 1 summarizes median and mean concentrations and concentration ranges for OC, EC, WSOC, and the selected organic species in the fine size fraction of the HVDS filter samples for the dry, transition, and wet periods of the LBA-SMOCC 2002 campaign. In addition, Table 1 presents mean percentages of the fine OC that is attributable to the carbon in the organic compounds. Figure 2 shows the time series for fine PM (PM $_2$), and OC, EC, and levoglucosan for the fine size fraction of the HVDS samples. It can be seen that all four parameters show substantial variation throughout the campaign and are fairly well correlated with each other. The correlations between the PM (PM $_2$) and OC, EC, and levoglucosan for the dry period were 0.83, 0.84, and 0.75, respectively. During the dry period, which is characterized by intense deforestation fires, high PM $_{2.5}$ levels of levoglucosan are measured (mean value 2.1 μ g m $^{-3}$), while during the transition and wet periods, the mean levels decrease to 0.40 μ g m $^{-3}$ and 0.06 μ g m $^{-3}$, respectively. It can also be seen in Fig. 2 that diel differences are observed for the fine PM (PM $_2$), OC, EC, and levoglucosan during the dry period when separate day- and nighttime sampling was carried out and that the highest concentrations are found at night. The higher nighttime concentrations can be partly explained by trapping of the pyrogenic aerosol under the shallow nocturnal

Table 1. Median and mean concentrations and concentration ranges for OC, EC, WSOC, and selected organic species (and mean percentages of the OC attributable to the carbon in the organic compounds) in the front filters of the fine size fraction of the HVDS filter samples for the dry, transition, and wet periods of the LBA-SMOCC 2002 campaign.

Species	Dry period ($N = 53$)				Transition period ($N = 20$)				Wet period ($N = 7$)			
	Conc., ng m^{-3} (* $\mu\text{g m}^{-3}$)			Mean % OC	Conc., ng m^{-3} (* $\mu\text{g m}^{-3}$)			Mean % OC	Conc., ng m^{-3} (* $\mu\text{g m}^{-3}$)			Mean % OC
	Median	Mean	Range		Median	Mean	Range		Median	Mean	Range	
OC*	27	32	4.1–79	n/a	8.4	9.1	3.9–15.7	n/a	1.80	1.60	0.93–2.3	n/a
EC*	0.98	1.11	0.30–2.4	n/a	0.42	0.42	0.18–0.66	n/a	0.07	0.09	0.04–0.18	n/a
WSOC*	17.5	21	2.6–53	66	6.0	6.6	2.5–10.5	73	0.98	1.04	0.65–1.92	64
levoglucosan	1380	2100	126–7500	2.63	350	400	106–1860	1.91	26	58	15.7–150	1.46
mannosan	88	148	10.1–540	0.18	27	31	7.3–70	0.15	2.8	4.1	1.9–7.4	0.11
galactosan	26	57	4.3–260	0.07	10.1	11.4	2.8–32	0.05	0.9	1.1	<0.5–2.4	0.03
arabitol	14.7	16.8	<2.0–41	0.03	9.8	9.8	4.5–22	0.05	8.2	8.7	5.3–11.8	0.27
mannitol	19.4	23	3.9–52	0.05	8.3	20	9.5–47	0.10	19.2	17.7	11.1–20	0.50
erythritol	12.8	14.4	2.3–37	0.02	4.1	4.4	1.6–8.0	0.02	1.1	1.0	0.7–1.3	0.03
glucose	47	52	15.1–130	0.09	34	34	16.6–53	0.17	27	27	16.3–37	0.74
fructose	13.9	15.2	<2.0–44	0.03	8.5	8.0	2.5–13.2	0.04	4.8	5.1	1.2–12.5	0.14
2-methylthreitol	51	52	4.8–98	0.09	19.0	26	7.6–89	0.13	8.2	9.1	3.0–20	0.26
2-methylerythritol	145	143	13.7–320	0.25	68	94	22–310	0.48	29	34	13.3–66	1.00
C ₅ -alkene triols	42	54	5.3–164	0.11	29	37	9.9–93	0.22	6.3	8.7	4.3–16.0	0.29
malic acid	390	400	138–860	0.57	260	270	163–410	1.15	74	76	37–110	1.69
succinic acid	500	640	53–2200	0.83	270	280	100–610	1.23	26	28	8.5–48	0.69

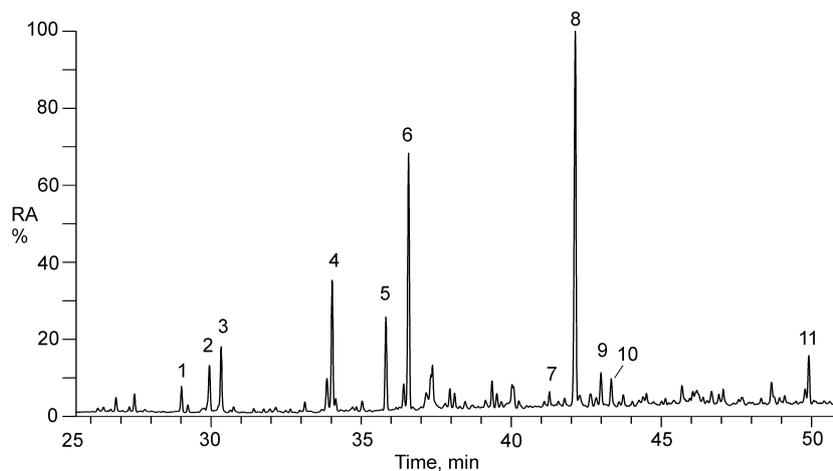


Fig. 1. GC/MS total ion chromatogram (TIC) obtained for a fine daytime HVDS filter sample collected during the transition period (26–27 October). (1) *cis*-2-methyl-1,3,4-trihydroxy-1-butene; (2) 3-methyl-2,3,4-trihydroxy-1-butene; (3) *trans*-2-methyl-1,3,4-trihydroxy-1-butene; (4) malic acid; (5) 2-methylerythritol; (6) 2-methylthreitol; (7) mannosan; (8) levoglucosan; (9) 1,6-anhydro- β -D-glucofuranose; (10) arabitol; and (11) mannitol.

boundary layer. This concentration effect is due to evolution of the boundary layer, which is much thinner at night, as a result of decreased vertical mixing and dilution (Fish et al., 2004; Rissler et al., 2006). An additional explanation for the higher nighttime concentrations of levoglucosan is photochemical degradation during daytime. In this respect, it has recently been shown that levoglucosan decays upon a time-scale relevant to particle lifetimes by heterogeneous OH radical-initiated oxidation (Hoffmann et al., 2010; Hennigan et al., 2010).

Figure 3 shows levoglucosan carbon as a percentage of the OC. It is clear that levoglucosan contributes more to the OC during the night, on average $3.1 \pm 0.9\%$ at night versus $1.8 \pm 0.7\%$ during the daytime. This diel variation can be explained by a different combustion stage with flaming combustion taking place during daytime when fires are started and smoldering combustion resulting in a less complete oxidation of biomass dominating at night, as has been discussed in more detail by Schkolnik et al. (2005). Our results can also be compared with those of Gao et al. (2003)

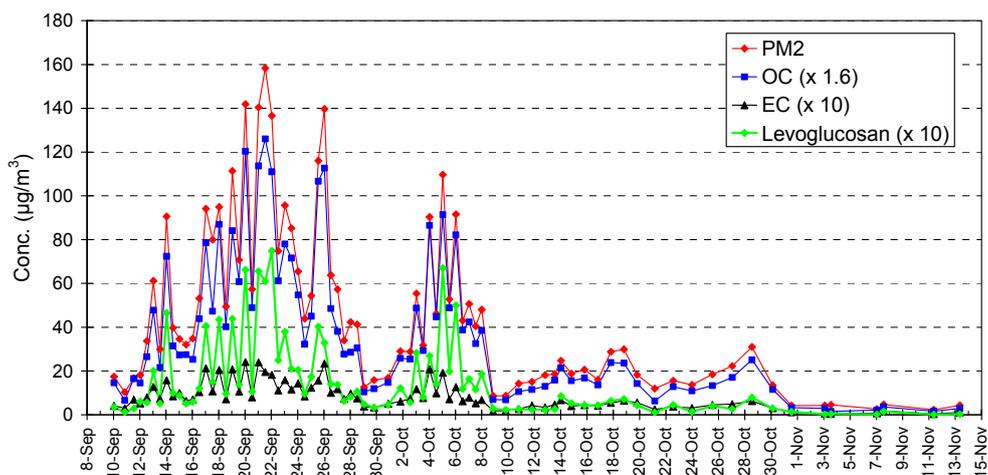


Fig. 2. Time series for fine PM (PM_2), and for OC, EC, and levoglucosan in the fine filters of the HVDS samples.

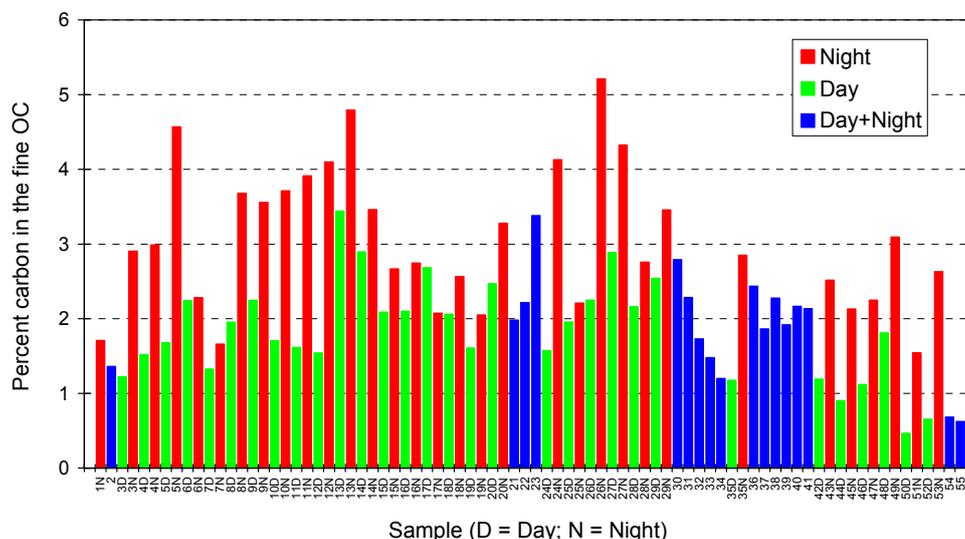


Fig. 3. Time series for the levoglucosan carbon as percent of the fine OC in the HVDS samples. Samples 1N through 29N are from the dry period, 30 through 48D from the transition period, and 49N through 55 from the wet period.

for smoke aerosol from the SAFARI 2000 experiment in southern Africa, which showed that certain organic species including levoglucosan are more enriched in smoke aerosol from the smoldering than the flaming phase. In addition, the diel variation of levoglucosan can to some extent also be explained by photochemical degradation of levoglucosan during daytime (Hoffmann et al., 2010; Hennigan et al., 2010). However, the data obtained within this field study do not allow to determine which of the two processes, i.e., the combustion stage or the photochemical degradation of levoglucosan during daytime, govern the atmospheric concentrations of levoglucosan, since flaming combustion which is prevalent during daytime is in itself a highly oxidative process. We also examined the diel variation of levoglucosan by expressing its carbon as a percentage of the water-insoluble

OC ($WIOC = OC - WSOC$), which can be considered as a rough proxy for non-SOA OC. Following this procedure, we see that levoglucosan carbon (be it that it is itself water-soluble) represents only a slightly larger percentage of the WIOC fraction during night than during the day, i.e., on average $8.6 \pm 2.1\%$ at night versus $6.4 \pm 2.6\%$ during the daytime. This night/day difference is (in relative terms; the ratio between the two percentages is 1.34) substantially smaller than that found for the difference in the percentage of levoglucosan carbon to the OC between night and day (the ratio between the two percentages is here 1.72). It may well be that only the difference in levoglucosan carbon to the WIOC between day and night is attributable to further oxidation of levoglucosan during the daytime.

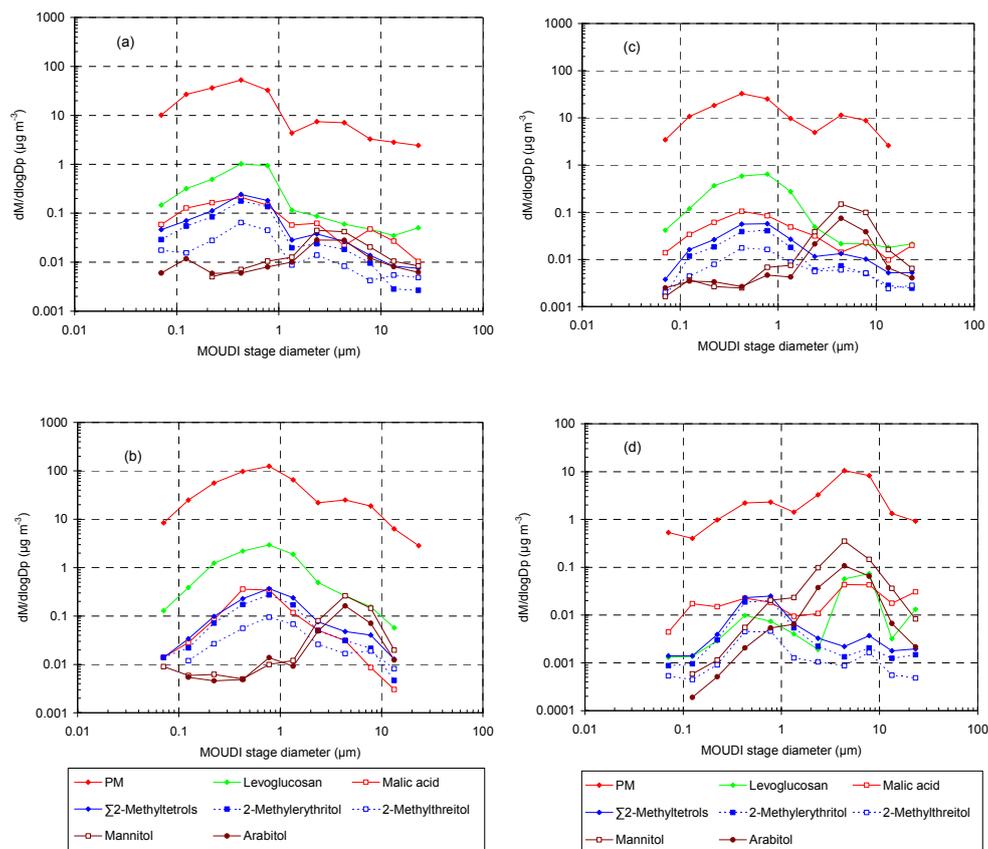


Fig. 4. Mass-size distributions of selected polar organic marker compounds and the PM during the 17 September 2002 day (a) and night (b) of the dry period, a 24-h sampling on 17 October 2002 of the transition period (c), and a 48-h sampling, 10–12 November 2002, of the wet period (d).

Figure 4a–d present typical size distributions of the PM and levoglucosan, as well as of malic acid, the 2-methyltetrols, mannitol and arabitol, for the dry, transition, and wet periods of the LBA-SMOCC 2002 campaign. Other indicator compounds such as glucose, fructose, erythritol, galactosan, and mannosan were also detected. However, a detailed examination of those compounds was not performed since they correspond to minor compounds; some of them (galactosan and mannosan) are known to accompany the emission of levoglucosan (Shafizadeh, 1984). It can be seen that the mass size distribution of the PM depends strongly on the period: during the dry period most of the PM is in the fine mode (Fig. 4a and b), while in the transition period a substantial fraction of it is in the coarse mode (Fig. 4c), and in the wet period the coarse mode has become more abundant than the fine one (Fig. 4d). Furthermore, it can be noted that there is a clear difference in the day- and nighttime mass-size distributions for the dry period with a more pronounced coarse mode at night than during daytime. Levoglucosan follows quite closely the PM and is mainly associated with the fine size mode, except in the wet period where it peaks in the coarse mode. The latter phenomenon can be explained

by a lack of pre-existing fine aerosol surface that is required for condensation of biomass smoke and by the hydrophilic properties of levoglucosan that facilitates its adsorption on the wet surface of coarse biological particles. A similar size distribution as ours for levoglucosan during the dry period was reported by Blazsó et al. (2003) for the LBA-EUSTACH 1999 dry season experiment at the same site.

3.2.2 Malic acid, 2-methyltetrols and C₅-alkene triols

Figure 5 shows the time series of malic acid, the 2-methyltetrols and the C₅-alkene triol derivatives of isoprene [sum of 2-methyl-1,3,4-trihydroxy-1-butene (*cis* and *trans*) and 3-methyl-2,3,4-trihydroxy-1-butene]. The time series of malic acid and the 2-methyltetrols are quite different from those of levoglucosan (Fig. 3), consistent with different aerosol sources or source processes. It can be seen that the concentrations of both malic acid and the 2-methyltetrols are higher in the dry and transition periods than in the wet period. The mass-size distributions of malic acid (Fig. 4a–d) show that it follows quite closely that of levoglucosan; it is mainly associated with the fine size mode, except in the wet

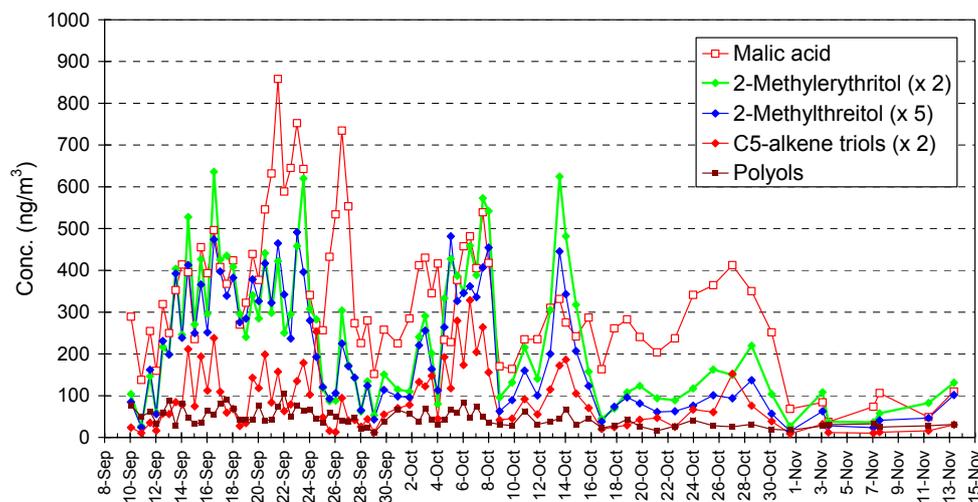


Fig. 5. Time series for malic acid, 2-methyltetrols (2-methylthreitol and 2-methylerythritol), C₅-alkene triol derivatives of isoprene (sum of 2-methyl-1,3,4-trihydroxy-1-butene (*cis* and *trans*) and 3-methyl-2,3,4-trihydroxy-1-butene) and polyols (sum of arabitol, mannitol, and erythritol) in the fine filters of the HVDS samples.

period where it is also more abundant in the coarse mode. The similar behaviors of levoglucosan and malic acid suggest the same aerosol formation process, namely, condensation of low-volatile organic vapors that are either emitted during deforestation fires by a high temperature process (in the case of levoglucosan) or formed by photooxidation of biogenic emissions and vapors released during the fires (in the case of malic acid). The different size distributions of malic acid and levoglucosan during the wet season, where both compounds are mainly associated with the coarse size mode, can be explained by a lack of fine aerosol surface onto which low-volatile organic vapors can condense. As to the origin of malic acid, it has been proposed that it is formed from C_n ($n \leq 6$) semivolatile carboxylic acids, i.e., further photooxidation of succinic acid (Kawamura and Gagosian, 1990; Kawamura and Ikushima, 1993), which in the present case can be explained by daytime photooxidation of semivolatile carboxylic acids that are emitted during biomass burning (Kundu et al., 2010). A fairly good correlation was found between the concentrations of malic and succinic acid during the dry and transition periods ($r = 0.76$), supporting that both tracers have the same aerosol source and are formed through photooxidation of C_n ($n \leq 6$) semivolatile carboxylic acids. It is noted that an even better correlation ($r = 0.92$) between the concentrations of malic and succinic acid has been reported for PM_{2.5} aerosols collected from K-pusztá, Hungary, during a 2003 summer period (Kourtchev et al., 2009). As can be seen in Fig. 5, malic acid does not reveal a diel variation; this behavior of malic acid has been noted in previous field studies such as, for example, during a 2003 summer campaign in K-pusztá, Hungary (Ion et al., 2005), and has been explained by its formation from both anthropogenic and biogenic sources over a relatively long time scale.

It can be seen in Fig. 5 that the 2-methyltetrols, 2-methylthreitol and 2-methylerythritol, closely follow each other. The ratio between the *threo* and *erythro* isomers was on average 0.30 and a statistically significant correlation was found between them ($r = 0.94$), consistent with their formation through the same aerosol formation process, namely, photooxidation of isoprene. The ratio *threo/erythro* of 0.30 compares well with the ratio of between 0.33 and 0.58 found for aerosol (PM_{2.5}, PM₁, or total aerosol) collected at other forested sites (e.g., 0.37, Ion et al., 2005; 0.40, Cahill et al., 2006; 0.48, Kourtchev et al., 2008a; 0.33, Clements and Seinfeld, 2007; 0.58, Xia and Hopke, 2006; 0.41, Kourtchev et al., 2008b). The higher concentrations of the 2-methyltetrols during the dry and transition periods compared to the wet period can in part be explained by a difference in the acidity of the aerosol. Smog chamber studies with isoprene (Edney et al., 2005; Surratt et al., 2007a, b) as well as field studies (Kourtchev et al., 2008a; Lewandowski et al., 2007) have demonstrated that the formation of 2-methyltetrols is strongly affected by the acidity of the aerosol. It is noted that during the LBA-SMOCC 2002 experiment the mixing ratios of the acidic trace gases HNO₃ and SO₂ were considerably higher during the dry and transition periods than the wet period, and that the same trends were found for aerosol NO₃⁻ and SO₄²⁻ anions showing maxima of 1.25 ppb and 0.6 ppb, respectively (Trebs et al., 2004). In addition, the higher concentrations of the 2-methyltetrols during the dry and transition periods compared to the wet period may in part be explained by differences in the emission rate of isoprene, the NO_x concentration and the removal by wet deposition. As to seasonal variations in the emission rate of isoprene in the Amazon basin, only slightly higher emissions in the dry than in the wet season were measured

(i.e., at National Forest of the Tapajos mean isoprene mixing ratios were 2.8 ± 0.9 ppb, 1.4 ± 0.5 ppb and 1.9 ± 1.2 ppb in the dry, transition, and wet periods, respectively, Trostdorf et al., 2004), so that other factors such as the aerosol acidity, the NO_x concentration and wet deposition mainly determine the concentrations of the 2-methyltetrols. As to seasonal variations in the NO_x concentration, substantial differences were reported by Trebs et al. (2006), who measured median NO_x mixing ratios in the dry, transition, and wet periods of 4.6 ppb, 3.0 ppb, and 0.9 ppb, respectively. It is very likely that the 2-methyltetrol concentrations were also affected by the NO_x concentration, since NO_x is known to play a role in their formation (Sato, 2008; Szmigielski et al., 2010). During the dry period, the 2-methyltetrol concentrations show a clear diel variation with highest concentrations during daytime. This is in accordance to observations made for aerosol (PM_{10} or $\text{PM}_{2.5}$) from other forested sites (Ion et al., 2005; Plewka et al., 2006; Kourtchev et al., 2008a), where a diel pattern was found for the 2-methyltetrol concentrations with maxima during daytime, which is consistent with their fast photochemical formation from locally emitted isoprene. The 2-methyltetrols were poorly correlated with malic acid ($r = 0.55$), as could be expected since they have a different aerosol source. No conclusions could be made regarding diel variations in the 2-methyltetrol concentrations during the transition and wet periods, since there were not sufficient day/night samples taken during these periods. In addition to the 2-methyltetrols, the C_5 -alkene triols were detected at significant concentrations during the dry and transition periods, and also exhibited higher concentrations during daytime. The latter photooxidation products of isoprene have been reported at high concentrations in PM_{10} aerosol from a boreal forest site, Hyytiälä, southern Finland, during 2004 and 2005 summer periods (Kourtchev et al., 2005, 2008a), especially during an episode that was characterized by a higher acidity. The percentage concentration ratios C_5 -alkene triols/2-methyltetrols were 28%, 31%, and 20% for the dry, transition, and wet periods of the LBA-SMOCC campaign, respectively, and are thus higher than the percentage ratios of less than 10% measured in laboratory isoprene photooxidation experiments performed in the absence of NO_x (Kleindienst et al., 2009). Possible reasons for this discrepancy are that the NO_x regimes are different under the ambient conditions and that the RH in the moist tropical atmosphere is much higher (it was, on average, 78% during the SMOCC campaign) than that employed in the latter laboratory study (i.e., <3%). It is worth noting that during all periods of the LBA-SMOCC 2002 campaign the NO_x regime cannot be regarded as a low- NO_x one (<10 ppt) since the median NO_x mixing ratios in the dry, transition and wet periods were 4.6 ppb, 3.0 ppb and 0.9 ppb, respectively (Trebs et al., 2006). With respect to the effect of the RH, it has been reported in a recent laboratory study in the absence of NO_x (considered as low- NO_x) by Surratt et al. (2010) that the concentration ratio C_5 -alkene triols/2-methyltetrols

is strongly affected by the RH. The mass size distributions of the 2-methyltetrols (Fig. 4a–d) show that they have the same pattern as those of levoglucosan and malic acid, and are mainly associated with the fine size mode during the dry and transition periods. However, it is noted that the mass size distributions of the 2-methyltetrols are distinctly different from those of levoglucosan and malic acid during the wet period, where the 2-methyltetrols remain associated with the fine size mode. The latter behavior of the 2-methyltetrols is consistent with an aerosol formation process that is different from that for levoglucosan and malic acid; in the case of the 2-methyltetrols a heterogeneous process is suggested, while that for levoglucosan and malic acid involves condensation of low-volatile organic vapors onto pre-existing aerosol particles. The C_5 -alkene triols in the MOUDI sample sets from the dry and transition periods were below the detection limit, but could be measured in the fine size fractions of the wet period MOUDI sample set, where their concentrations were about 20% of those of the 2-methyltetrols (results not shown).

Both the 2-methyltetrols and C_5 -alkene triols are isoprene SOA tracers under low- NO_x conditions (Surratt et al., 2006; Kleindienst et al., 2009); the formation of 2-methyltetrols can be explained by acid-catalyzed degradation of C_5 -trihydroxyhydroperoxides (Kleindienst et al., 2009) and/or C_5 -epoxydiols (Paulot et al., 2009; Surratt et al., 2010), while that of the C_5 -alkene triols can be explained by acid-catalyzed degradation of C_5 -epoxydiols (Wang et al., 2005; Surratt et al., 2010). It is noted that during the dry and transition periods of the LBA-SMOCC campaign the NO_x mixing ratios were in the 1–5 ppb range (Trebs et al., 2006), which can be considered as an intermediate NO_x regime, suggesting that the C_5 -alkene triols may not be as unique to low- NO_x conditions as originally thought (Surratt et al., 2006). It can be seen that the size distribution observed during the wet season for the 2-methyltetrols (Fig. 4d) differs from that of other polar compounds that partition from the gas to the particle phase such as levoglucosan and malic acid. A possible explanation is that only the freshly generated fine particles are sufficiently acidic to generate the 2-methyltetrols from their gas-phase precursors through acid-catalyzed reactions. In this context, it is worth noting that both the 2-methyltetrols (Fig. 4a–d) and inorganic sulfate (Fig. 4 in Fuzzi et al., 2007) are mainly associated with the fine size mode.

3.2.3 Arabitol, mannitol, and erythritol

Arabitol, mannitol, and erythritol are marker compounds for airborne fungal spores (Lewis and Smith, 1967; Bielecki, 1982) that are expected to be mainly associated with the coarse aerosol (Matthias-Maser and Jaenicke, 1995; Bauer et al., 2002a, b). However, together with fungal spores also fragments may be released from moldy surfaces (Górny et al., 2002), explaining why these polyols are also present in

the PM_{2.5} HVDS samples, as has been reported in previous studies (Graham et al., 2003; Yttri et al., 2007). The time series for the polyols (arabitol, mannitol, and erythritol) (Fig. 5) reveals little variation throughout the dry, transition, and wet periods of the LBA-SMOCC 2002 campaign, as could be expected for these compounds since the humid tropical rain forest remains active throughout the whole year in producing fungal material. In addition, no clear day/night variations could be noted for their PM_{2.5} concentrations (Fig. 5).

The mass size distributions of arabitol and mannitol (Fig. 4a–d) show that they have similar patterns and are mainly associated with the coarse mode. The day- and nighttime data for samplings in the dry period (Fig. 4a and b) show that the concentrations of arabitol and mannitol are about two times higher at night than during daytime, consistent with observations made by Graham et al. (2003) during the LBA-CLAIRE 2001 wet season campaign on the coarse size fractions of HVDS samples. These day/night differences have been explained by a nocturnal increase in wet spore discharging fungi such as *Ascomycota* and *Basidiomycota* (Elbert et al., 2007); an alternative explanation for this phenomenon, however, is trapping of the released fungal material under the shallow nocturnal boundary layer. The mass size distributions of arabitol and mannitol for the 48-h sampling during the wet period (Fig. 4d) clearly show a tail into the fine size mode, suggesting an enhanced release of fungal fragments from the biota during this period compared to the transition and dry periods. Size-fractionated aerosol data revealing similar patterns for arabitol and/or mannitol were reported for samples from a rural meadow site in Melpitz, Germany (Carvalho et al., 2003) and from urban sites in Norway (Yttri et al., 2007), where arabitol and/or mannitol clearly peaked in the coarse mode between 1.3 and 4.2 μm, which is the size range for spores of typical airborne fungal strains (Bauer et al., 2002b).

4 Conclusions

Sources, source processes, time series, diel variations, and size distributions of organic marker compounds were investigated for carbonaceous aerosols that were collected during the LBA-SMOCC field experiment, conducted in Rondônia, Brazil, in 2002 during dry, intermediate, and wet periods. During all three periods levoglucosan was found to be the most dominant organic species in PM_{2.5} samples and reached up to 7.5 μg m⁻³ during the dry period, which was characterized by intense deforestation fires. During the dry period, levoglucosan exhibited diel variations with a nighttime prevalence. In the size-segregated samples, levoglucosan was found to be closely associated with the PM and mainly found in the fine mode, except during the wet period, where it peaked in the coarse mode. Isoprene oxidation products were found to be important species in PM_{2.5} at this pas-

ture site (on average 250 ng m⁻³ during the dry period versus 157 ng m⁻³ during the transition period and 52 ng m⁻³ during the wet period) and the seasonal differences were mainly attributed to differences in the acidity of the aerosols, the NO_x concentration and wet deposition. In addition, during the dry period clear diel variations were observed for the isoprene oxidation products with a daytime prevalence, which is consistent with their fast formation from locally emitted isoprene. In size-segregated samples, malic acid and the 2-methyltetrols exhibited a different distribution pattern. While the 2-methyltetrols were found to be mainly associated with the fine mode during all periods, malic acid was found to be prevalent in the fine mode only during the dry and transition periods and in the coarse mode during the wet period, indicating that the aerosol formation processes for those species are distinctly different. The unique behavior of the 2-methyltetrols is explained by heterogeneous chemistry, likely involving acid-catalyzed degradation of their gas-phase precursors onto an acidic particle surface. Marker compounds for airborne fungi included arabitol, mannitol, and erythritol. The sum of these polyols in PM_{2.5} during the dry, transition, and wet periods was, on average, 54 ng m⁻³, 34 ng m⁻³, and 27 ng m⁻³, respectively and revealed minor day/night variation. The mass size distributions of arabitol and mannitol during all periods showed similar patterns and an association with the coarse mode, which is consistent with their primary source origin.

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