



Title	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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1 **Diurnal variation in the water-soluble inorganic ions, organic carbon and isotopic**  
2 **compositions of total carbon and nitrogen in biomass burning aerosols from the**  
3 **LBA-SMOCC campaign in Rondônia, Brazil**

4

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27 **Abstract**

28           Aerosol particles (PM<sub>2.5</sub>) were collected during the day (n=6) and nighttime (n=9)  
29 from a tropical pasture site in Rondônia, Brazil during an intensive biomass burning  
30 period (16-26 September, 2002). Higher normalized (by K<sup>+</sup>, levoglucosan, or apparent  
31 elemental carbon, EC<sub>a</sub>) mass concentrations of SO<sub>4</sub><sup>2-</sup> and CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> in daytime suggest  
32 their photochemical production, while the opposite trend for NO<sub>3</sub><sup>-</sup> suggests its transfer to  
33 the aerosol phase at lower temperatures and higher humidities, as well as possibly  
34 production through hydrolysis of N<sub>2</sub>O<sub>5</sub> on aqueous aerosol particles. About 4.2-7.5% of  
35 OC (5-13% of water-soluble organic carbon (WSOC)) could be characterized at the  
36 molecular level using GC-MS and GC-FID. Among the detected organic compound  
37 classes, the relative abundances of anhydrosugars and aromatics were higher in night  
38 samples, but sugars/sugar alcohols, diacids, oxoacids and α-dicarbonyls were more  
39 abundant in day samples. Consecutive day and night samples showed that δ<sup>13</sup>C values of  
40 total carbon (TC) were lower in daytime samples, which can be interpreted as resulting  
41 from higher contributions of refractory TC depleted in <sup>13</sup>C due to predominantly flaming  
42 combustion. The δ<sup>15</sup>N values of total nitrogen (TN) ranged from +23.5‰ to +25.7‰,  
43 however, there was no trend in day and night samples. Higher values of δ<sup>13</sup>C and δ<sup>15</sup>N for  
44 biomass burning particles than those of unburned vegetation reflect positive isotopic  
45 enrichment either during the formation of particles or after the emission of particles in the  
46 atmosphere.

47

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

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## 52 **1. Introduction**

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

60           Carbonaceous materials in biomass burning aerosols constitute as much as 70-90%  
61 of total aerosol mass (Andreae and Crutzen, 1997; Yamasoe et al., 2000; Fuzzi et al.,  
62 2007). About 45-75% of the carbonaceous material represents water-soluble organic  
63 carbon (WSOC) (Graham et al., 2002; Mayol-Bracero et al., 2002a; Decesari et al., 2006).  
64 This suggests that the emission of WSOC from biomass burning is regionally and globally  
65 important. The significant fraction of WSOC in smoke aerosols (Mayol-Bracero et al.,  
66 2002b) can take up water vapor from the atmosphere and affect the light absorption  
67 efficiency (Redemann et al., 2001). The WSOC in biomass burning particles contributes to  
68 the cloud condensation nuclei (CCN) activity (Roberts et al., 2002; Andreae et al., 2004)  
69 and may also participate in aqueous phase chemical reactions occurring in droplets  
70 nucleated by smoke particles.

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

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

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

88 Stable carbon and nitrogen isotopic composition of total carbon (TC) and total  
89 nitrogen (TN) of aerosols from the LBA-SMOCC biomass burning experiment have not  
90 reported, although comprehensive investigations on the chemical composition and  
91 physical properties of aerosols are available in the literature (Fuzzi et al., 2007 and  
92 references therein). The  $\delta^{13}\text{C}$  of bulk organic carbon has been successfully used to better  
93 understand the contributions of marine and continental sources to aerosol carbon  
94 (Chesselet et al., 1981; Cachier et al., 1986, 1989; Narukawa et al., 1999, 2008; Martinelli  
95 et al., 2002; Turekian et al., 2003; Kawamura et al., 2004; Kelly et al., 2005; Ho et al.,  
96 2006; Huang et al., 2006). Stable carbon and nitrogen isotopic ratios in biomass burning  
97 aerosols have not previously been studied extensively. They can provide information not  
98 only on the origin and biomass burning mechanisms, but also on the isotopic fractionation  
99 that is likely during biomass burning and after the emission of particles in the atmosphere.

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

109

## 110 **2. Instrumentation and methods**

### 111 *2.1. Site description and aerosol sampling*

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

116 Aerosol sampling procedures have been described in detail elsewhere (Solomon et  
117 al., 1983; Hoffer et al., 2006). Briefly, fine aerosol particles (PM<sub>2.5</sub>) were collected on pre-  
118 combusted (~10 h at 600 °C) Pallflex quartz fiber filters using a dichotomous virtual  
119 impactor (Solomon et al., 1983) mounted on a 10 m high tower. Daytime samples (n=6)  
120 were collected from ~7:45 to ~17:45 LT (local time) and nighttime samples (n=9) from  
121 ~18:30 to ~7:00 LT. The aerosol filters were placed in pre-baked (~10 h at 600 °C) glass  
122 jars and stored in a freezer at -20 °C at the Max Planck Institute for Chemistry in Mainz,  
123 Germany. Small fractions of the filter discs were wrapped in pre-baked thick aluminum  
124 foil and transported to our laboratory in Sapporo, Japan. Filter discs were transferred into

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

127

## 128 2.2. Analytical Methods

129 For the water-soluble inorganic ion and WSOC measurements, aliquots of the filter  
130 samples were extracted with Milli Q water. One part was used for the analyses of  
131 inorganic ions using a Metrohm 761 ion chromatography (IC) system (Metrohm, Herisau,  
132 Switzerland). Anions were separated on a Shodex SI-90 4E column with 1.8 mM Na<sub>2</sub>CO<sub>3</sub>  
133 and 1.7 mM NaHCO<sub>3</sub> (Kanto Chemical, Japan) as eluent, and cations on a Shodex YK-  
134 421 column with 4 mM H<sub>3</sub>PO<sub>4</sub> as eluent (Kanto Chemical, Japan). The injection loop  
135 volume was 200 µl. Both cations and anions were quantified against a standard calibration  
136 curve. Another part of the filtered water extract was acidified with 1.2 M HCl and purged  
137 with pure air in order to remove dissolved inorganic carbon and volatile organics, and then  
138 WSOC was measured with a carbon analyzer (Shimadzu, TOC-5000). The reproducibility  
139 for WSOC measurements using a laboratory standard was 10%.

140 The concentrations of organic carbon (OC) and apparent elemental carbon (EC<sub>a</sub>)  
141 were measured using a semi-continuous OC/EC analyzer (Sunset Laboratory Inc.,  
142 Portland, OR, USA). For a discussion and definition of EC<sub>a</sub> see the review paper by  
143 Andreae and Gelencsér (2006). Aliquots of the sample filters (diameter 11 mm) were  
144 mounted into the oven port using a flat-faced forceps. The oven temperature was  
145 programmed as follows: under He, at 250 °C for 2 min, at 450 °C for 2 min and at 550 °C  
146 for 2 min, then under He with 10% O<sub>2</sub>, at 550 °C for 2 min, at 700 °C for 2 min and at 870  
147 °C for 3.5 min. The carbon content of the sample that evolves to CO<sub>2</sub> between 250 °C and  
148 700 °C was defined as OC, and that which is combusted between 700 °C and 870 °C as  
149 EC<sub>a</sub>.

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  $\mu$ l of pyridine and 50  $\mu$ l 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<sup>2</sup>) 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<sub>2</sub>). The N<sub>2</sub> and CO<sub>2</sub> derived during this process were isolated on-line using a gas



175 chromatograph and then measured with a thermal conductivity detector. Aliquots of the N<sub>2</sub>  
 176 and CO<sub>2</sub> gases were then introduced into an isotope ratio mass spectrometer  
 177 (ThermoQuest, Delta Plus) through an interface (ThermoQuest, ConFlo II). The isotopic  
 178 composition of δ<sup>13</sup>C and δ<sup>15</sup>N was determined using the following standard isotopic  
 179 conversion equations (1) and (2), respectively:

$$180 \quad \delta^{13}\text{C} (\text{‰}) = \left[ \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right] \times 1000 \quad (1)$$

$$181 \quad \delta^{15}\text{N} (\text{‰}) = \left[ \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} - 1 \right] \times 1000 \quad (2)$$

182 Acetanilide was used as an external standard to determine TC, TN and their  
 183 isotopic ratios. The reproducibility for TC, TN, and their stable isotopes for the LBA-  
 184 SMOCC samples could not be determined due to a lack of sample materials. But, the  
 185 reproducibility in our laboratory of TC and TN in atmospheric aerosol samples collected  
 186 from different parts of the world ranged between 0.7-9% (av. 2.5%) and 1.4-4.8% (av.  
 187 3%), whereas standard deviations of δ<sup>13</sup>C and δ<sup>15</sup>N measurements ranged between 0.08-  
 188 0.24‰ (av. 0.12‰) and 0.03-0.45‰ (av. 0.13‰).

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

193

### 194 **3. Results and discussion**

#### 195 *3.1. Atmospheric conditions during the sampling period*

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

198 °C (av. 24.2 °C) at nighttime. The boundary layer in daytime was very well mixed with an  
199 average height of  $1690\pm 250$  m, whereas the nocturnal boundary layer decreased to 200-  
200 250 m (Fuzzi et al., 2007). Many active fires were observed in the province of Rondônia,  
201 where our sampling site is located, as well as in other adjacent and distant provinces of  
202 Brazil (Figure 1, upper panel). The values of relative humidity in day- and night-time were  
203 about 70% and 100%, respectively. Three-dimensional backward air mass trajectories at  
204 250 m agl (above ground level), used for explaining the compositional and isotopic  
205 variations, were drawn using the Hybrid Single-Particle Lagrangian Integrated Trajectory  
206 (HYSPLIT) model (Draxler et al., 2006). Horizontal transport of 3-day air mass back  
207 trajectories for day and night samples indicates that air masses at our sampling site are  
208 mainly influenced by air masses transported from Rondônia and its neighbor provinces  
209 (Figure 1, upper panel). The vertical trajectories show that the air masses were usually  
210 transported within the boundary layer (Figure 1, lower panel).

211

### 212 3.2. Water-soluble inorganic ions

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

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

223 biomass combustion. The average relative abundance of  $\text{SO}_4^{2-}$  is about 50% higher in day  
224 samples than in night samples, being consistent with daytime versus nighttime variations  
225 of  $\text{SO}_2$ , from which  $\text{SO}_4^{2-}$  is mainly produced. Trebs et al. (2004) observed a higher  
226 mixing ratio of  $\text{SO}_2$  in daytime than in nighttime during our aerosol collection time at the  
227 FNS site in Rondônia. A higher abundance of  $\text{SO}_4^{2-}$  in daytime aerosols can be explained  
228 by enhanced chemical production as well as the transfer of  $\text{SO}_4^{2-}$  from the free troposphere  
229 to the boundary layer due to turbulent mixing in daytime. The main explanation for higher  
230 concentrations of  $\text{NO}_3^-$  at nighttime is that humidity is higher and temperature lower,  
231 which thermodynamically favors the reaction between gaseous  $\text{NH}_3$  and  $\text{HNO}_3$  to form  
232 aerosol nitrate. This logic can be strongly substantiated by the observed lower mixing ratio  
233 of  $\text{HNO}_3$  at nighttime during our sampling period at the FNS site (Trebs et al., 2004). The  
234 higher concentration and relative abundance of  $\text{NO}_3^-$  in nighttime aerosols also suggests  
235 that  $\text{NO}_3^-$  production due to the reactions of  $\text{HNO}_3$  and hydrolysis of  $\text{N}_2\text{O}_5$  on aqueous  
236 aerosol particles in nighttime may be more pronounced than in daytime during the biomass  
237 burning period in Amazonia.

238 Both the mass concentration and relative abundance of  $\text{CH}_3\text{SO}_3^-$  ( $\text{MSA}^-$ ) is 1.4 and  
239 2.5 times, respectively, higher in day samples than night samples (Figure 2a and 2b),  
240 suggesting the enhanced chemical production of this species from its precursors  
241 (dimethylsulphide and methylmercaptan).  $\text{MSA}^-$  can also be emitted directly from biomass  
242 burning (Andreae and Andreae, 1988).  $\text{NO}_2^-$  in aerosols is produced from its gaseous  
243 precursor  $\text{HNO}_2$ , which is derived from the heterogeneous reactions of  $\text{NO}_2$  with surface  
244 moisture (Kleffman et al., 2003). This reaction should be favorable in the nighttime at our  
245 sampling site due to high nighttime humidity. A higher concentration, or relative  
246 abundance, of  $\text{NO}_2^-$  in aerosols at nighttime was expected, but the opposite was observed  
247 (Table 1, Figure 2a and 2b). Alternatively, due to rapid photo-production and subsequent

248 photolysis of  $\text{HNO}_2$  in the daytime (Harrison et al., 1996),  $\text{NO}_2^-$  in the aerosol phase  
249 should not be higher. The higher concentration of  $\text{NO}_2^-$  we found in daytime aerosols  
250 suggests that complete depletion of  $\text{HNO}_2$  did not occur in the daytime in the Amazon  
251 Basin. HCl is known to be emitted directly from biomass fires, accounting for a large  
252 fraction of total emitted chlorine (Andreae et al., 1996). The higher mass concentration  
253 and relative abundance of aerosol  $\text{Cl}^-$  observed in nighttime samples (Table 1, Figure 2b)  
254 can be explained by the expansion and dilution of the boundary layer in the daytime due to  
255 turbulent mixing, and an enhanced condensation/dissolution/chemical reaction of gaseous  
256 HCl on aerosol surfaces at night under the conditions of lower temperature, high humidity,  
257 and stable thermal stratification.

258 Ammonium ( $\text{NH}_4^+$ ) in aerosol is produced from the reaction between  $\text{NH}_3$  and  
259 acidic species present in either the gas or aerosol phase. Trebs et al. (2004), using a wet-  
260 annular denuder and a Steam-Jet aerosol collector followed by on-line flow injection  
261 analysis (Wyers et al., 1993) during the same campaign at the FNS site, reported that  $\text{NH}_3$   
262 started to increase in the early morning (07:00 to 10:00) followed by the usual decrease  
263 during the rest of a day. This trend was interpreted as being due to the re-evaporation of  
264 deposited  $\text{NH}_3$  from wet surfaces (grass leaves) as the temperature began to increase. In  
265 our study, we have observed slightly higher relative abundances of  $\text{NH}_4^+$  in daytime than  
266 in nighttime samples (Figure 2c and 2d), suggesting that diel variations of  $\text{NH}_3$  and  
267 increased availability of  $\text{H}_2\text{SO}_4$  due to daytime photo-production influence  $\text{NH}_4^+$   
268 formation. Potassium ( $\text{K}^+$ ) showed slightly higher relative abundances in night samples  
269 (Figure 2c and 2d). We have observed higher relative abundance of  $\text{Na}^+$  (Figure 2c and 2d)  
270 in both day and night samples. Such a large contribution was not reported in the previous  
271 studies on the same experiment. Although the concentration of  $\text{Na}^+$  in field blank samples

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

274 Potassium, levoglucosan and  $EC_a$  are considered to be conservative tracers for  
275 biomass burning. Variations in potassium, levoglucosan and  $EC_a$ -normalized diel mass  
276 concentrations for inorganic secondary aerosols ( $SO_4^{2-}$ ,  $NO_3^-$ ,  $MSA^-$  and  $NH_4^+$ ) are  
277 presented in Figure 3. Higher normalized mass concentrations for  $SO_4^{2-}$ ,  $MSA^-$  and  $NH_4^+$   
278 were observed in daytime (Figure 3), further suggesting the enhanced photo-production of  
279 the sulfur species and consequent uptake of  $NH_3$ . In contrast, normalized mass  
280 concentrations for  $NO_3^-$  showed the opposite trend (Figure 3) suggesting transfer of  
281 gaseous  $HNO_3$  into the aerosol phase at lower temperatures and higher humidities at night,  
282 as well as possible  $NO_3^-$  production through nighttime chemistry in Amazonia. Fuzzi et al.  
283 (2007) observed similar diurnal variation for the ratio of  $SO_4^{2-}/K^+$  and  $NO_3^-$  for size-  
284 segregated biomass burning samples of the same campaign collected by different  
285 impactors.

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

292 A clear diel variability was also observed for the  $K^+/levoglucosan$  ratio (Figure  
293 4b). Gao et al. (2003) found a  $K^+/levoglucosan$  ratio of 33.3 during the flaming phase, and  
294 lower ratios (0.2-0.6) for the smoldering phase in savanna fires. A higher ratio during  
295 intensive biomass burning in summer and a lower one in winter at Aveiro, Portugal has  
296 been reported (Pio et al., 2008). Thus, the relatively higher  $K^+/levoglucosan$  ratio in

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

302

### 303 3. 3. *Anhydrosugars*

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

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

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

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

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

350         The carbon content of levoglucosan, the most abundant anhydrosugar, accounts for  
351 1.9-3.8% (av. 2.6%) of OC in daytime versus 2.5-5.3% (av. 4%) in nighttime, while it  
352 accounts for 2-6.4% (av. 3.8%) of WSOC in daytime versus 4.1-9.1% (av. 6.9%) in  
353 nighttime, being comparable to values (0.1-10% of OC and 0.2-16% of WSOC) of  
354 biomass burning aerosols of the LBA-SMOCC campaign (Decesari et al., 2006) and  
355 similar to values (1-6% of TC and 2-8% of WSOC) reported for the aerosol samples  
356 collected at the same site during the biomass burning period in 1999 (Graham et al., 2002).  
357 Overall, these three anhydrosugars account for 48% and 62% of individually detected  
358 organic species in day and night samples, respectively (Figure 6a and 6b).

359

#### 360 *3.4. Sugars and sugar alcohols*

361         Two sugars (fructose and sucrose) and a few sugar alcohols including glycerol,  
362 threitol, erythritol, arabitol, mannitol, sorbitol and inositol were also detected in the  
363 biomass burning aerosols (Table 2). The concentrations of sugars were 3.6-33 ng m<sup>-3</sup> (av.  
364 28 ng m<sup>-3</sup>) in daytime versus 1.4-49 ng m<sup>-3</sup> (av. 31 ng m<sup>-3</sup>) in nighttime, while the  
365 concentrations of sugar alcohols were 50-173 ng m<sup>-3</sup> (av. 93 ng m<sup>-3</sup>) in daytime versus 84-  
366 357 ng m<sup>-3</sup> (av. 206 ng m<sup>-3</sup>) in nighttime (Table 2). The average concentration of sugars is  
367 about 2 times higher, while the average concentration of sugar alcohols is almost equal to  
368 the previous measurements on biomass burning aerosols of the same campaign (Decesari  
369 et al., 2006). The mean concentration of sugar alcohols is 1.2-2.7 times higher than those  
370 reported for aerosols collected at the same site in October 1999 (Graham et al., 2002). The  
371 contribution of sugars and sugar alcohols to OC ranged between 0.02-0.05% (av. 0.03%)



372 and 0.07-0.13% (av. 0.1%) in daytime versus 0.01-0.06% (av. 0.02%) and 0.06-0.17% (av.  
373 0.14%) in nighttime, whereas their contribution to WSOC ranged between 0.03-0.06%  
374 (av. 0.04%) and 0.11-0.18% (av. 0.14%) in daytime versus 0.02-0.09% (av. 0.04%) and  
375 0.11-0.3% (av. 0.23%) in nighttime.

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

392

### 393 *3.5. Aromatic compounds*

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

397 possibly towards more refractory compounds (HULIS), based on the decrease in their  
398 ratios from the biomass burning to the transition period. Here, we focus on the absolute  
399 concentrations of this group of compounds. Syringyl compounds (syringic acid,  
400 syringaldehyde), vanillyl compounds (vanillic acid and vanillin), coumaryl compounds (4-  
401 hydroxybenzoic acid, 4-hydroxybenzaldehyde and 3, 4-dihydroxybenzoic acid) as well as  
402 3-hydroxy benzoic acid and 4-methylbenzocatechin were determined in all day and night  
403 samples. Their concentrations were 77-550 ng m<sup>-3</sup> (av. 190 ng m<sup>-3</sup>) in daytime versus 210-  
404 940 ng m<sup>-3</sup> (av. 520 ng m<sup>-3</sup>) in nighttime (Table 2). Decesari et al. (2006) also reported  
405 these compounds for biomass burning period samples of the same campaign using  
406 different analytical protocols, giving a range of concentrations of 200-360 ng m<sup>-3</sup>. Total  
407 aromatics accounted for 0.18-0.36% (av. 0.26%) of OC and 0.24-0.61% (av. 0.37%) of  
408 WSOC in daytime samples, and 0.3-0.67% (av. 0.48%) of OC and 0.51-1.2% (av. 0.81%)  
409 of WSOC in nighttime samples.

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

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

427

### 428 *3.6. Diacids, oxoacids and dicarbonyls*

429 We determined the concentrations of diacids and related compounds in the range  
430 of C<sub>2</sub>-C<sub>11</sub> in the aerosol particles collected during the intensive biomass burning period in  
431 Rondônia. Molecular distributions, loadings, and evidence for photo-production of diacids  
432 and related compounds in biomass burning aerosols will be reported in another paper  
433 (Kundu et al., 2009, Molecular distributions of dicarboxylic acids, ketocarboxylic acids  
434 and dicarbonyls in biomass burning aerosols: Implications for photochemical production  
435 and degradation in smoke layer, submitted). Here, we focus only on the contributions of  
436 total diacids, oxoacids and dicarbonyls in bulk and detected molecular organics.

437 The mean contribution of total diacids-carbon to OC was 1.7% in the daytime  
438 versus 1.4% in the nighttime, while its contribution to WSOC was similar (2.3%) in the  
439 day- and night-time. The average percentage of total oxoacids to OC was 0.15% in the  
440 daytime versus 0.11% in the nighttime, while the percentage of total oxoacids to WSOC  
441 was 0.19% in the daytime and 0.18% in the nighttime. The average contribution of total  
442 dicarbonyls accounted for 0.07% and 0.09% to OC and WSOC, respectively, in the  
443 daytime versus 0.05% and 0.08% in the nighttime. Decesari et al. (2006) reported diacids  
444 in the range of C<sub>2</sub>-C<sub>9</sub> and oxoacid (glyoxylic acid) in the aerosols collected during the dry  
445 period for the LBA-SMOCC campaign using four different analytical techniques, which

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

450

### 451 *3.7. Stable carbon isotopes of total carbon and nitrogen isotopes of total nitrogen*

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

461 The average value of  $\delta^{13}\text{C}$  for TC in daytime samples was  $-25.5\text{‰}$  with a range of -  
462  $26.1$  to  $-24.3\text{‰}$ , while it was  $-24.4\text{‰}$  in night samples with a range of  $-25.2\text{‰}$  to  $-23.6\text{‰}$ .  
463 The  $\delta^{13}\text{C}$  values for consecutive day and night samples are significantly different (Figure  
464 7). The average  $\delta^{13}\text{C}$  value in aerosols collected from the  $\text{C}_3$  plant dominated Santarém  
465 region of Brazil was reported to be  $-25.8 \pm 0.5\text{‰}$  with a range of  $-26.9\text{‰}$  to  $-24.9\text{‰}$   
466 (Martinelli et al., 2002).

467 The daytime  $\delta^{13}\text{C}$  values of TC were lower than in the nighttime (Figure 7). One  
468 possible explanation for this clear diel cycle is that there are isotopic differences between  
469 the labile and refractory fractions within  $\text{C}_3$  and  $\text{C}_4$  vegetation relative to their bulk  $\delta^{13}\text{C}$   
470 values. Nadelhoffer and Fry (1988) have shown that the  $\delta^{13}\text{C}$  of bulk leaf material is a

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

482         We obtained a very good anti-correlation between  $\delta^{13}\text{C}$  and TC for nighttime  
483 samples, but not for day samples (Figure 8). Wide varieties of volatile and semi-volatile  
484 organics (e.g., alkanes, alkenes, aldehydes, ketones, furans, esters, organic acids,  
485 polycyclic compounds, etc.) are emitted directly (Koppmann et al., 1997; Rudolph et al.,  
486 2000) or produced secondarily in the atmosphere during biomass burning. Rudolph et al.  
487 (2000) reported the kinetic isotope effect (KIE) associated with the reaction of several  
488 hydrocarbons including normal chain  $\text{C}_3\text{-C}_6$  alkanes, alkenes, isoprene and ethyne with  
489 OH radicals. All measured KIEs are positive, that is, molecules containing only  $^{12}\text{C}$  react  
490 faster than  $^{13}\text{C}$ -containing molecules. On the other hand, we can say that products  
491 produced from the reactions between OH radicals and NMHC have a lower  $\delta^{13}\text{C}$  than the  
492 reactants. Irei et al. (2006) reported that the  $\delta^{13}\text{C}$  of secondary particulate organic matter  
493 produced from the OH-radical-induced reactions of toluene is lower by 5.8‰ than those of  
494 the parent toluene. Thus, volatile and semi-volatile organics produced secondarily  
495 (photochemically) from the products of biomass combustion should be depleted in  $^{13}\text{C}$ . If

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

501 The average  $\delta^{15}\text{N}$  values of TN for day and night samples were  $23.3\pm 1.7\text{‰}$  and  
502  $23.7\pm 1.4\text{‰}$ , respectively, and are not statistically different. Our average  $\delta^{15}\text{N}$  values in day  
503 and night samples are about 2 times higher than those in the atmospheric aerosols  
504 ( $11.5\pm 2.1\text{‰}$ ) collected from the Santarém region (Martinelli et al., 2002). This region is  
505 located in the northeast region of the Amazon basin, and is covered mostly by primary  
506 tropical rain forest although there are a few pasture areas. The reported average  $\delta^{15}\text{N}$  value  
507 ( $10.6\pm 2.8\text{‰}$ ) in aerosol collected from Piracicaba during August 1999 to September 2000  
508 is about 13‰ lower than our values as well (Martinelli et al., 2002). Piracicaba is located  
509 in São Paulo State, Brazil, in an area covered predominantly with  $\text{C}_4$  plants.

510 To better understand the sources of aerosol carbon and nitrogen by using their  
511 isotopic compositions, it is mandatory to know whether or not a significant isotope  
512 fractionation occurs during the combustion process (Currie et al., 1999). If so, the extent  
513 of the fractionation has to be considered when particles and their sources are evaluated.  
514 Such a fractionation is very likely, because particles produced from combustion are  
515 composed of a wide variety of compound classes, and volatile compounds are condensed  
516 onto the existing particles and thermally altered plant debris (Turekian et al., 1998). Based  
517 on laboratory experiments, Turekian et al. (1998) reported that the  $\delta^{13}\text{C}$  values of particles  
518 produced during combustion of  $\text{C}_3$  plants (Eucalyptus sp. and Colosperum mopane) were  
519 approximately 0.5‰ higher than the unburned plant. On the other hand, the  $\delta^{13}\text{C}$  of  
520 particles produced during the combustion of  $\text{C}_4$  plants (Cenchrus ciliaris, Antephora

521 pubescence, and *Saccharum officinarum*, sugarcane) were approximately 3.5‰ lower than  
522 the source. Another combustion experiment conducted under laboratory conditions (Currie  
523 et al., 1999) reported that the  $\delta^{13}\text{C}$  values of particles were on average 0.5‰ lower than  
524 the unburned  $\text{C}_3$  plants (pine and oak). These are relatively minor changes, however,  
525 compared with the large isotopic difference that exists between  $\text{C}_3$  and  $\text{C}_4$  plants. The  
526 isotopic fractionation of nitrogen during combustion was higher than that for carbon.  
527 Particles produced during biomass combustion showed higher  $\delta^{15}\text{N}$  values by 5 and 7.8‰  
528 than those of unburned  $\text{C}_3$  and  $\text{C}_4$  plants, respectively (Turekian et al., 1998).

529         The stable carbon and nitrogen isotopic compositions of soil in primary forest  
530 areas and  $\text{C}_3$  vegetation tissues collected from the Amazon basin were reported by  
531 Martinelli et al. (2002). These values, along with the isotopic data for aerosols from this  
532 study and the isotopic data of the aerosol collected from Santarém, Brazil (Martinelli et al.,  
533 2002) are presented in Figure 9. Our nitrogen and carbon isotopic data show significant  
534 enrichment of  $^{15}\text{N}$  and  $^{13}\text{C}$  compared to vegetation tissues and soil from the Amazon basin,  
535 supporting that biomass burning rather than vegetation tissue debris and soil organics is  
536 the dominant contributor to our samples. Even applying the fractionation of 5‰, the  $\delta^{15}\text{N}$   
537 values of aerosols collected from Rondônia are still statistically different than the foliar  
538 and soil  $\delta^{15}\text{N}$  values found in the region of the Amazon basin dominated by primary forest  
539 (Figure 9). Based on this difference, it is reasonable to hypothesize that soils are not an  
540 important source of organic matter to aerosol particles in Rondônia and that particles  
541 produced due to burning of the foliar tissues are much more important than direct  
542 emissions from unburned tissues. Atmospheric sources of nitrogen (e. g.,  $\text{NO}_3^-$  from the  
543 oxidative reaction of  $\text{NO}_x$  that is directly produced from  $\text{N}_2$  and  $\text{O}_2$  inside the flame) do  
544 not affect the above hypothesis because the temperatures in biomass burning are not high

545 enough to cause significant NO<sub>x</sub> production from air. As a result, almost all of the NO<sub>x</sub>  
 546 and NH<sub>3</sub> in biomass smoke comes from the fuel nitrogen.

547 Because Figure 9 suggests that biomass burning is the main contributor of TC in  
 548 our aerosols, we can roughly calculate the relative contribution of C<sub>3</sub> and C<sub>4</sub> plants to TC  
 549 by the following isotopic mass balance equation.

$$550 \quad f_{\text{TC-C}_3} = \frac{\text{TC}_{\text{C}_3}}{\text{TC}_{\text{aerosol}}} \quad f_{\text{TC-C}_4} = \frac{1 - \text{TC}_{\text{C}_3}}{\text{TC}_{\text{aerosol}}}$$

$$551 \quad \delta^{13}\text{C}_{\text{TC-aerosol}} = f_{\text{TC-C}_3} \times \delta^{13}\text{C}_{\text{TC-C}_3} + f_{\text{TC-C}_4} \times \delta^{13}\text{C}_{\text{TC-C}_4}$$

552 In the equations above,  $f_{\text{TC-C}_3}$  and  $f_{\text{TC-C}_4}$  refer to a fraction TC from C<sub>3</sub> and C<sub>4</sub> plants in  
 553 TC<sub>aerosol</sub>, respectively, while  $\delta^{13}\text{C}_{\text{TC-aerosol}}$ ,  $\delta^{13}\text{C}_{\text{TC-C}_3}$  and  $\delta^{13}\text{C}_{\text{TC-C}_4}$  stand for the stable  
 554 carbon isotopic composition of aerosol particles, and tissues of C<sub>3</sub> and C<sub>4</sub> plants,  
 555 respectively. The  $\delta^{13}\text{C}_{\text{TC-C}_3}$  and  $\delta^{13}\text{C}_{\text{TC-C}_4}$  values are assumed to be -31.5‰ and -13.5‰  
 556 based on the average  $\delta^{13}\text{C}$  values found for leaves of C<sub>3</sub> and C<sub>4</sub> vegetations in the Amazon  
 557 basin (Martinelli et al., 2002).

558 Based on the above equation, the average contribution of C<sub>3</sub> and C<sub>4</sub> plants to TC is  
 559 60% and 40%, respectively, suggesting a predominance of deforestation burning over  
 560 pasture maintenance burning as sources of smoke aerosols during our experiment. The  
 561 minimum and maximum contribution is 67% and 33%, and 54% and 46%, respectively  
 562 (Figure 10). A higher contribution from C<sub>3</sub> plants to TC than from C<sub>4</sub> plants in daytime  
 563 samples was observed, which can be interpreted as being due to the flaming phase of  
 564 biomass combustion in the daytime. Higher K<sup>+</sup>/levoglucosan ratio in the daytime than in  
 565 the nighttime (Figure 4b) provides evidence that the flaming phase of combustion is more  
 566 important in daytime.

567

#### 568 4. Conclusion



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

588

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602

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Table 1. Concentrations ( $\text{ng m}^{-3}$ ) 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.

Species	Day samples (n=6)		Night samples (n=9)		Total (n=15)	
	Mean <sup>b</sup>	Median	Mean <sup>b</sup>	Median	Mean <sup>b</sup>	Median
F <sup>-</sup>	110±50	95	154±18	157	135±41	139
MSA <sup>-a</sup>	420±122	420	290±99	290	340±122	330
Cl <sup>-</sup>	57±17	51	200±98	196	144±105	94
NO <sub>2</sub> <sup>-</sup>	168±126	192	148±193	33	156±165	69
NO <sub>3</sub> <sup>-</sup>	800±580	570	3010±1060	2930	2130±1420	1910
SO <sub>4</sub> <sup>2-</sup>	2690±300	2570	2780±370	2810	2740±340	2740
Na <sup>+</sup>	2370±1030	1800	2740±97	2740	2590±650	2720
NH <sub>4</sub> <sup>+</sup>	1040±123	1030	1410±610	1440	1260±510	1120
K <sup>+</sup>	1500±800	1030	2410±350	2420	2040±710	2080
Ca <sup>2+</sup>	80±67	53	115±27	114	101±48	106
Mg <sup>2+</sup>	38±25	32	33±17	30	35±20	30

<sup>a</sup>Methanesulfonate ion ( $\text{CH}_3\text{SO}_3^-$ )

<sup>b</sup>Standard deviation ( $\pm 1$  SD)

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

Component	Day samples (n=6)			Night samples (n=9)		
	Range	Mean	Median	Range	Mean	Median
<b>Bulk organics (<math>\mu\text{g m}^{-3}</math>)</b>						
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
<b>Anhydrosugars (<math>\text{ng m}^{-3}</math>)</b>						
Levogluconan	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
<b>Subtotal</b>		<b>2687</b>	<b>1669</b>		<b>6020</b>	<b>5826</b>
<b>Sugars (<math>\text{ng m}^{-3}</math>)</b>						
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
<b>Subtotal</b>		<b>28</b>	<b>26</b>		<b>31</b>	<b>28</b>
<b>Sugar alcohols (<math>\text{ng m}^{-3}</math>)</b>						
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
<b>Subtotal</b>		<b>93</b>	<b>84</b>		<b>206</b>	<b>209</b>
<b>Aromatic compounds (<math>\text{ng m}^{-3}</math>)</b>						
4-Methylbenzocatechin	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
<b>Subtotal</b>		<b>191</b>	<b>125</b>		<b>519</b>	<b>432</b>

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.

Compound	$K^+$		CO		OC		EC	
	Day	Night	Day	Night	Day	Night	Day	Night
<b>Anhydrosugars</b>								
Levoglucozan	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
<b>Sugars/Sugar alcohols</b>								
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
<b>Aromatic compounds</b>								
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 ( $\mu\text{g m}^{-3}$ ).

**Figure 3.** Diurnal variations in (a) potassium ( $\text{K}^+$ ), (b) levoglucosan and (c) apparent elemental carbon ( $\text{EC}_a$ ) normalized by mass concentrations of sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), MSA ( $\text{CH}_3\text{SO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ). 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)  $\text{MSA}^-/\text{SO}_4^{2-}$  and (b)  $\text{K}^+/\text{levoglucosan}$  ratios in the biomass burning aerosols from Rondônia during 16-26 September 2002.

**Figure 5.** Relation of total anhydrosugars against (a) CO, (b) K<sup>+</sup>, (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<sup>-3</sup>).

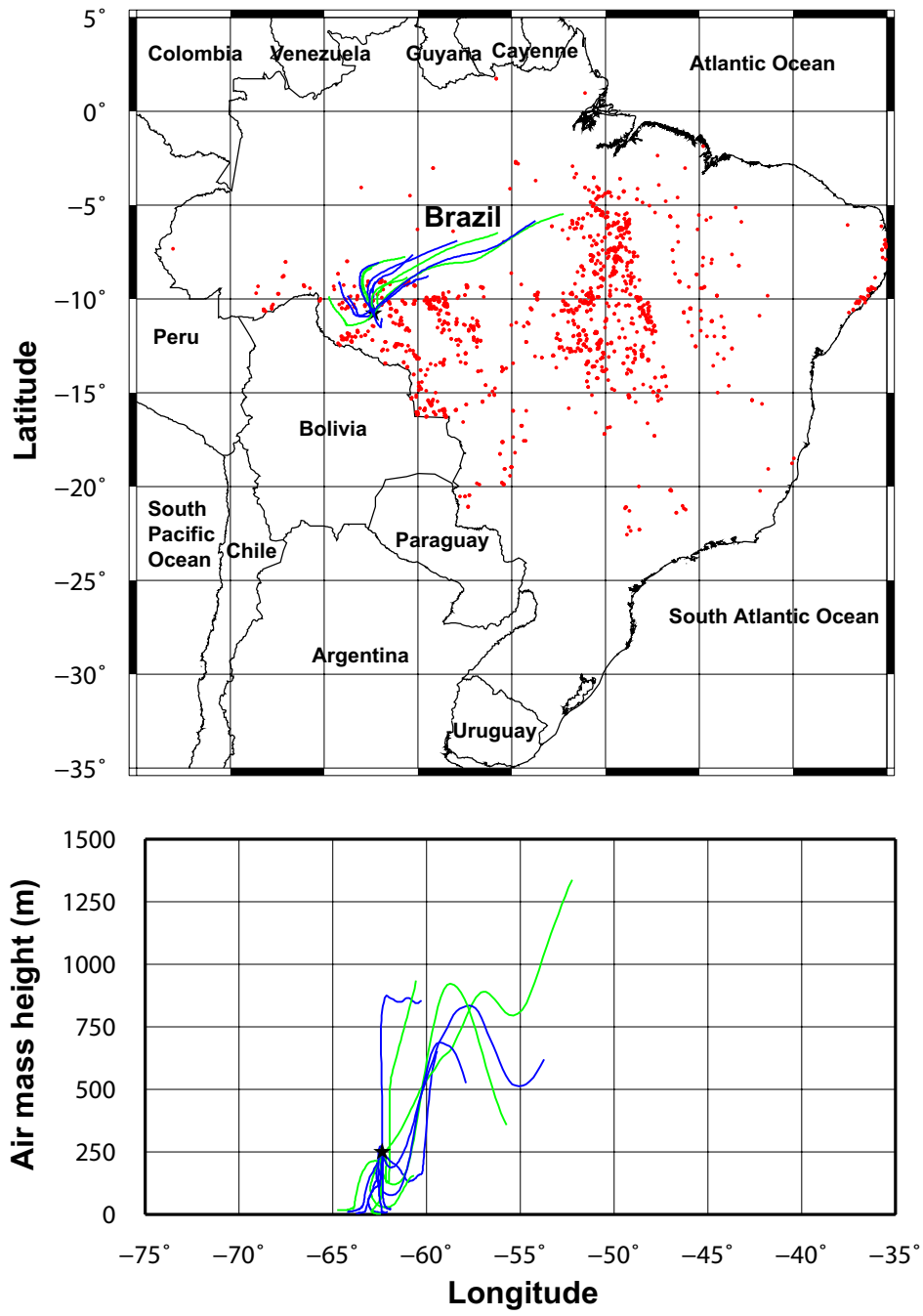
**Figure 7.** Diurnal variations of  $\delta^{13}\text{C}$  values of total carbon (TC) and TC in biomass burning aerosols collected during 16-26 September 2002.

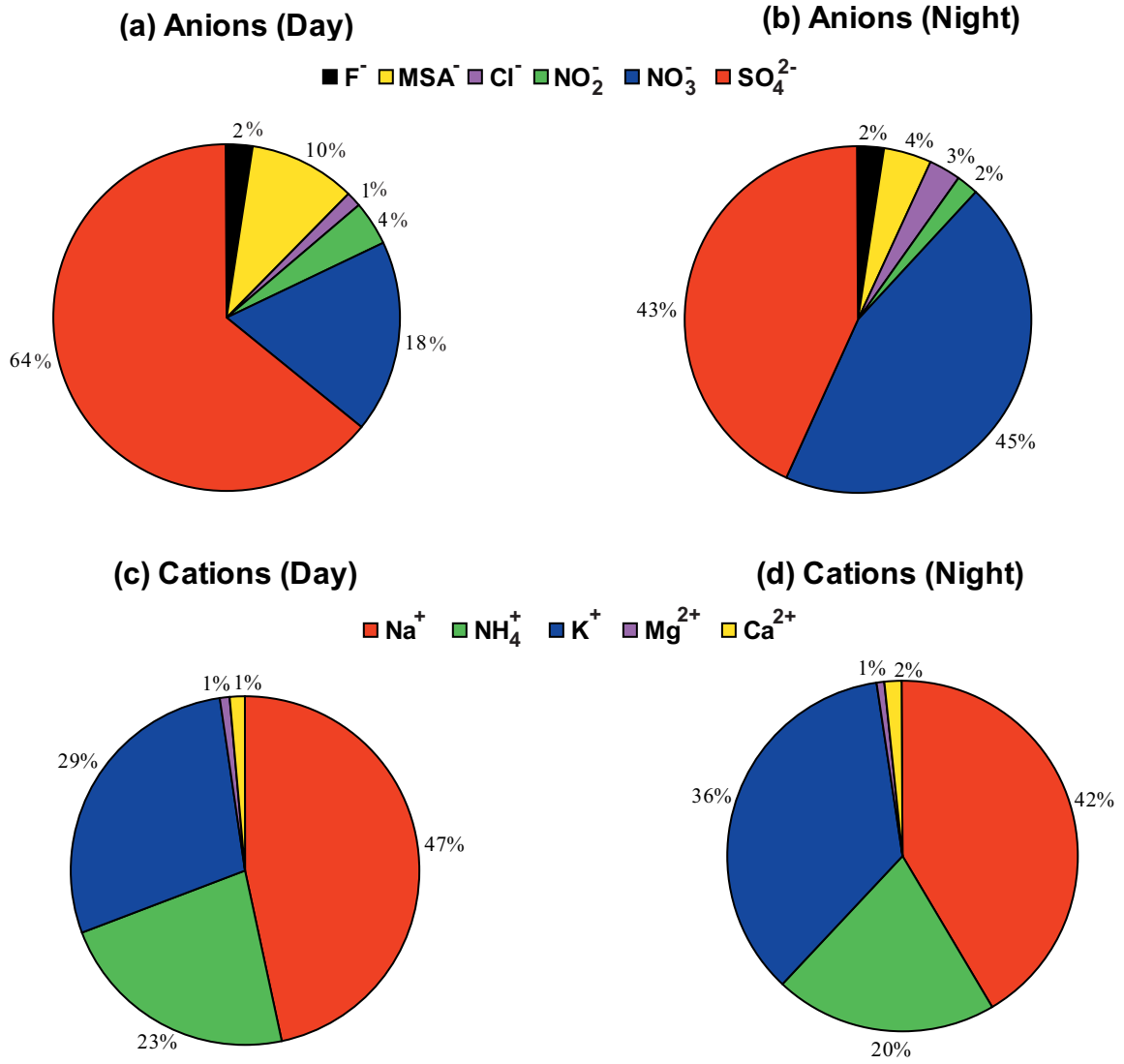
**Figure 8.** Relation between the concentrations of total carbon (TC) and  $\delta^{13}\text{C}$  values of biomass burning aerosols. One nighttime sample has been excluded as no analytical results are available.

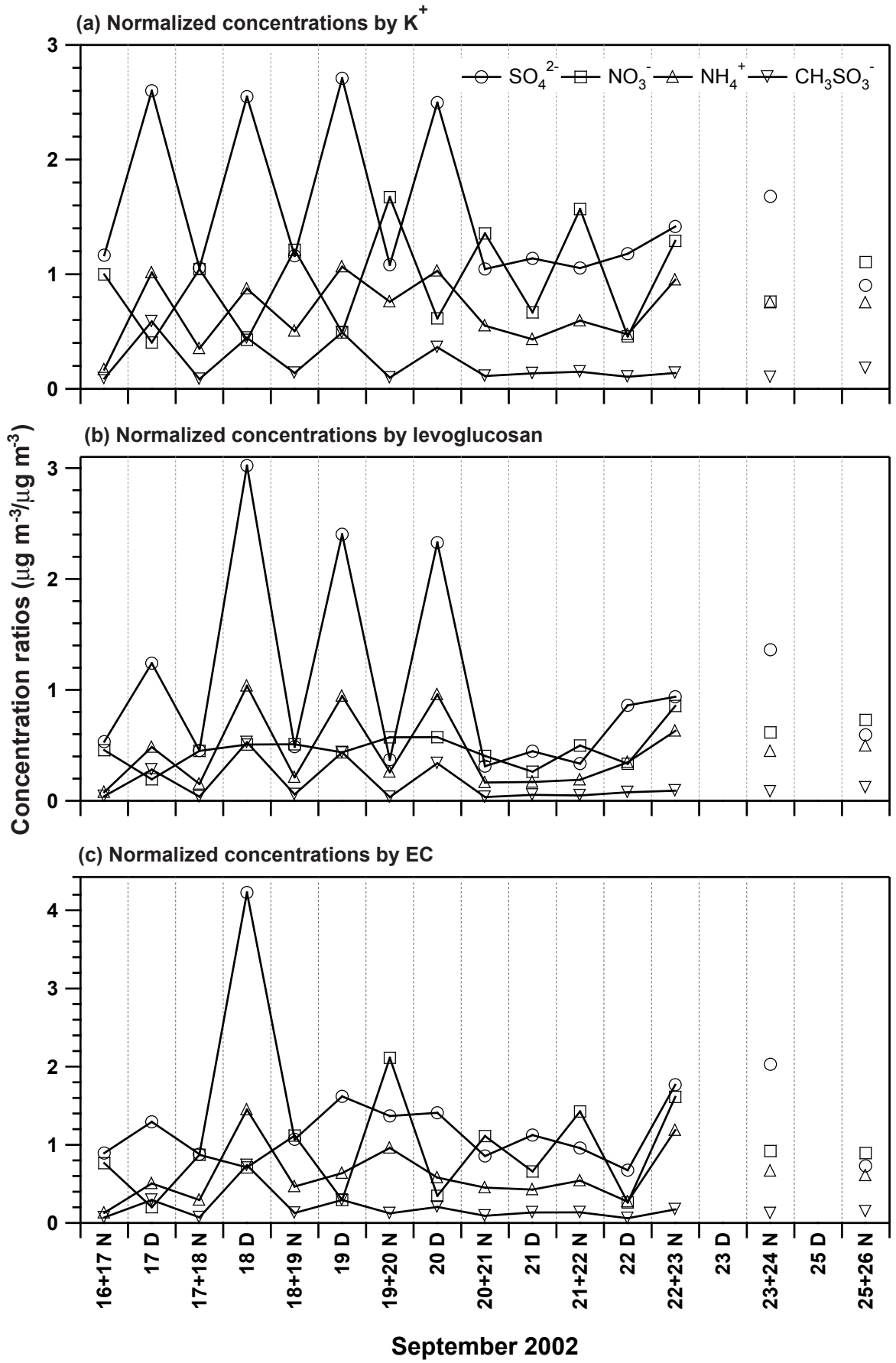
**Figure 9.**  $\delta^{13}\text{C}$  versus  $\delta^{15}\text{N}$  for the aerosol particles collected in this study and for aerosol particles collected from Santarém, Brazil (Martinelli et al., 2002) along with soil and vegetation tissues (Martinelli et al. (2002). “Aerosol-fractionation” means that  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  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).

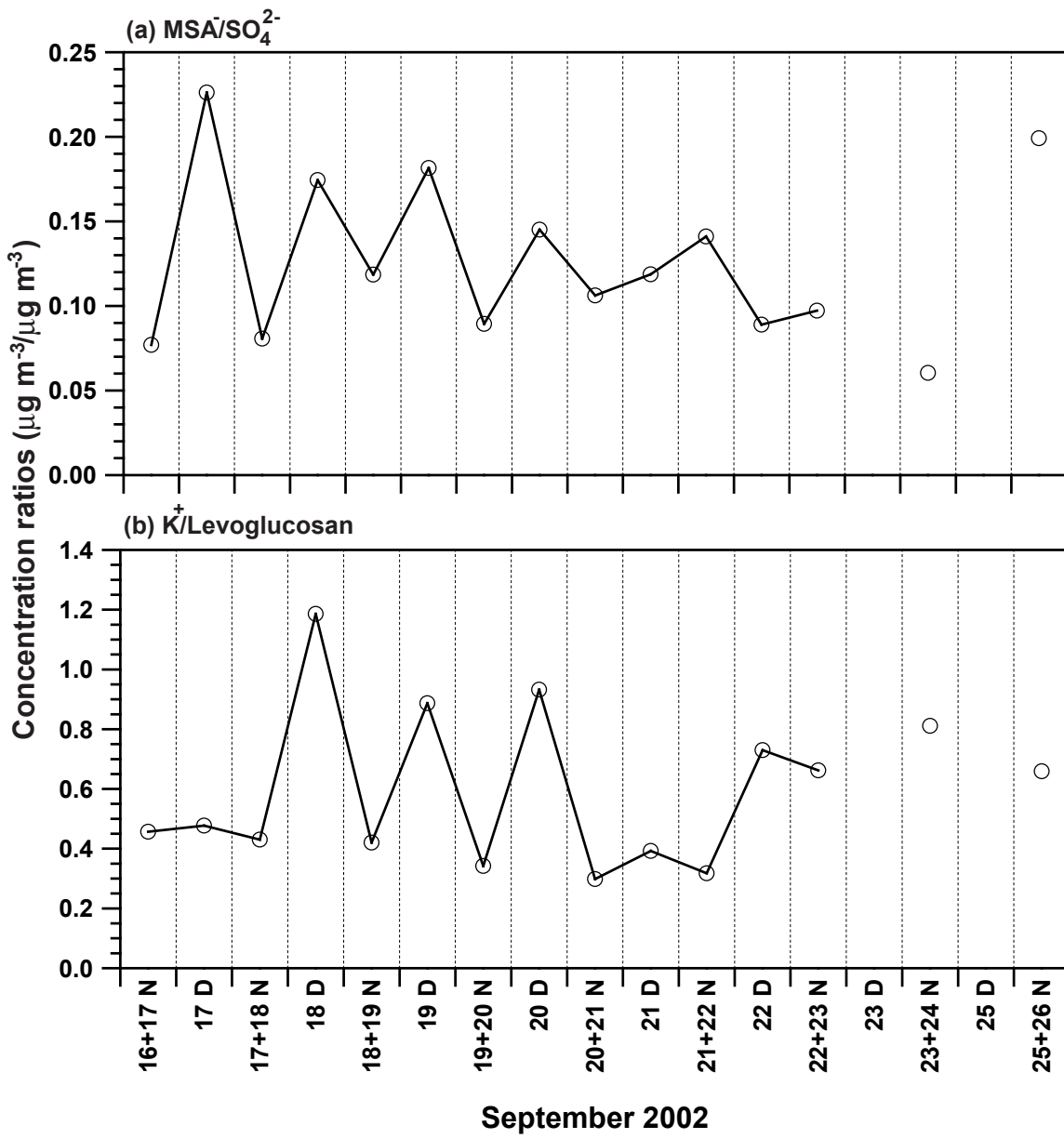


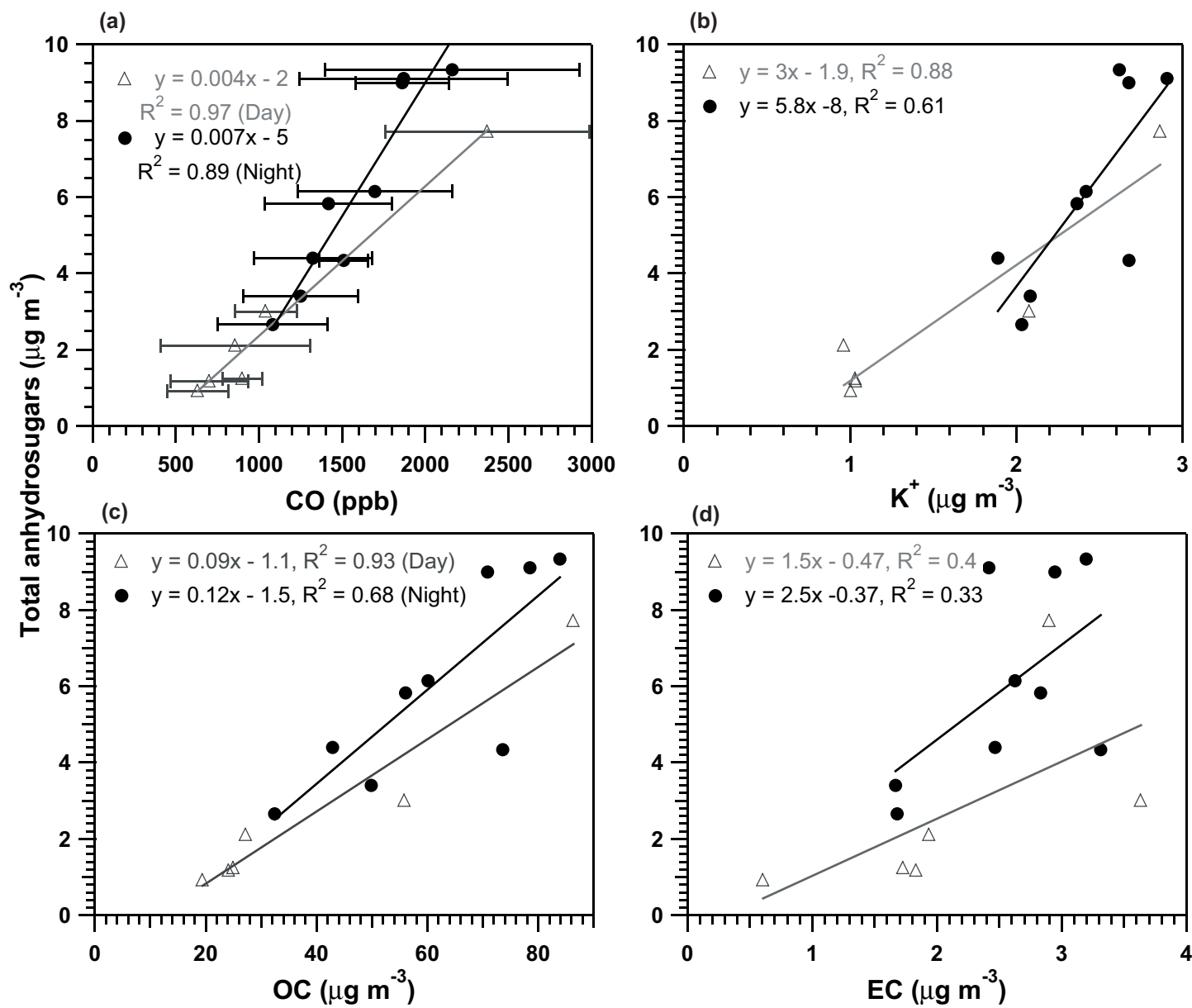
**Figure 10.** Contribution of C<sub>3</sub> and C<sub>4</sub> plants to total carbon (TC) in biomass burning aerosols.











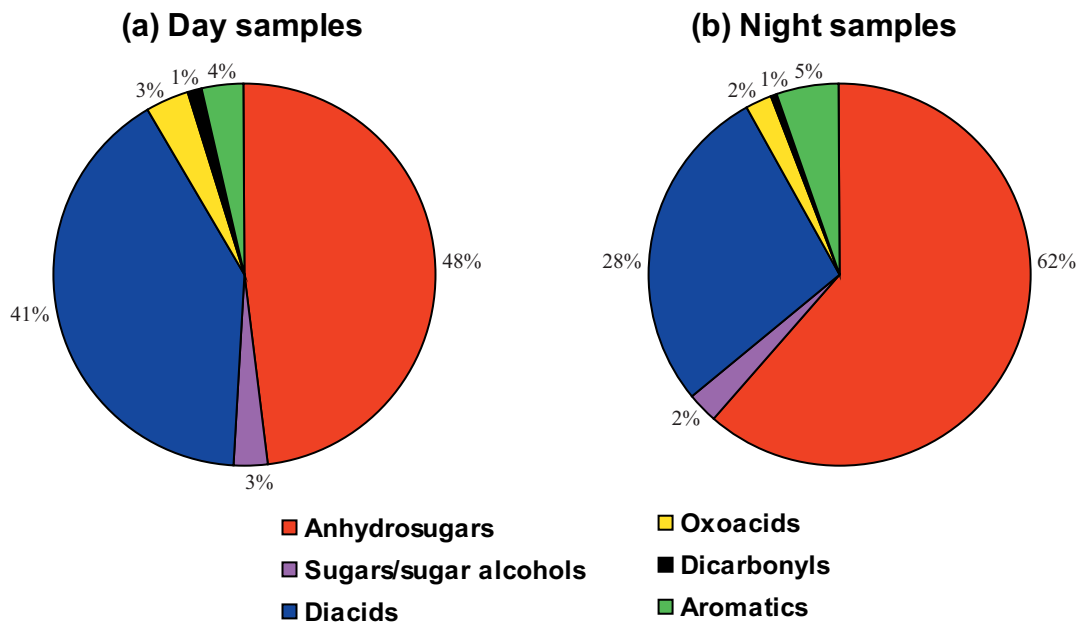


Figure 7.

