Diurnal variation in the water-soluble inorganic ions, organic carbon and isotopic compositions of total carbon and nitrogen in biomass burning aerosols from the LBA-SMOCC campaign in Rondônia, Brazil

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Abstract

Aerosol particles ($PM_{2.5}$) were collected during the day (n=6) and nighttime (n=9) from a tropical pasture site in Rondônia, Brazil during an intensive biomass burning period (16-26 September, 2002). Higher normalized (by K^+, levoglucosan, or apparent elemental carbon, EC_a) mass concentrations of SO_4^{2-} and $CH_3SO_3^-$ in daytime suggest their photochemical production, while the opposite trend for NO_3^- suggests its transfer to the aerosol phase at lower temperatures and higher humidities, as well as possibly production through hydrolysis of N_2O_5 on aqueous aerosol particles. About 4.2-7.5% of OC (5-13% of water-soluble organic carbon (WSOC)) could be characterized at the molecular level using GC-MS and GC-FID. Among the detected organic compound classes, the relative abundances of anhydrosugars and aromatics were higher in night samples, but sugars/sugar alcohols, diacids, oxoacids and α-dicarbonyls were more abundant in day samples. Consecutive day and night samples showed that $\delta^{13}C$ values of total carbon (TC) were lower in daytime samples, which can be interpreted as resulting from higher contributions of refractory TC depleted in ^{13}C due to predominantly flaming combustion. The $\delta^{15}N$ values of total nitrogen (TN) ranged from +23.5‰ to +25.7‰, however, there was no trend in day and night samples. Higher values of $\delta^{13}C$ and $\delta^{15}N$ for biomass burning particles than those of unburned vegetation reflect positive isotopic enrichment either during the formation of particles or after the emission of particles in the atmosphere.

Keywords: Biomass burning; Water-soluble inorganic ions; Organic aerosols; Stable carbon and nitrogen isotopes; Kinetic isotope effect; LBA-SMOCC; Rondônia

1. Introduction

The Large-Scale Biosphere-Atmosphere Experiment in Amazonia – Smoke, Aerosols, Clouds, Rainfall, and Climate (LBA-SMOCC) campaign took place at a pasture site in Rondônia, southwestern Amazonia, Brazil during the late dry (September) to early wet season (November), and included the transition period (October) in 2002. The main goal was to explore the relationship between the chemical and physical properties of biomass burning aerosols, and its role in perturbing the microphysical properties of clouds at regional and mesoscale levels.

Carbonaceous materials in biomass burning aerosols constitute as much as 70-90% of total aerosol mass (Andreae and Crutzen, 1997; Yamasoe et al., 2000; Fuzzi et al., 2007). About 45-75% of the carbonaceous material represents water-soluble organic carbon (WSOC) (Graham et al., 2002; Mayol-Bracero et al., 2002a; Decesari et al., 2006). This suggests that the emission of WSOC from biomass burning is regionally and globally important. The significant fraction of WSOC in smoke aerosols (Mayol-Bracero et al., 2002b) can take up water vapor from the atmosphere and affect the light absorption efficiency (Redemann et al., 2001). The WSOC in biomass burning particles contributes to the cloud condensation nuclei (CCN) activity (Roberts et al., 2002; Andreae et al., 2004) and may also participate in aqueous phase chemical reactions occurring in droplets nucleated by smoke particles.

Together with the particle size, their chemical composition (both inorganic and organic) is one of the most important factors determining the ability of aerosols to act as CCN (Charlson et al., 2001; Nenes et al., 2002; Dusek et al., 2006), which are directly associated with modulating the cloud microphysical properties and as a result the radiative properties of clouds (Ramanathan et al., 2001; Kaufman et al., 2002; Roberts et al., 2003).

It is therefore important to study the chemical composition of biomass burning particles and its chemical transformations.

A series of papers on aerosol chemistry have already been published from the LBA-SMOCC biomass burning experiment (Trebs et al., 2004; Falkovich et al., 2005; Decesari et al., 2006; Hoffer et al., 2006; Fuzzi et al., 2007). These studies have comprehensively discussed the diurnal variation, size distribution and chemical evolution of water-soluble and insoluble inorganics, bulk organics, water-soluble oxygenated molecular organics as well as the gas phase chemical composition of inorganic compounds. Significant variations in the aerosol composition and concentrations were explained by diurnal oscillations of boundary layer height, type of combustion phases, and differences in emission strength of pollutants and in meteorological conditions between the dry and wet periods.

Stable carbon and nitrogen isotopic composition of total carbon (TC) and total nitrogen (TN) of aerosols from the LBA-SMOCC biomass burning experiment have not reported, although comprehensive investigations on the chemical composition and physical properties of aerosols are available in the literature (Fuzzi et al., 2007 and references therein). The $\delta^{13}C$ of bulk organic carbon has been successfully used to better understand the contributions of marine and continental sources to aerosol carbon (Chesselet et al., 1981; Cachier et al., 1986, 1989; Narukawa et al., 1999, 2008; Martinelli et al., 2002; Turekian et al., 2003; Kawamura et al., 2004; Kelly et al., 2005; Ho et al., 2006; Huang et al., 2006). Stable carbon and nitrogen isotopic ratios in biomass burning aerosols have not previously been studied extensively. They can provide information not only on the origin and biomass burning mechanisms, but also on the isotopic fractionation that is likely during biomass burning and after the emission of particles in the atmosphere.

In this study, we collected daytime and nighttime aerosols during intensive biomass burning, under the framework of the LBA-SMOCC campaign, from a pasture site in Rondônia, Brazil, located on the southwestern periphery of the Amazon basin. Here, we report on diel variations in the concentrations and compositions of water-soluble inorganic ions, bulk organic carbon, water-soluble organic carbon and molecular organics, as well as the stable carbon and nitrogen isotopic composition of biomass burning aerosols. Based on our chemical and isotopic data, we discuss the evidence for photochemical processes in the smoke layers, and the isotopic fractionation that is likely to occur either during particle formation from biomass burning or after the emission of particles to the atmosphere.

2. Instrumentation and methods

2.1. Site description and aerosol sampling

The samples discussed in this study were collected during an intensive biomass burning period in the dry season, from 16-26 September 2002, at the FNS (Fazenda Nossa Senhora Aparecida) site (10°45'44" S, 62°21' 27" W, 315 m asl) located in the southwestern province of Rondônia in Brazil (Figure 1).

Aerosol sampling procedures have been described in detail elsewhere (Solomon et al., 1983; Hoffer et al., 2006). Briefly, fine aerosol particles ($PM_{2.5}$) were collected on pre-combusted (~10 h at 600 °C) Pallflex quartz fiber filters using a dichotomous virtual impactor (Solomon et al., 1983) mounted on a 10 m high tower. Daytime samples (n=6) were collected from ~7:45 to ~17:45 LT (local time) and nighttime samples (n=9) from ~18:30 to ~7:00 LT. The aerosol filters were placed in pre-baked (~10 h at 600 °C) glass jars and stored in a freezer at -20 °C at the Max Planck Institute for Chemistry in Mainz, Germany. Small fractions of the filter discs were wrapped in pre-baked thick aluminum foil and transported to our laboratory in Sapporo, Japan. Filter discs were transferred into

pre-baked glass vials (~480 °C, overnight) and stored in our laboratory at -20 °C until analysis.

2.2. Analytical Methods

For the water-soluble inorganic ion and WSOC measurements, aliquots of the filter samples were extracted with Milli Q water. One part was used for the analyses of inorganic ions using a Metrohm 761 ion chromatography (IC) system (Metrohm, Herisau, Switzerland). Anions were separated on a Shodex SI-90 4E column with 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ (Kanto Chemical, Japan) as eluent, and cations on a Shodex YK-421 column with 4 mM H_3PO_4 as eluent (Kanto Chemical, Japan). The injection loop volume was 200 µl. Both cations and anions were quantified against a standard calibration curve. Another part of the filtered water extract was acidified with 1.2 M HCl and purged with pure air in order to remove dissolved inorganic carbon and volatile organics, and then WSOC was measured with a carbon analyzer (Shimadzu, TOC-5000). The reproducibility for WSOC measurements using a laboratory standard was 10%.

The concentrations of organic carbon (OC) and apparent elemental carbon (EC_a) were measured using a semi-continuous OC/EC analyzer (Sunset Laboratory Inc., Portland, OR, USA). For a discussion and definition of EC_a see the review paper by Andreae and Gelencsér (2006). Aliquots of the sample filters (diameter 11 mm) were mounted into the oven port using a flat-faced forceps. The oven temperature was programmed as follows: under He, at 250 °C for 2 min, at 450 °C for 2 min and at 550 °C for 2 min, then under He with 10% O_2, at 550 °C for 2 min, at 700 °C for 2 min and at 870 °C for 3.5 min. The carbon content of the sample that evolves to CO_2 between 250 °C and 700 °C was defined as OC, and that which is combusted between 700 °C and 870 °C as EC_a.

150 Detailed analytical procedures for the determination of polar compounds
151 (anhydrosugars, sugars, sugar alcohols and aromatic compounds) are available elsewhere
152 (Graham et al., 2002; Hoffer et al., 2006). Briefly, aliquots of the filters were extracted
153 with acetonitrile followed by derivatization with 50 μl of pyridine and 50 μl of
154 bis(trimethylsilyl)trifluoroacetamide (BSTFA), containing 1% trimethylchlorosilane
155 (TMCS) as a catalyst at 70 °C for 30 minutes, and peak identification and quantification
156 was made with a GC-MS.
157 Analytical procedures for the analyses of the diacids and related compounds are
158 described by Kawamura and Ikushima (1993) in detail. Briefly, almost dried water
159 extracts of the filter samples were derivatized with 14% borontrifluoride in n-butanol at
160 100 °C. The derived dibutyl esters and dibutoxy acetals were determined using a GC
161 (Hewlett-Packard, HP6890) equipped with a capillary column and a FID detector.
162 Authentic diacid dibutyl esters were used as external standards for the peak identification.
163 The compounds were also identified using a GC/mass spectrometer (Thermoquest, Trace
164 MS).
165 For TC and TN analyses, a small disc (area 0.95 cm^2) was cut out of each filter
166 sample. The disc was put into a tin cup and shaped into a rounded ball using a pair of flat-
167 tipped tweezers. The samples were introduced into the elemental analyzer (EA; model:
168 NA 1500 NCS, Carlo Erba Instruments) using an auto-sampler, and were oxidized in a
169 combustion column packed with chromium trioxide at 1020 °C, in which the tin container
170 burns to promote the intensive oxidation of sample materials in an atmosphere of pure
171 oxygen. The combustion products are transferred to a reduction column packed with
172 metallic copper that was maintained at 650 °C. Here excess oxygen is removed and
173 nitrogen oxides coming from the combustion column are reduced to molecular nitrogen
174 (N_2). The N_2 and CO_2 derived during this process were isolated on-line using a gas

chromatograph and then measured with a thermal conductivity detector. Aliquots of the N_2 and CO_2 gases were then introduced into an isotope ratio mass spectrometer (ThermoQuest, Delta Plus) through an interface (ThermoQuest, ConFlo II). The isotopic composition of $\delta^{13}C$ and $\delta^{15}N$ was determined using the following standard isotopic conversion equations (1) and (2), respectively:

$$\delta^{13}\mathrm{C}\ (‰) = \left[\frac{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{sample}}}{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{standard}}} - 1 \right] \times 1000 \qquad (1)$$

$$\delta^{15}\mathrm{N}\ (‰) = \left[\frac{(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{sample}}}{(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{standard}}} - 1 \right] \times 1000 \qquad (2)$$

Acetanilide was used as an external standard to determine TC, TN and their isotopic ratios. The reproducibility for TC, TN, and their stable isotopes for the LBA-SMOCC samples could not be determined due to a lack of sample materials. But, the reproducibility in our laboratory of TC and TN in atmospheric aerosol samples collected from different parts of the world ranged between 0.7-9% (av. 2.5%) and 1.4-4.8% (av. 3%), whereas standard deviations of $\delta^{13}C$ and $\delta^{15}N$ measurements ranged between 0.08-0.24‰ (av. 0.12‰) and 0.03-0.45‰ (av. 0.13‰).

Carbon monoxide, CO, was measured with a Thermo Environmental Instrument Inc. analyzer (Model 48C Gas Filter Correlation) with a detection limit of 40 ppb. Because of the high ambient humidity, a cooler was used to remove water from the sample stream prior to the CO analyzer.

3. Results and discussion

3.1. Atmospheric conditions during the sampling period

No rainfall was found to occur during our sampling period. Ambient temperature ranged between 30.3 and 34.2 °C (av. 32.1 °C) during daytime, and between 23.6 and 25.2

°C (av. 24.2 °C) at nighttime. The boundary layer in daytime was very well mixed with an average height of 1690±250 m, whereas the nocturnal boundary layer decreased to 200-250 m (Fuzzi et al., 2007). Many active fires were observed in the province of Rondônia, where our sampling site is located, as well as in other adjacent and distant provinces of Brazil (Figure 1, upper panel). The values of relative humidity in day- and night-time were about 70% and 100%, respectively. Three-dimensional backward air mass trajectories at 250 m agl (above ground level), used for explaining the compositional and isotopic variations, were drawn using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler et al., 2006). Horizontal transport of 3-day air mass back trajectories for day and night samples indicates that air masses at our sampling site are mainly influenced by air masses transported from Rondônia and its neighbor provinces (Figure 1, upper panel). The vertical trajectories show that the air masses were usually transported within the boundary layer (Figure 1, lower panel).

3.2. Water-soluble inorganic ions

In this study, six water-soluble inorganic anions (F^-, $CH_3SO_3^-$, Cl^-, NO_2^-, NO_3^- and SO_4^{2-}) and five cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were quantified. Their mass concentrations are summarized in Table 1, and their relative abundances in total inorganic ions are depicted in Figure 2.

For the anions in day samples, both the average concentrations and relative abundances of SO_4^{2-} were the greatest, followed by NO_3^-, $CH_3SO_3^-$, NO_2^-, F^- and Cl^-, while those of NO_3^- in night samples were the most abundant followed by SO_4^{2-}, $CH_3SO_3^-$, Cl^-, F^- and NO_2^- (Table 1, Figure 2a and 2b), indicating that day and night samples have a different inorganic composition and as a result different mixing states due to difference in daytime and nighttime chemistry and in the dominant phases (flaming and smoldering) of

biomass combustion. The average relative abundance of SO_4^{2-} is about 50% higher in day samples than in night samples, being consistent with daytime versus nighttime variations of SO_2, from which SO_4^{2-} is mainly produced. Trebs et al. (2004) observed a higher mixing ratio of SO_2 in daytime than in nighttime during our aerosol collection time at the FNS site in Rondônia. A higher abundance of SO_4^{2-} in daytime aerosols can be explained by enhanced chemical production as well as the transfer of SO_4^{2-} from the free troposphere to the boundary layer due to turbulent mixing in daytime. The main explanation for higher concentrations of NO_3^- at nighttime is that humidity is higher and temperature lower, which thermodynamically favors the reaction between gaseous NH_3 and HNO_3 to form aerosol nitrate. This logic can be strongly substantiated by the observed lower mixing ratio of HNO_3 at nighttime during our sampling period at the FNS site (Trebs et al., 2004). The higher concentration and relative abundance of NO_3^- in nighttime aerosols also suggests that NO_3^- production due to the reactions of HNO_3 and hydrolysis of N_2O_5 on aqueous aerosol particles in nighttime may be more pronounced than in daytime during the biomass burning period in Amazonia.

Both the mass concentration and relative abundance of $CH_3SO_3^-$ (MSA^-) is 1.4 and 2.5 times, respectively, higher in day samples than night samples (Figure 2a and 2b), suggesting the enhanced chemical production of this species from its precursors (dimethylsulphide and methylmercaptan). MSA^- can also be emitted directly from biomass burning (Andreae and Andreae, 1988). NO_2^- in aerosols is produced from its gaseous precursor HNO_2, which is derived from the heterogeneous reactions of NO_2 with surface moisture (Kleffman et al., 2003). This reaction should be favorable in the nighttime at our sampling site due to high nighttime humidity. A higher concentration, or relative abundance, of NO_2^- in aerosols at nighttime was expected, but the opposite was observed (Table 1, Figure 2a and 2b). Alternatively, due to rapid photo-production and subsequent

photolysis of HNO_2 in the daytime (Harrison et al., 1996), NO_2^- in the aerosol phase should not be higher. The higher concentration of NO_2^- we found in daytime aerosols suggests that complete depletion of HNO_2 did not occur in the daytime in the Amazon Basin. HCl is known to be emitted directly from biomass fires, accounting for a large fraction of total emitted chlorine (Andreae et al., 1996). The higher mass concentration and relative abundance of aerosol Cl^- observed in nighttime samples (Table 1, Figure 2b) can be explained by the expansion and dilution of the boundary layer in the daytime due to turbulent mixing, and an enhanced condensation/dissolution/chemical reaction of gaseous HCl on aerosol surfaces at night under the conditions of lower temperature, high humidity, and stable thermal stratification.

Ammonium (NH_4^+) in aerosol is produced from the reaction between NH_3 and acidic species present in either the gas or aerosol phase. Trebs et al. (2004), using a wet-annular denuder and a Steam-Jet aerosol collector followed by on-line flow injection analysis (Wyers et al., 1993) during the same campaign at the FNS site, reported that NH_3 started to increase in the early morning (07:00 to 10:00) followed by the usual decrease during the rest of a day. This trend was interpreted as being due to the re-evaporation of deposited NH_3 from wet surfaces (grass leaves) as the temperature began to increase. In our study, we have observed slightly higher relative abundances of NH_4^+ in daytime than in nighttime samples (Figure 2c and 2d), suggesting that diel variations of NH_3 and increased availability of H_2SO_4 due to daytime photo-production influence NH_4^+ formation. Potassium (K^+) showed slightly higher relative abundances in night samples (Figure 2c and 2d). We have observed higher relative abundance of Na^+ (Figure 2c and 2d) in both day and night samples. Such a large contribution was not reported in the previous studies on the same experiment. Although the concentration of Na^+ in field blank samples

in our study is about 10% of real samples, we cannot completely rule out the contamination of our samples during handling, transportation and extraction.

Potassium, levoglucosan and EC_a are considered to be conservative tracers for biomass burning. Variations in potassium, levoglucosan and EC_a-normalized diel mass concentrations for inorganic secondary aerosols (SO_4^{2-}, NO_3^-, MSA^- and NH_4^+) are presented in Figure 3. Higher normalized mass concentrations for SO_4^{2-}, MSA^- and NH_4^+ were observed in daytime (Figure 3), further suggesting the enhanced photo-production of the sulfur species and consequent uptake of NH_3. In contrast, normalized mass concentrations for NO_3^- showed the opposite trend (Figure 3) suggesting transfer of gaseous HNO_3 into the aerosol phase at lower temperatures and higher humidities at night, as well as possible NO_3^- production through nighttime chemistry in Amazonia. Fuzzi et al. (2007) observed similar diurnal variation for the ratio of SO_4^{2-}/K^+ and NO_3^- for size-segregated biomass burning samples of the same campaign collected by different impactors.

A clear diel variation of MSA^-/SO_4^{2-} ratio was observed (Figure 4a), which could be related to more rapid photo-production of MSA^- than SO_4^{2-} from their respective precursors. MSA^- is an oxidation product of dimethylsulfide (DMS) and methylmercaptan (MeSH). Our MSA^-/SO_4^{2-} ratio ranged between 0.06-0.23. Both lower and upper limits in our study are higher than that of mixed layer aerosols over the Amazon basin collected between July and August in 1985 (0.02-0.09) (Andreae and Andreae, 1988).

A clear diel variability was also observed for the K^+/levoglucosan ratio (Figure 4b). Gao et al. (2003) found a K^+/levoglucosan ratio of 33.3 during the flaming phase, and lower ratios (0.2-0.6) for the smoldering phase in savanna fires. A higher ratio during intensive biomass burning in summer and a lower one in winter at Aveiro, Portugal has been reported (Pio et al., 2008). Thus, the relatively higher K^+/levoglucosan ratio in

daytime than in nighttime tends to indicate the mostly flaming character of daytime fires. Ratios lower than 0.25-1 have been obtained for $PM_{2.5}$ emissions from wood stove combustion of USA tree species (Fine et al., 2004) and burning in an USA pine forest (Lee et al., 2005). In our study, this ratio ranged between 0.3-1.2, suggesting that biomass burning affecting the Rondônia site is a combination of smoldering and flaming phases.

3. 3. Anhydrosugars

Three anhydrosugars, i.e., levoglucosan, galactosan, and mannosan were measured in this study. Hoffer et al. (2006) had already reported some results on the same suite of samples used in this study. They reported that levoglucosan was the dominant anhydrosugar and that the anhydrosugar-carbon content normalized by TC was higher in nighttime than in daytime. Here, we focus on the absolute concentrations of anhydrosugars (Table 2), discuss their likely sources, and compare our dataset with the antecedent biomass burning experiments carried out at the same site and other sites.

The concentration of levoglucosan ranged between 850-7310 ng m^{-3} (av. 2550 ng m^{-3}) in daytime versus 2510-8790 ng m^{-3} (av. 5650 ng m^{-3}) in nighttime. Concentrations of mannosan were lower (av. 97 ng m^{-3}) in daytime than in nighttime (av. 236 ng m^{-3}). Galactosan also showed lower values in daytime (av. 40 ng m^{-3}) than in nighttime (av. 135 ng m^{-3}) (see Table 2). Mannosan is more abundant than galactosan in every sample, indicating the importance of primary forest burning. Galactosan is more abundant than mannosan in smoke particles derived from rice straw, biomass briquettes and grasses (Sheesley et al., 2003; Oros et al., 2006). Fuzzi et al. (2007) reported that anhydrosugars (levoglucosan and mannosan) in day and night biomass burning samples collected during our campaign were enriched in the submicrometer fraction, suggesting direct emissions of anhydrosugars from biomass burning. Decesari et al. (2006) also reported that the mean

concentration of anhydrosugars varied between 1160 and 4370 ng m^{-3} for biomass burning aerosols from the same campaign using different analytical techniques, pointing to large differences in the results from different analytical techniques. The mean value of our day and night samples is almost equal to the upper limit, but 3.7 times higher than the lower limit of the data of Decesari et al. (2006). The average concentrations of these anhydrosugars in both day- and night-time samples are higher than those reported from a previous study at the same site in Rondônia (Graham et al., 2002, Zdrahal et al., 2002). But the mean concentration of levoglucosan in day- and night-time samples is 2.6-5.8 times lower than that of smoke aerosol collected using an aircraft from savanna fires during the Southern African Regional Science Initiative 2000 (SAFARI 2000) field campaign in southern Africa (Gao et al., 2003). These differences reflect mostly the specific conditions (fire abundance, transport, and dilution of emissions) prevailing during sampling.

Polysaccharides present in the biomass break down during combustion, yielding anhydrosugars (Simoneit et al., 1999). As a result, anhydrosugars in day and night samples showed good correlation against the biomass burning tracers K^+ and CO, along with OC (Figure 5, Table 3). Another biomass burning tracer, EC_a, didn't show a strong correlation against anhydrosugars (r^2=0.3-0.4, Figure 5d), although Graham et al. (2002) reported very good correlation between anhydrosugars and EC_a for aerosol samples collected at the same site from 1-29 October 1999, as a part of Large-Scale Atmosphere-Biosphere Experiment in Amazonia (LBA-EUSTACH-2) campaign. This is probably due to differences in the emission ratios of EC_a and levoglucosan among the different types of fires and different atmospheric residence times of levoglucosan and EC_a. Systematically, correlation coefficients of anhydrosugars with K^+, CO, OC and EC_a were higher in daytime samples than in nighttime samples. This is to be expected, as daytime sampling

collects a more highly averaged blend of biomass smoke from a large number of fires along the airmass trajectories, whereas the samples collected at nighttime are more influenced by nearby fires with individually varying combustion conditions.

The carbon content of levoglucosan, the most abundant anhydrosugar, accounts for 1.9-3.8% (av. 2.6%) of OC in daytime versus 2.5-5.3% (av. 4%) in nighttime, while it accounts for 2-6.4% (av. 3.8%) of WSOC in daytime versus 4.1-9.1% (av. 6.9%) in nighttime, being comparable to values (0.1-10% of OC and 0.2-16% of WSOC) of biomass burning aerosols of the LBA-SMOCC campaign (Decesari et al., 2006) and similar to values (1-6% of TC and 2-8% of WSOC) reported for the aerosol samples collected at the same site during the biomass burning period in 1999 (Graham et al., 2002). Overall, these three anhydrosugars account for 48% and 62% of individually detected organic species in day and night samples, respectively (Figure 6a and 6b).

3.4. Sugars and sugar alcohols

Two sugars (fructose and sucrose) and a few sugar alcohols including glycerol, threitol, erythritol, arabitol, mannitol, sorbitol and inositol were also detected in the biomass burning aerosols (Table 2). The concentrations of sugars were 3.6-33 ng m^{-3} (av. 28 ng m^{-3}) in daytime versus 1.4-49 ng m^{-3} (av. 31 ng m^{-3}) in nighttime, while the concentrations of sugar alcohols were 50-173 ng m^{-3} (av. 93 ng m^{-3}) in daytime versus 84-357 ng m^{-3} (av. 206 ng m^{-3}) in nighttime (Table 2). The average concentration of sugars is about 2 times higher, while the average concentration of sugar alcohols is almost equal to the previous measurements on biomass burning aerosols of the same campaign (Decesari et al., 2006). The mean concentration of sugar alcohols is 1.2-2.7 times higher than those reported for aerosols collected at the same site in October 1999 (Graham et al., 2002). The contribution of sugars and sugar alcohols to OC ranged between 0.02-0.05% (av. 0.03%)

and 0.07-0.13% (av. 0.1%) in daytime versus 0.01-0.06% (av. 0.02%) and 0.06-0.17% (av. 0.14%) in nighttime, whereas their contribution to WSOC ranged between 0.03-0.06% (av. 0.04%) and 0.11-0.18% (av. 0.14%) in daytime versus 0.02-0.09% (av. 0.04%) and 0.11-0.3% (av. 0.23%) in nighttime.

Generally, good correlations of these classes of compounds against K^+, CO, OC and EC_a were observed in day samples (Table 3), suggesting a major contribution from biomass burning. These compounds are possibly formed either through direct volatilization of plant materials, or as breakdown products of polysaccharides (Graham et al., 2002). Some of the sugars can also be produced by hydrolysis of the corresponding anhydrosugars under the acidic atmospheric conditions created by biomass burning. In nighttime samples, although concentrations of these compound classes are higher due to the shallow boundary layer, weak correlations were usually observed against biomass burning tracers. This can be interpreted by the enhanced contribution of biological particles such as bacteria, viruses, spores of lichens and fungi, small algae and protozoan cysts (Simoneit and Mazurek, 1981), or re-suspension of organic-rich soil particles (Simoneit at al., 2004), which all can become trapped in the shallow boundary layer at night. Bacteria, fungi, lower plants and invertebrates contain polyols, which serve as reserve of carbohydrate and/or cell protectants against stressful conditions (Eleutherio et al., 1993; Chaturvedi et al., 1997). Sugar and sugar alcohols accounted for 2.7% and 2.5% of the detected organic species in day and night samples respectively (Figure 6a and 6b).

3.5. Aromatic compounds

Hoffer et al. (2006) suggested for the same group of samples used in this study that TC (total carbon) and levoglucosan-normalized phenolic acids (syringic acid, vanillic acid and 4-hydroxybenzoic acid) may undergo chemical transformations in the aerosol phase,

possibly towards more refractory compounds (HULIS), based on the decrease in their ratios from the biomass burning to the transition period. Here, we focus on the absolute concentrations of this group of compounds. Syringyl compounds (syringic acid, syringaldehyde), vanillyl compounds (vanillic acid and vanillin), coumaryl compounds (4-hydroxybenzoic acid, 4-hydroxybenzaldehyde and 3, 4-dihydroxybenzoic acid) as well as 3-hydroxy benzoic acid and 4-methylbenzcatechin were determined in all day and night samples. Their concentrations were 77-550 ng m^{-3} (av. 190 ng m^{-3}) in daytime versus 210-940 ng m^{-3} (av. 520 ng m^{-3}) in nighttime (Table 2). Decesari et al. (2006) also reported these compounds for biomass burning period samples of the same campaign using different analytical protocols, giving a range of concentrations of 200-360 ng m^{-3}. Total aromatics accounted for 0.18-0.36% (av. 0.26%) of OC and 0.24-0.61% (av. 0.37%) of WSOC in daytime samples, and 0.3-0.67% (av. 0.48%) of OC and 0.51-1.2% (av. 0.81%) of WSOC in nighttime samples.

The combustion of hardwoods releases predominantly syringyl compounds, whereas softwood and grasses yield predominantly vanillyl and coumaryl compounds, respectively (Simoneit et al., 1993; Kjallstrand et al., 1998). On average, syringyl compounds in both day and night samples are higher by a factor of 1.6 and 2.3, respectively, than vanillyl compounds, suggesting the dominant combustion of hardwood, which is the typical vegetation of the tropical forests in Amazonia (Abas et al., 1995). The average concentrations of syringyl and vanillyl compounds are 1.7 and 1.1 times higher in daytime samples and 2.9 and 1.2 times higher in night samples than those of coumaryl compounds. This suggests that hardwood combustion is dominant, but that softwood and grass combustion also contribute, being consistent with the type of vegetation in Amazonia.

In general, all the aromatic compounds determined in daytime samples correlated better with biomass burning tracers and OC than those determined in nighttime samples, being similar to the sugar compounds. These aromatic compounds are probably derived from the combustion of lignin that constitutes 20-35% of the dry weight of wood. The organic compounds identified were observed to account for 3.6% and 5.2% of individually detected organic species in day and night samples, respectively (Figure 6a and 6b).

3.6. Diacids, oxoacids and dicarbonyls

We determined the concentrations of diacids and related compounds in the range of C_2-C_{11} in the aerosol particles collected during the intensive biomass burning period in Rondônia. Molecular distributions, loadings, and evidence for photo-production of diacids and related compounds in biomass burning aerosols will be reported in another paper (Kundu et al., 2009, Molecular distributions of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in biomass burning aerosols: Implications for photochemical production and degradation in smoke layer, submitted). Here, we focus only on the contributions of total diacids, oxoacids and dicarbonyls in bulk and detected molecular organics.

The mean contribution of total diacids-carbon to OC was 1.7% in the daytime versus 1.4% in the nighttime, while its contribution to WSOC was similar (2.3%) in the day- and night-time. The average percentage of total oxoacids to OC was 0.15% in the daytime versus 0.11% in the nighttime, while the percentage of total oxoacids to WSOC was 0.19% in the daytime and 0.18% in the nighttime. The average contribution of total dicarbonyls accounted for 0.07% and 0.09% to OC and WSOC, respectively, in the daytime versus 0.05% and 0.08% in the nighttime. Decesari et al. (2006) reported diacids in the range of C_2-C_9 and oxoacid (glyoxylic acid) in the aerosols collected during the dry period for the LBA-SMOCC campaign using four different analytical techniques, which

are different from ours. Using their analytical techniques, diacids accounted, on average, for 4.1-4.9% of OC (1.9-7.6% of WSOC). The contributions of total diacids, oxoacids and dicarbonyls were 41%, 3.4% and 1.2% in the daytime and 28.2%, 2.1% and 0.7% in the nighttime, respectively, of detected organic compounds in this study (Figure 6a and 6b).

3.7. Stable carbon isotopes of total carbon and nitrogen isotopes of total nitrogen

Particulate matter produced from the combustion of biomass is composed of the condensation products of gaseous compounds (emitted directly or secondarily produced) onto primary smoke particles or pre-existing aerosols (Cocks and McElroy, 1984) as well as the uplift of thermally altered plant debris (char) due to the turbulence of air masses during burning (Cachier et al., 1985; Lobert and Warnatz, 1993). The carbon and nitrogen isotopic signature of these particles will depend upon the relative importance of these two sources and the physical and chemical alterations that affect different carbon and nitrogen pools (cellulose, hemicellulose, lignin, wax, proteins, etc.) as a result of the combustion process.

The average value of $\delta^{13}C$ for TC in daytime samples was -25.5‰ with a range of -26.1 to -24.3‰, while it was -24.4‰ in night samples with a range of -25.2‰ to -23.6‰. The $\delta^{13}C$ values for consecutive day and night samples are significantly different (Figure 7). The average $\delta^{13}C$ value in aerosols collected from the C_3 plant dominated Santarém region of Brazil was reported to be -25.8±0.5‰ with a range of -26.9‰ to -24.9‰ (Martinelli et al., 2002).

The daytime $\delta^{13}C$ values of TC were lower than in the nighttime (Figure 7). One possible explanation for this clear diel cycle is that there are isotopic differences between the labile and refractory fractions within C_3 and C_4 vegetation relative to their bulk $\delta^{13}C$ values. Nadelhoffer and Fry (1988) have shown that the $\delta^{13}C$ of bulk leaf material is a

function of the fractional contributions of refractory compounds such as lipids and lignins and more labile (oxidizable) starches, proteins, sugars and holocellulose (the acid soluble fibers of the vegetation) each with their own $\delta^{13}C$ signals. Lipids and lignins tend to be depleted in ^{13}C content relative to the bulk leaf whereas starches, proteins, sugars, and holocellulose tend to be enriched in ^{13}C relative to bulk leaf. If the refractory carbon content contributes a greater fraction to TC in the daytime due to the prevalence of flaming phases of biomass burning, as indicated by the higher K^+/levoglucosan ratio than in nighttime, it is likely that daytime TC will be more depleted in ^{13}C than nighttime TC. The increase of the $\delta^{13}C$ after 20 September during the day can result from the accumulation of organic aerosols produced by nocturnal sources in the residual mixing layer, as already observed by Fuzzi et al. (2007).

We obtained a very good anti-correlation between $\delta^{13}C$ and TC for nighttime samples, but not for day samples (Figure 8). Wide varieties of volatile and semi-volatile organics (e.g., alkanes, alkenes, aldehydes, ketones, furans, esters, organic acids, polycyclic compounds, etc.) are emitted directly (Koppmann et al., 1997; Rudolph et al., 2000) or produced secondarily in the atmosphere during biomass burning. Rudolph et al. (2000) reported the kinetic isotope effect (KIE) associated with the reaction of several hydrocarbons including normal chain C_3-C_6 alkanes, alkenes, isoprene and ethyne with OH radicals. All measured KIEs are positive, that is, molecules containing only ^{12}C react faster than ^{13}C-containing molecules. On the other hand, we can say that products produced from the reactions between OH radicals and NMHC have a lower $\delta^{13}C$ than the reactants. Irei et al. (2006) reported that the $\delta^{13}C$ of secondary particulate organic matter produced from the OH-radical-induced reactions of toluene is lower by 5.8‰ than those of the parent toluene. Thus, volatile and semi-volatile organics produced secondarily (photochemically) from the products of biomass combustion should be depleted in ^{13}C. If

the condensation of volatile and semi-volatile organics on pre-existing particles were the major process in enhancing TC in aerosols, we should not observe an anti-correlation between $\delta^{13}C$ and TC. Our results suggest an enhanced contribution of TC from the labile fractions of organics (enriched with ^{13}C) in nighttime when the smoldering phases of biomass burning prevail, (Figure 4b).

The average $\delta^{15}N$ values of TN for day and night samples were 23.3±1.7‰ and 23.7±1.4‰, respectively, and are not statistically different. Our average $\delta^{15}N$ values in day and night samples are about 2 times higher than those in the atmospheric aerosols (11.5±2.1‰) collected from the Santarém region (Martinelli et al., 2002). This region is located in the northeast region of the Amazon basin, and is covered mostly by primary tropical rain forest although there are a few pasture areas. The reported average $\delta^{15}N$ value (10.6±2.8‰) in aerosol collected from Piracicaba during August 1999 to September 2000 is about 13‰ lower than our values as well (Martinelli et al., 2002). Piracicaba is located in São Paulo State, Brazil, in an area covered predominantly with C_4 plants.

To better understand the sources of aerosol carbon and nitrogen by using their isotopic compositions, it is mandatory to know whether or not a significant isotope fractionation occurs during the combustion process (Currie et al., 1999). If so, the extent of the fractionation has to be considered when particles and their sources are evaluated. Such a fractionation is very likely, because particles produced from combustion are composed of a wide variety of compound classes, and volatile compounds are condensed onto the existing particles and thermally altered plant debris (Turekian et al., 1998). Based on laboratory experiments, Turekian et al. (1998) reported that the $\delta^{13}C$ values of particles produced during combustion of C_3 plants (Eucalyptus sp. and Colospherum mopane) were approximately 0.5‰ higher than the unburned plant. On the other hand, the $\delta^{13}C$ of particles produced during the combustion of C_4 plants (Cenchris cilliarus, Antephora

pubesence, and Saccharum officinarum, sugarcane) were approximately 3.5‰ lower than the source. Another combustion experiment conducted under laboratory conditions (Currie et al., 1999) reported that the $\delta^{13}C$ values of particles were on average 0.5‰ lower than the unburned C_3 plants (pine and oak). These are relatively minor changes, however, compared with the large isotopic difference that exists between C_3 and C_4 plants. The isotopic fractionation of nitrogen during combustion was higher than that for carbon. Particles produced during biomass combustion showed higher $\delta^{15}N$ values by 5 and 7.8‰ than those of unburned C_3 and C_4 plants, respectively (Turekian et al., 1998).

The stable carbon and nitrogen isotopic compositions of soil in primary forest areas and C_3 vegetation tissues collected from the Amazon basin were reported by Martinelli et al. (2002). These values, along with the isotopic data for aerosols from this study and the isotopic data of the aerosol collected from Santarém, Brazil (Martinelli et al., 2002) are presented in Figure 9. Our nitrogen and carbon isotopic data show significant enrichment of ^{15}N and ^{13}C compared to vegetation tissues and soil from the Amazon basin, supporting that biomass burning rather than vegetation tissue debris and soil organics is the dominant contributor to our samples. Even applying the fractionation of 5‰, the $\delta^{15}N$ values of aerosols collected from Rondônia are still statistically different than the foliar and soil $\delta^{15}N$ values found in the region of the Amazon basin dominated by primary forest (Figure 9). Based on this difference, it is reasonable to hypothesize that soils are not an important source of organic matter to aerosol particles in Rondônia and that particles produced due to burning of the foliar tissues are much more important than direct emissions from unburned tissues. Atmospheric sources of nitrogen (e. g., NO_3^- from the oxidative reaction of NO_x that is directly produced from N_2 and O_2 inside the flame) do not affect the above hypothesis because the temperatures in biomass burning are not high

enough to cause significant NO_x production from air. As a result, almost all of the NO_x and NH_3 in biomass smoke comes from the fuel nitrogen.

Because Figure 9 suggests that biomass burning is the main contributor of TC in our aerosols, we can roughly calculate the relative contribution of C_3 and C_4 plants to TC by the following isotopic mass balance equation.

$$f_{TC-C3} = \frac{TC_{C3}}{TC_{aerosol}} \qquad f_{TC-C4} = \frac{1 - TC_{C3}}{TC_{aerosol}}$$

$$\delta^{13}C_{TC-aerosol} = f_{TC-C3} \times \delta^{13}C_{TC-C3} + f_{TC-C4} \times \delta^{13}C_{TC-C4}$$

In the equations above, f_{TC-C3} and f_{TC-C4} refer to a fraction TC from C_3 and C_4 plants in $TC_{aerosol}$, respectively, while $\delta^{13}C_{TC-aerosol}$, $\delta^{13}C_{TC-C3}$ and $\delta^{13}C_{TC-C4}$ stand for the stable carbon isotopic composition of aerosol particles, and tissues of C_3 and C_4 plants, respectively. The $\delta^{13}C_{TC-C3}$ and $\delta^{13}C_{TC-C4}$ values are assumed to be -31.5‰ and -13.5‰ based on the average $\delta^{13}C$ values found for leaves of C_3 and C_4 vegetations in the Amazon basin (Martinelli et al., 2002).

Based on the above equation, the average contribution of C_3 and C_4 plants to TC is 60% and 40%, respectively, suggesting a predominance of deforestation burning over pasture maintenance burning as sources of smoke aerosols during our experiment. The minimum and maximum contribution is 67% and 33%, and 54% and 46%, respectively (Figure 10). A higher contribution from C_3 plants to TC than from C_4 plants in daytime samples was observed, which can be interpreted as being due to the flaming phase of biomass combustion in the daytime. Higher K^+/levoglucosan ratio in the daytime than in the nighttime (Figure 4b) provides evidence that the flaming phase of combustion is more important in daytime.

4. Conclusion

Day- and night-time aerosols collected during intensive biomass burning at the FNS site in Rondônia, Brazil, under the framework of the LBA-SMOCC campaign were investigated for water-soluble inorganic ions, organics (bulk and molecular) and the stable carbon and nitrogen isotopic composition of total carbon (TC) and total nitrogen (TN). Based on the day- and night-time variations of different chemical species, we provide clear evidence for the chemical evolution of smoke aerosols. As the ability of organic-rich biomass burning particles to act as cloud condensation nuclei (CCN) depends upon their molecular composition, we extended our efforts to speciate different classes of organic compounds including anhydrosugars, sugars/sugar alcohols, aromatics, diacids, oxoacids and dicarbonyls. We are able to speciate only 4-7.5% of OC (5-13% of WSOC), indicating that more efforts are needed in order to understand the complex molecular composition of biomass burning aerosols. Stable carbon isotopes of TC were found as very effective tools for understanding the biomass burning mechanism, as different pools of organics in biomass have different isotopic signatures and are combusted at different temperatures. Stable carbon and nitrogen isotopic compositions of TC and TN also provide additional information about the sources of aerosols and the isotopic fractionation that happens during biomass burning. This study showed that the $\delta^{15}N$ value of aerosol particles produced from field biomass burning was higher than that of aerosol particles produced from biomass burning experiments in the laboratory.

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Table

Table 1. Concentrations (ng m^{-3}) of water-soluble inorganic ions in atmospheric aerosols collected during the intensive biomass burning period (16-26 September 2002) under the framework of the LBA-SMOCC campaign at the FNS site in Rondônia, Brazil.

	Day samples (n=6)		**Night samples (n=9)**		**Total (n=15)**	
Species	**Mean[b]**	**Median**	**Mean[b]**	**Median**	**Mean[b]**	**Median**
F^-	110±50	95	154±18	157	135±41	139
MSA^{-a}	420±122	420	290±99	290	340±122	330
Cl^-	57±17	51	200±98	196	144±105	94
NO_2^-	168±126	192	148±193	33	156±165	69
NO_3^-	800±580	570	3010±1060	2930	2130±1420	1910
SO_4^{2-}	2690±300	2570	2780±370	2810	2740±340	2740
Na^+	2370±1030	1800	2740±97	2740	2590±650	2720
NH_4^+	1040±123	1030	1410±610	1440	1260±510	1120
K^+	1500±800	1030	2410±350	2420	2040±710	2080
Ca^{2+}	80±67	53	115±27	114	101±48	106
Mg^{2+}	38±25	32	33±17	30	35±20	30

[a]Methanesulfonate ion ($CH_3SO_3^-$)

[b]Standard deviation (±1 SD)

Table

Table 2. Concentrations of bulk organics and organic compounds in the atmospheric aerosols ($PM_{2.5}$) collected during the intensive biomass burning period (16-26 September 2002) from Rondônia, Brazil (BDL: below detection limit).

	Day samples (n=6)			Night samples (n=9)		
Component	**Range**	**Mean**	**Median**	**Range**	**Mean**	**Median**
Bulk organics (μg m^{-3})						
EC	0.6-3.6	2.1	1.9	1.7-3.3	2.6	2.6
OC	19.5-86.4	39.7	26.1	32.4-83.9	60.9	60.1
WSOC	18.4-51	26.2	21.5	22.2-45.6	35.8	35.9
Anhydrosugars (ng m^{-3})						
Levoglucosan	850-7310	2550	1593	2510-8790	5650	5500
Galactosan	18.7-110.5	39.7	21.4	62.8-215	134.5	119.6
Mannosan	37.8-288.5	97.4	55.4	85.6-385	235.5	206
Subtotal		**2687**	**1669**		**6020**	**5826**
Sugars (ng m^{-3})						
Fructose	12.5-33	19.9	17.4	20.5-49.3	27.3	24.6
Sucrose	3.6-12.2	7.8	8.4	1.4-5.7	3.8	3.5
Subtotal		**28**	**26**		**31**	**28**
Sugar alcohols (ng m^{-3})						
Glycerol	7.3-17.2	10.2	9.0	11.5-39.8	21.2	21.6
Threitol	1.5-24.9	7.7	4.8	7.5-26.7	18.2	19.7
Erythritol	22.1-44.9	30.3	28.6	20.6-172.7	86	83.2
Arabitol	10-43.7	21.6	19.6	25.9-63.9	45.3	46.9
Mannitol	8.3-38.4	20.9	20.1	17.9-49.6	33.1	34.9
Sorbitol	0.4-1.5	0.8	0.8	0.5-2.1	1.2	1.2
Inositol	0.7-2.3	1.2	1	BDL-1.7	1.1	1.1
Subtotal		**93**	**84**		**206**	**209**
Aromatic compounds (ng m^{-3})						
4-Methylbenzcatechin	1.2-6.1	2.6	2.1	3.5-18.5	8.7	7.7
4-Hydroxybenzaldehyde	0.7-6.6	2.8	1.6	2.8-17.8	7.3	5.6
3-Hydroxybenzoic acid	3.1-21.4	7.2	4.1	7.9-25.1	16.3	15.1
4-Hydroxybenzoic acid	16.7-80	31.8	21.6	38.3-137.8	77.2	70.5
3, 4-Dihydroxybenzoic acid	25.8-121	48.6	33	29.2-105.9	65.6	67.6
Vanillin	1.4-9.9	4.1	3.1	11-30.7	17.4	13.1
Vanillic acid	13.8-106	33.6	18.5	37.6-151.1	85.6	67.3
Syringaldehyde	6.9-48	20.6	18.3	28.9-240	119.6	75.5
Syringic acid	7.6-147	39.7	22.9	48.1-216.3	121.5	109.1
Subtotal		**191**	**125**		**519**	**432**

Table

Table 3. Regression coefficients (R^2) for concentrations of anhydrosugars, sugars, sugar alcohols and aromatic compounds against potassium (K^+), carbon monoxide (CO), organic carbon (OC) and elemental carbon (EC) in the atmospheric aerosols collected in day- and night-time during the intensive biomass burning period (16-26 September 2002) from Rondônia, Brazil under the framework of the LBA-SMOCC campaign.

	K^+		CO		OC		EC	
Compound	**Day**	**Night**	**Day**	**Night**	**Day**	**Night**	**Day**	**Night**
				Anhydrosugars				
Levoglucosan	0.94	0.78	0.99	0.95	0.97	0.83	0.61	0.58
Galactosan	0.96	0.78	0.98	0.89	0.97	0.78	0.59	0.42
Mannosan	0.93	0.82	0.99	0.94	0.95	0.86	0.55	0.53
				Sugars/Sugar alcohols				
Fructose	0.97	-0.24	0.88	-0.36	0.96	-0.50	0.77	-0.42
Sucrose	0.76	0.41	0.64	0.75	0.75	0.51	0.74	0.56
Glycerol	0.94	0.33	0.93	0.28	0.93	0.30	0.48	0.30
Threitol	0.91	0.42	0.99	0.80	0.94	0.54	0.56	0.28
Erythritol	0.71	0.57	0.46	0.57	0.69	0.53	0.92	0.003
Arabitol	0.89	0.44	0.97	0.63	0.93	0.50	0.58	0.52
Mannitol	0.80	0.02	0.88	0.40	0.87	0.16	0.71	0.32
Sorbitol	0.90	-0.10	0.92	0.25	0.94	0.07	0.75	0.30
Inositol	0.87	0.37	0.93	0.64	0.87	0.43	0.35	0.25
				Aromatic compounds				
4-Methylbenzcatechin	0.86	0.36	0.92	0.57	0.87	0.37	0.34	0.22
4-Hydroxybenzaldehyde	0.34	0.70	0.38	0.55	0.30	0.61	-0.31	0.31
3-Hydroxybenzoic acid	0.92	0.87	0.99	0.94	0.94	0.87	0.51	0.57
4-Hydroxybenzoic acid	0.95	0.76	0.98	0.77	0.96	0.75	0.58	0.48
3, 4-Dihydroxybenzoic acid	0.93	0.83	0.99	0.62	0.95	0.87	0.55	0.73
Vanillin	0.80	0.46	0.92	0.52	0.84	0.49	0.37	0.23
Vanillic acid	0.92	0.85	0.99	0.93	0.94	0.85	0.51	0.48
Syringaldehyde	0.86	0.75	0.85	0.91	0.84	0.80	0.34	0.39
Syringic acid	0.88	0.68	0.98	0.89	0.91	0.71	0.47	0.39

Figure captions

Figure 1. Sampling location of the LBA-SMOCC campaign at the FNS (Fazenda Nossa Senhora Aparecida) site in Rondônia, Brazil. The star indicates the FNS site. Horizontal and vertical transport along 3-days air mass back trajectories for each filter sample are also shown in the upper and lower panels, respectively. Green and blue lines are the trajectories of the day and night samples, respectively. Solid red circles represent the fire spots in Brazil during our sampling period (16-26 September 2002). Air mass trajectories were drawn using the HYSPLIT model. Fire location data are from http://dup.esrin.esa.int/ionia/wfa.

Figure 2. Pie diagrams showing the mean relative abundances of water-soluble inorganic anions (a, b) in total anions, and cations (c, d) in total cations for day and night samples. The relative abundances of cations and anions are calculated based on the mass concentrations (μg m^{-3}).

Figure 3. Diurnal variations in (a) potassium (K^+), (b) levoglucosan and (c) apparent elemental carbon (EC_a) normalized by mass concentrations of sulfate (SO_4^{2-}), nitrate (NO_3^-), MSA ($CH_3SO_3^-$) and ammonium (NH_4^+). Daytime samples were collected from ~7:45 to ~17:45 (LT, local time) while nighttime samples from ~18:30 to 7:00 LT.

Figure 4. Diurnal variations of (a) MSA^-/SO_4^{2-} and (b) K^+/levoglucosan ratios in the biomass burning aerosols from Rondônia during 16-26 September 2002.

Figure 5. Relation of total anhydrosugars against (a) CO, (b) K^+, (c) OC and (d) EC for day and night samples. The error bars represent one standard deviation.

Figure 6. Pie diagrams showing the relative abundances of different organic compound classes detected in (a) day and (b) night samples. The relative abundances of individual compound classes are calculated based on the mass concentrations (ng m^{-3}).

Figure 7. Diurnal variations of $\delta^{13}C$ values of total carbon (TC) and TC in biomass burning aerosols collected during 16-26 September 2002.

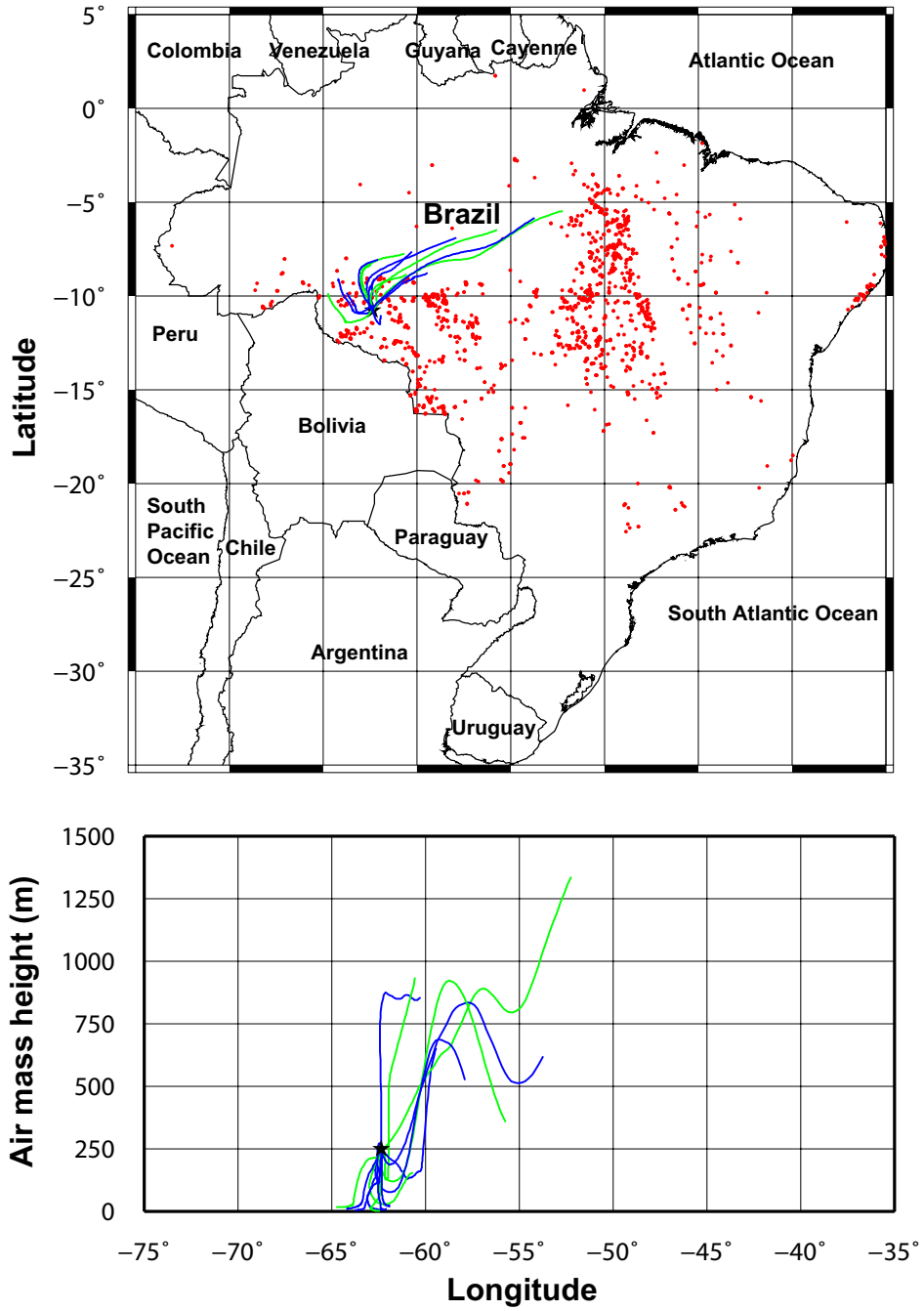
Figure 8. Relation between the concentrations of total carbon (TC) and $\delta^{13}C$ values of biomass burning aerosols. One nighttime sample has been excluded as no analytical results are available.

Figure 9. $\delta^{13}C$ versus $\delta^{15}N$ for the aerosol particles collected in this study and for aerosol particles collected from Santarém, Brazil (Martinelli et al., 2002) along with soil and vegetation tissues (Martinelli et al. (2002). "Aerosol-fractionation" means that $\delta^{13}C$ and $\delta^{15}N$ values of 0.5‰ and 5‰ respectively have been subtracted from each sample. These values represent the amount of positive isotopic fractionation between biomass burning particles and plant tissues from which particles are produced by combustion (Turekian et al., 1998).

Figure 10. Contribution of C_3 and C_4 plants to total carbon (TC) in biomass burning aerosols.

Figure

Figure 1.



Figure

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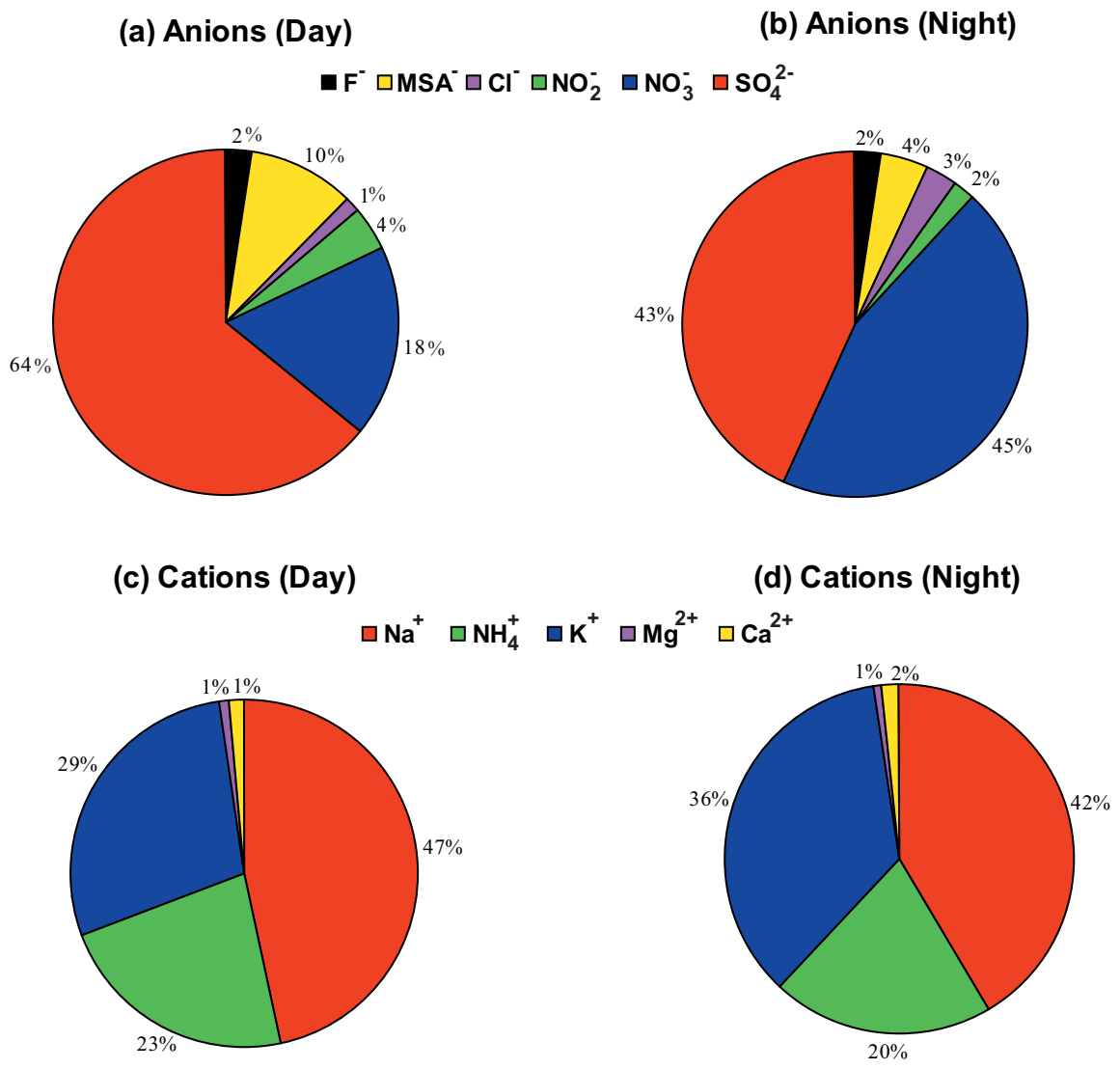

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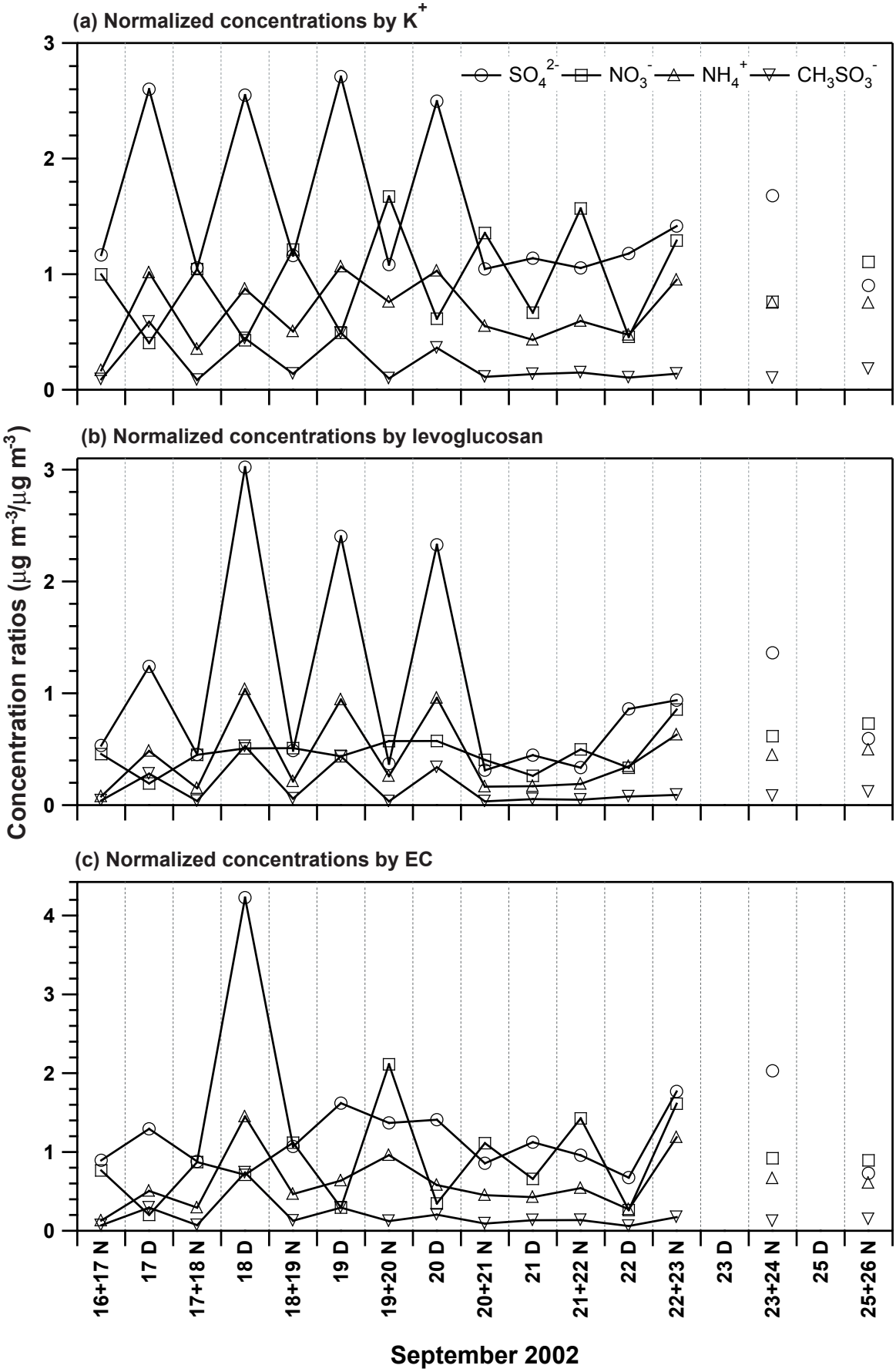

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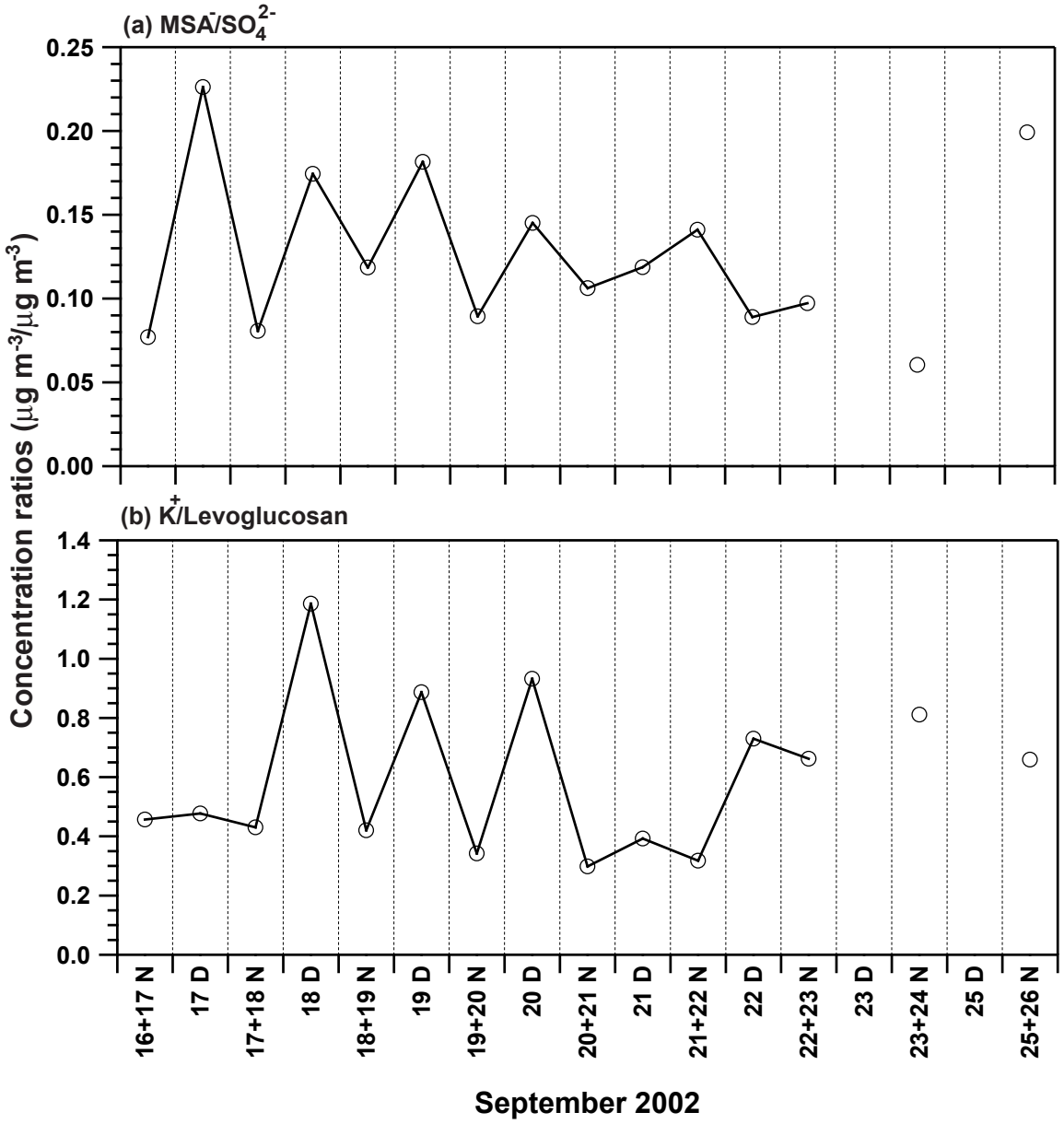

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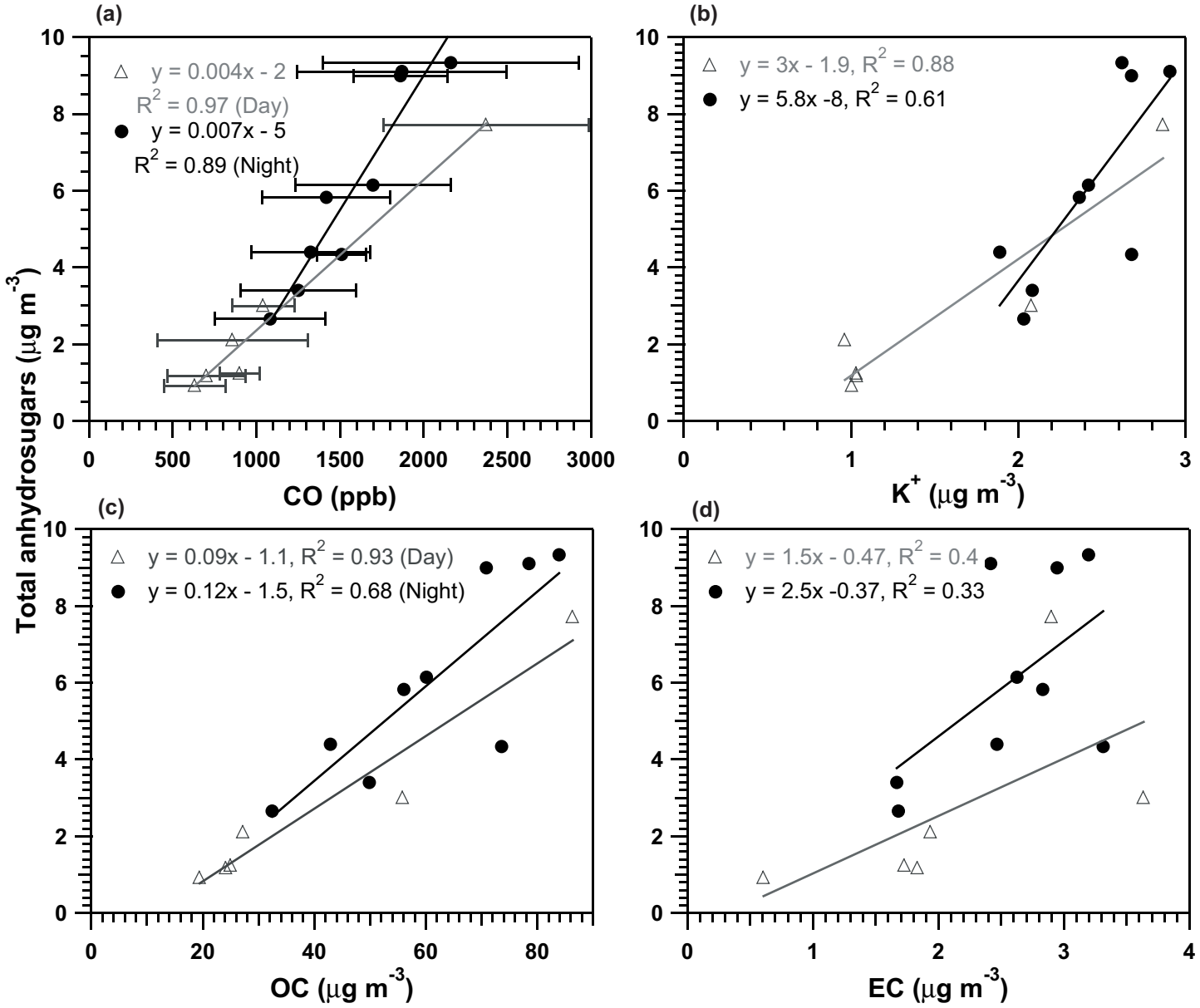

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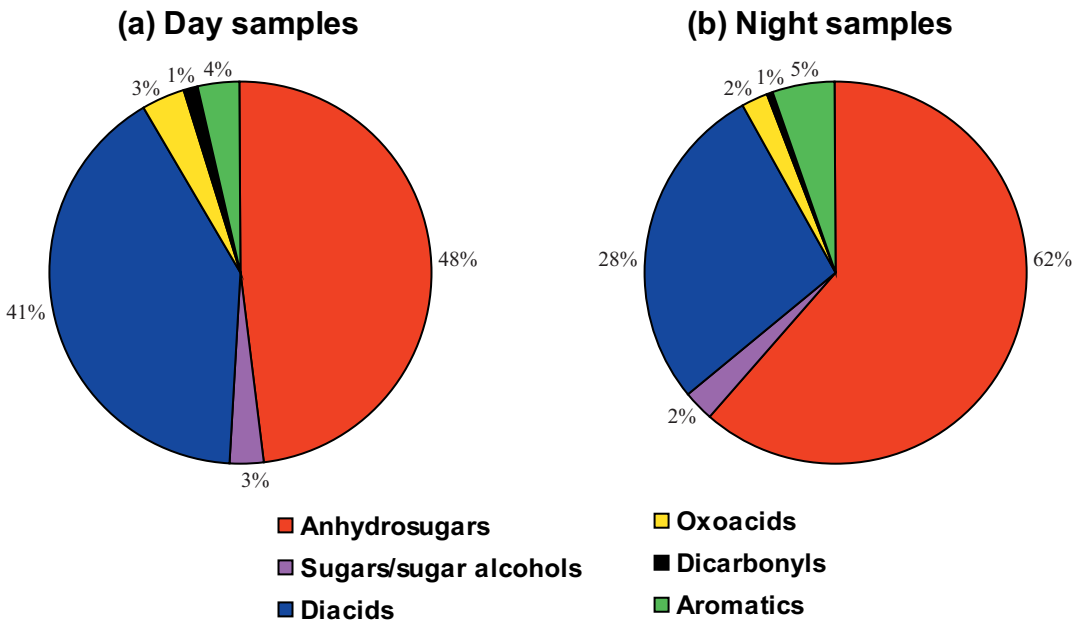

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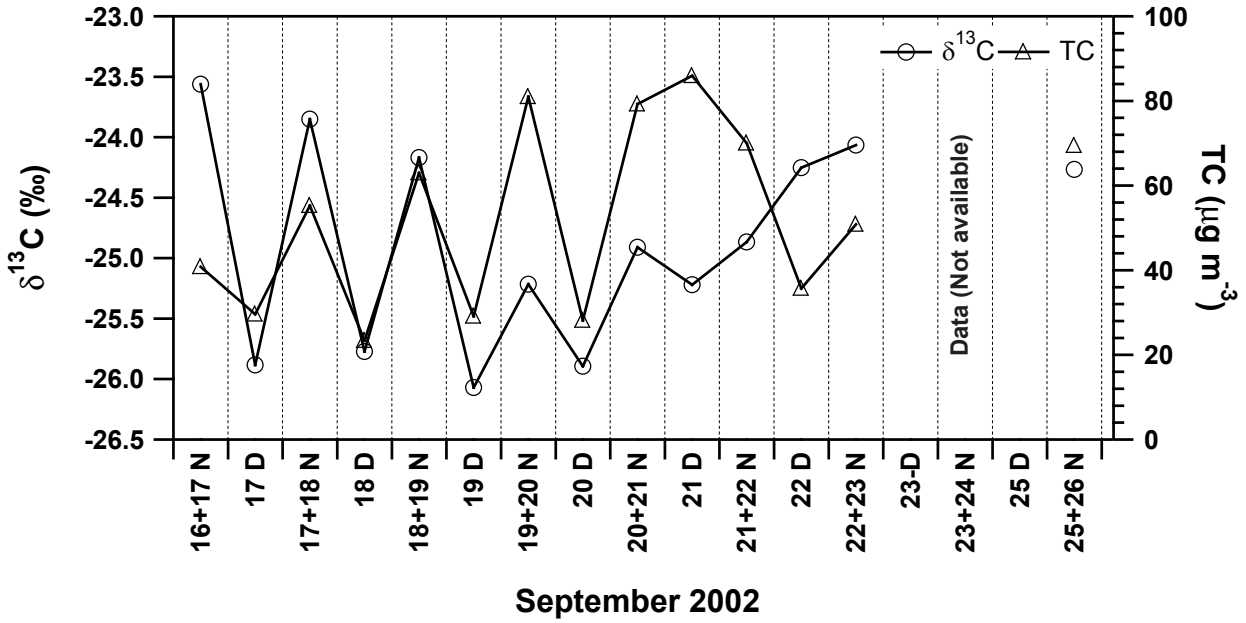

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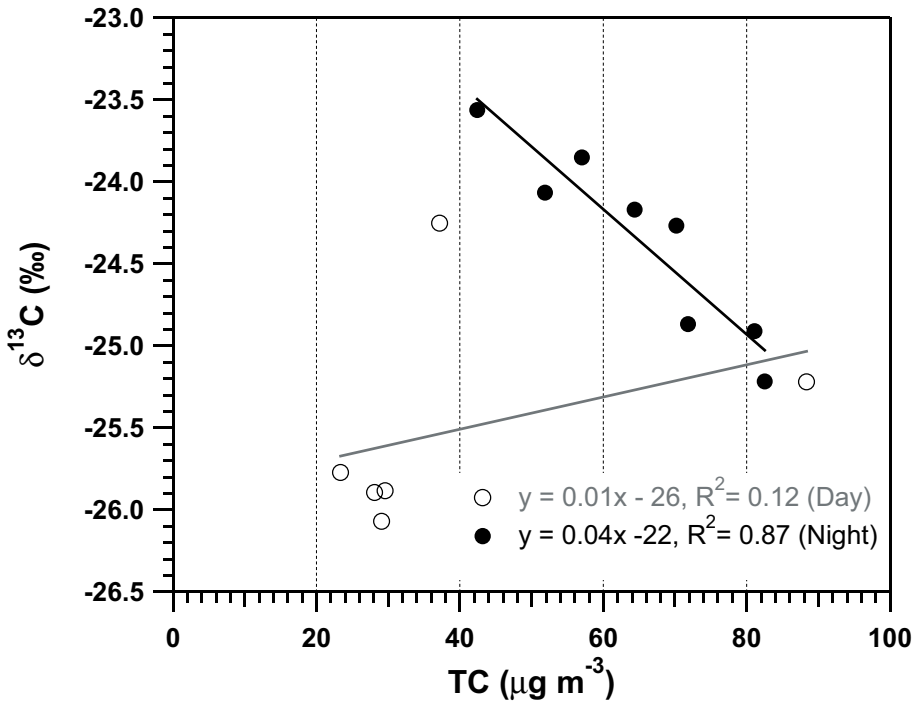

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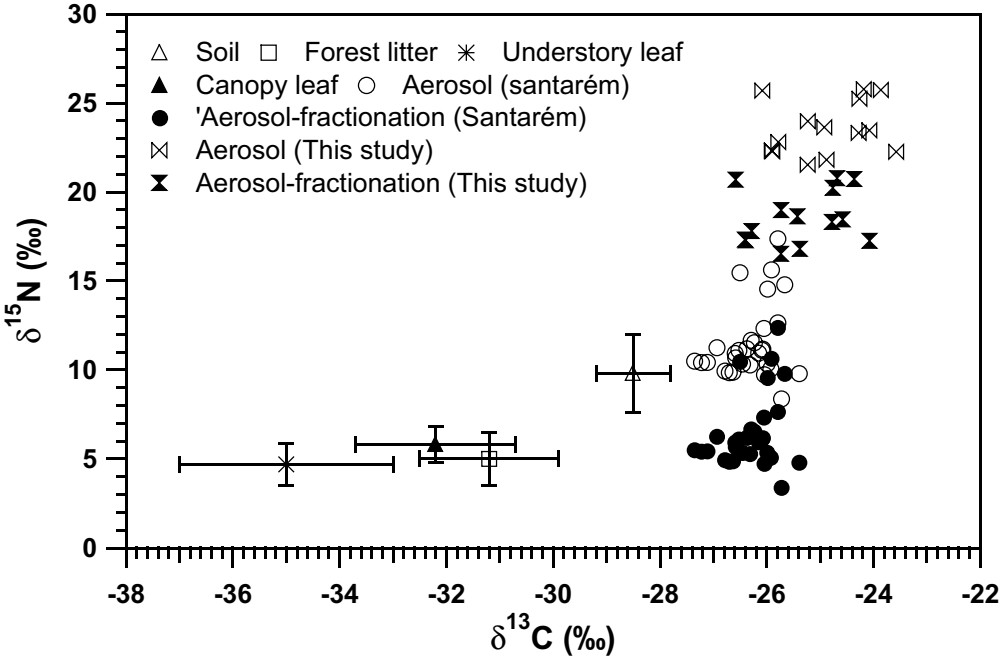

Figure

Figure 10.