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**

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27 **Abstract**

28   Aerosol particles ($PM_{2.5}$) 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^+, levoglucosan, or apparent

31 elemental carbon, EC_a) mass concentrations of SO_4^{2-} and $CH_3SO_3^-$ in daytime suggest

32 their photochemical production, while the opposite trend for NO_3^- suggests its transfer to

33 the aerosol phase at lower temperatures and higher humidities, as well as possibly

34 production through hydrolysis of N_2O_5 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 $\delta^{13}C$ 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 ^{13}C due to predominantly flaming

42 combustion. The $\delta^{15}N$ 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 $\delta^{13}C$ and $\delta^{15}N$ 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.

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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 $\delta^{13}C$ 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 ($PM_{2.5}$) 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_2CO_3

133   and 1.7 mM $NaHCO_3$ (Kanto Chemical, Japan) as eluent, and cations on a Shodex YK-

134   421 column with 4 mM H_3PO_4 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_a)

141   were measured using a semi-continuous OC/EC analyzer (Sunset Laboratory Inc.,

142   Portland, OR, USA). For a discussion and definition of EC_a 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_2, 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_2 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_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

175 chromatograph and then measured with a thermal conductivity detector. Aliquots of the N_2

176 and CO_2 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 $\delta^{13}C$ and $\delta^{15}N$ was determined using the following standard isotopic

179 conversion equations (1) and (2), respectively:

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

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

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 $\delta^{13}C$ and $\delta^{15}N$ 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±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 SO_4^{2-} is about 50% higher in day

224 samples than in night samples, being consistent with daytime versus nighttime variations

225 of SO_2, from which SO_4^{2-} is mainly produced. Trebs et al. (2004) observed a higher

226 mixing ratio of SO_2 in daytime than in nighttime during our aerosol collection time at the

227 FNS site in Rondônia. A higher abundance of SO_4^{2-} in daytime aerosols can be explained

228 by enhanced chemical production as well as the transfer of 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 NO_3^- at nighttime is that humidity is higher and temperature lower,

231 which thermodynamically favors the reaction between gaseous NH_3 and HNO_3 to form

232 aerosol nitrate. This logic can be strongly substantiated by the observed lower mixing ratio

233 of HNO_3 at nighttime during our sampling period at the FNS site (Trebs et al., 2004). The

234 higher concentration and relative abundance of NO_3^- in nighttime aerosols also suggests

235 that NO_3^- production due to the reactions of HNO_3 and hydrolysis of N_2O_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 $CH_3SO_3^-$ (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). MSA^- can also be emitted directly from biomass

242 burning (Andreae and Andreae, 1988). NO_2^- in aerosols is produced from its gaseous

243 precursor HNO_2, which is derived from the heterogeneous reactions of 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 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 HNO_2 in the daytime (Harrison et al., 1996), NO_2^- in the aerosol phase

249   should not be higher. The higher concentration of NO_2^- we found in daytime aerosols

250   suggests that complete depletion of 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 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 (NH_4^+) in aerosol is produced from the reaction between 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 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 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 NH_4^+ in daytime than

266   in nighttime samples (Figure 2c and 2d), suggesting that diel variations of NH_3 and

267   increased availability of H_2SO_4 due to daytime photo-production influence NH_4^+

268   formation. Potassium (K^+) showed slightly higher relative abundances in night samples

269   (Figure 2c and 2d). We have observed higher relative abundance of 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 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 $PM_{2.5}$ 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^{-3} (av. 2550 ng

312   m^{-3}) in daytime versus 2510-8790 ng m^{-3} (av. 5650 ng m^{-3}) in nighttime. Concentrations of

313   mannosan were lower (av. 97 ng m^{-3}) in daytime than in nighttime (av. 236 ng m^{-3}).

314   Galactosan also showed lower values in daytime (av. 40 ng m^{-3}) than in nighttime (av. 135

315   ng m^{-3}) (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^{-3} 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^+ and CO, along with OC

338 (Figure 5, Table 3). Another biomass burning tracer, EC_a, 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_a 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_a and levoglucosan among the different types of

344 fires and different atmospheric residence times of levoglucosan and EC_a. Systematically,

345 correlation coefficients of anhydrosugars with K^+, CO, OC and EC_a 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 airmass 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^{-3} (av.

364   28 ng m^{-3}) in daytime versus 1.4-49 ng m^{-3} (av. 31 ng m^{-3}) in nighttime, while the

365   concentrations of sugar alcohols were 50-173 ng m^{-3} (av. 93 ng m^{-3}) in daytime versus 84-

366   357 ng m^{-3} (av. 206 ng m^{-3}) 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 at 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-methylbenzcatechin were determined in all day and night

403 samples. Their concentrations were 77-550 ng m^{-3} (av. 190 ng m^{-3}) in daytime versus 210-

404 940 ng m^{-3} (av. 520 ng m^{-3}) 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^{-3}. 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_2-C_{11} 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_2-C_9 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 $\delta^{13}C$ for TC in daytime samples was -25.5‰ with a range of -

462   26.1 to -24.3‰, while it was -24.4‰ in night samples with a range of -25.2‰ to -23.6‰.

463   The $\delta^{13}C$ values for consecutive day and night samples are significantly different (Figure

464   7). The average $\delta^{13}C$ value in aerosols collected from the C_3 plant dominated Santarém

465   region of Brazil was reported to be -25.8±0.5‰ with a range of -26.9‰ to -24.9‰

466   (Martinelli et al., 2002).

467   The daytime $\delta^{13}C$ 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 C_3 and C_4 vegetation relative to their bulk $\delta^{13}C$

470   values. Nadelhoffer and Fry (1988) have shown that the $\delta^{13}C$ 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 $\delta^{13}C$ signals. Lipids and lignins tend to be

474 depleted in ^{13}C content relative to the bulk leaf whereas starches, proteins, sugars, and

475 holocellulose tend to be enriched in ^{13}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 K^+/levoglucosan ratio than

478 in nighttime, it is likely that daytime TC will be more depleted in ^{13}C than nighttime TC.

479 The increase of the $\delta^{13}C$ 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 $\delta^{13}C$ 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 C_3-C_6 alkanes, alkenes, isoprene and ethyne with

489 OH radicals. All measured KIEs are positive, that is, molecules containing only ^{12}C react

490 faster than ^{13}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 $\delta^{13}C$ than the

492 reactants. Irei et al. (2006) reported that the $\delta^{13}C$ 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}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 $\delta^{13}C$ and TC. Our results suggest an enhanced contribution of TC from the labile

499   fractions of organics (enriched with ^{13}C) in nighttime when the smoldering phases of

500   biomass burning prevail, (Figure 4b).

501   The average $\delta^{15}N$ values of TN for day and night samples were 23.3±1.7‰ and

502   23.7±1.4‰, respectively, and are not statistically different. Our average $\delta^{15}N$ values in day

503   and night samples are about 2 times higher than those in the atmospheric aerosols

504   (11.5±2.1‰) 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 $\delta^{15}N$ value

507   (10.6±2.8‰) 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 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 $\delta^{13}C$ values of particles

518   produced during combustion of C_3 plants (Eucalyptus sp. and Colospherum mopane) were

519   approximately 0.5‰ higher than the unburned plant. On the other hand, the $\delta^{13}C$ of

520   particles produced during the combustion of C_4 plants (Cenchris cilliarus, Antephora

521   pubesence, 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 $\delta^{13}C$ values of particles were on average 0.5‰ lower than

524   the unburned C_3 plants (pine and oak). These are relatively minor changes, however,

525   compared with the large isotopic difference that exists between C_3 and 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 $\delta^{15}N$ values by 5 and 7.8‰

528   than those of unburned C_3 and C_4 plants, respectively (Turekian et al., 1998).

529   The stable carbon and nitrogen isotopic compositions of soil in primary forest

530   areas and 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}N and ^{13}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 $\delta^{15}N$

537   values of aerosols collected from Rondônia are still statistically different than the foliar

538   and soil $\delta^{15}N$ 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., NO_3^- from the

543   oxidative reaction of NO_x that is directly produced from N_2 and 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_x production from air. As a result, almost all of the NO_x

546   and NH_3 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_3 and C_4 plants to TC

549   by the following isotopic mass balance equation.

550
$$f_{TC-C3} = \frac{TC_{C3}}{TC_{aerosol}} \qquad f_{TC-C4} = \frac{1 - TC_{C3}}{TC_{aerosol}}$$

551
$$\delta^{13}C_{TC-aerosol} = f_{TC-C3} \times \delta^{13}C_{TC-C3} + f_{TC-C4} \times \delta^{13}C_{TC-C4}$$

552   In the equations above, f_{TC-C3} and f_{TC-C4} refer to a fraction TC from C_3 and C_4 plants in

553    $TC_{aerosol}$, respectively, while $\delta^{13}C_{TC-aerosol}$, $\delta^{13}C_{TC-C3}$ and $\delta^{13}C_{TC-C4}$ stand for the stable

554   carbon isotopic composition of aerosol particles, and tissues of C_3 and C_4 plants,

555   respectively. The $\delta^{13}C_{TC-C3}$ and $\delta^{13}C_{TC-C4}$ values are assumed to be -31.5‰ and -13.5‰

556   based on the average $\delta^{13}C$ values found for leaves of C_3 and C_4 vegetations in the Amazon

557   basin (Martinelli et al., 2002).

558   Based on the above equation, the average contribution of C_3 and C_4 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_3 plants to TC than from C_4 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^+/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 δ^{15}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 (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[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$_3$SO$_3^-$)

[b]Standard deviation (±1 SD)

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).

Component	Day samples (n=6)			Night samples (n=9)		
	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 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
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 ($\mu g\ m^{-3}$).

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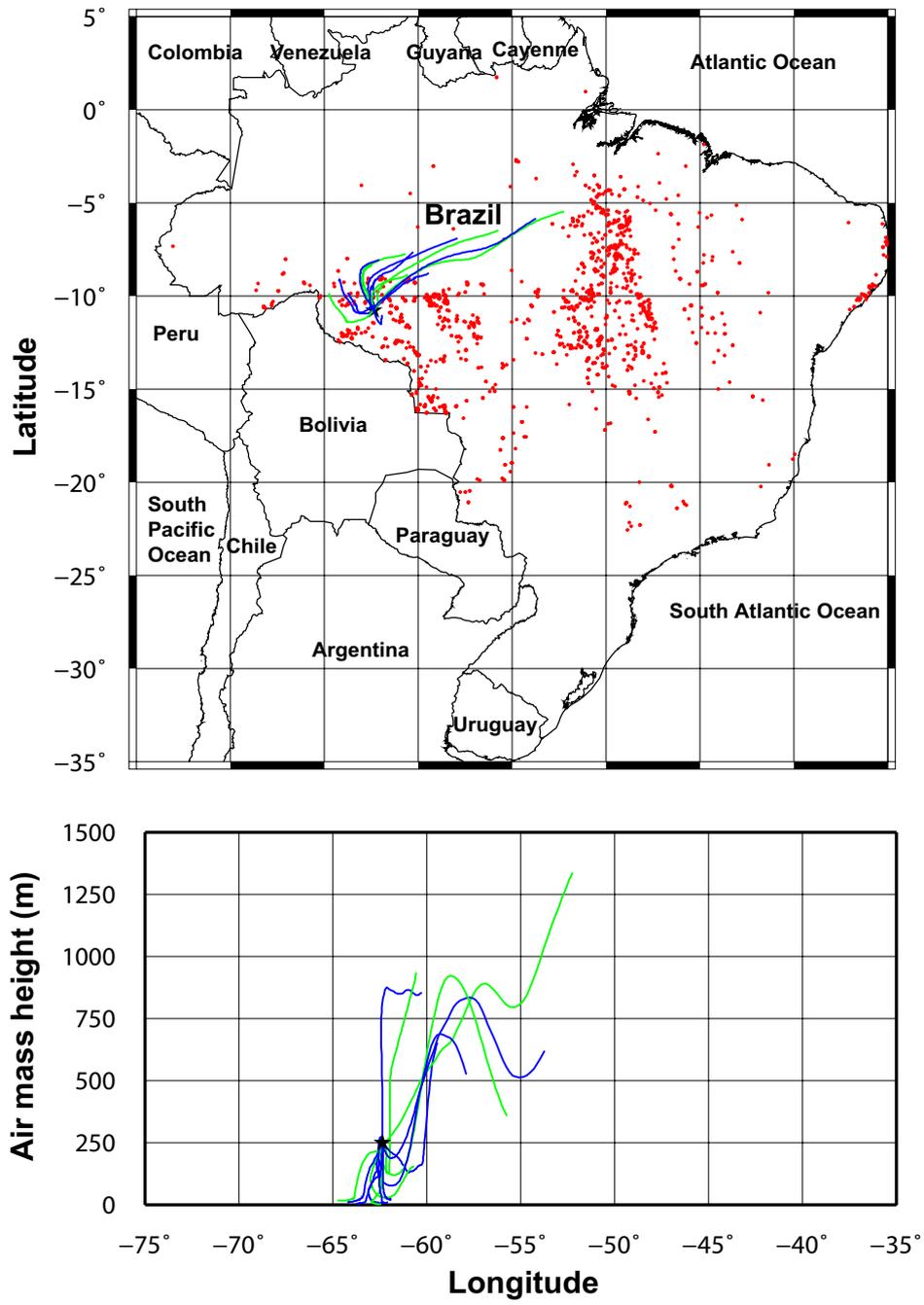
Figure 6. Pie diagrams showing the relative abundances of different organic compound classes detected in (a) day and (b) night samples. The relative abundances of individual compound classes are calculated based on the mass concentrations (ng m^{-3}).

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).

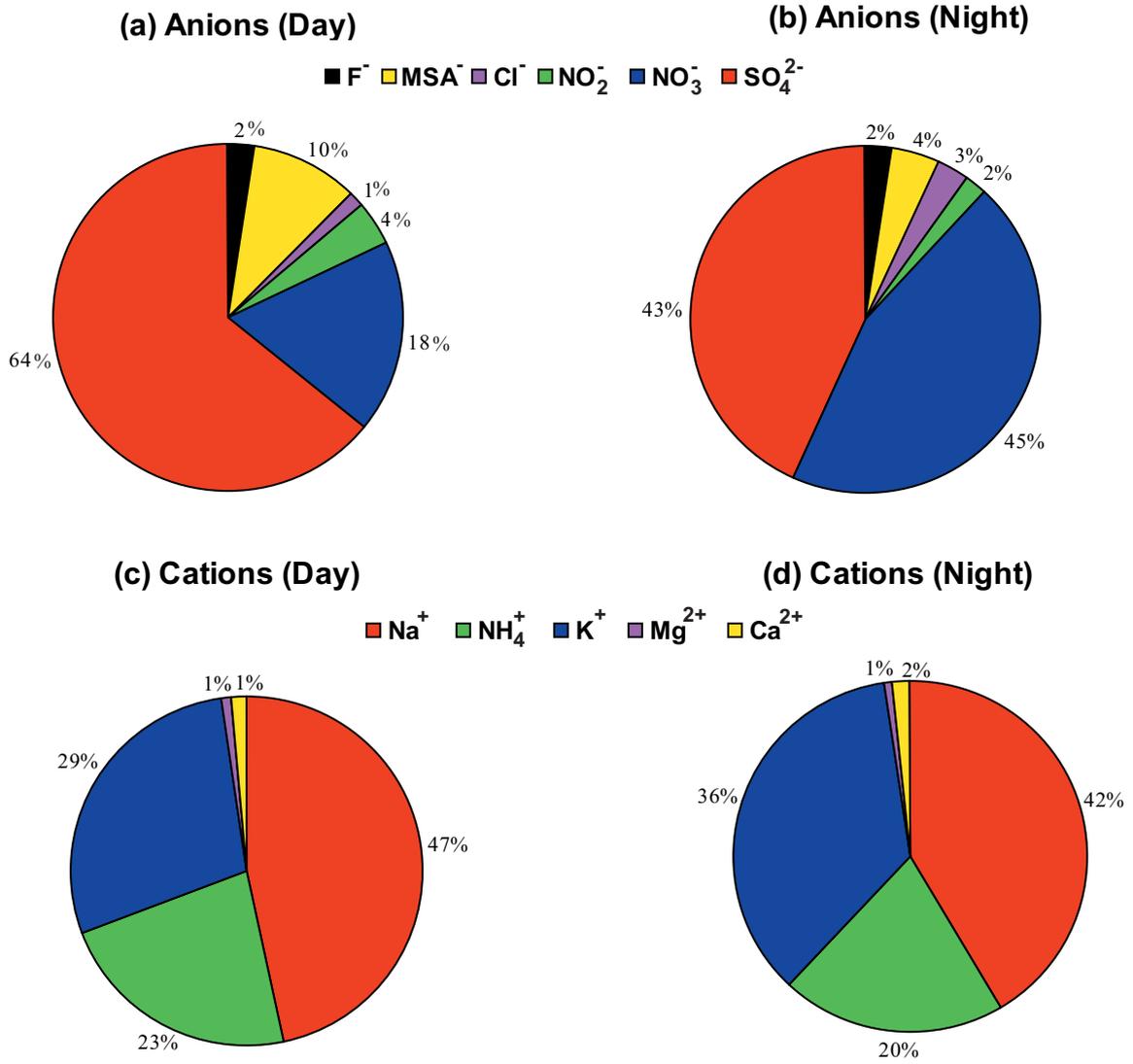**Figure 10.** Contribution of C_3 and C_4 plants to total carbon (TC) in biomass burning aerosols.
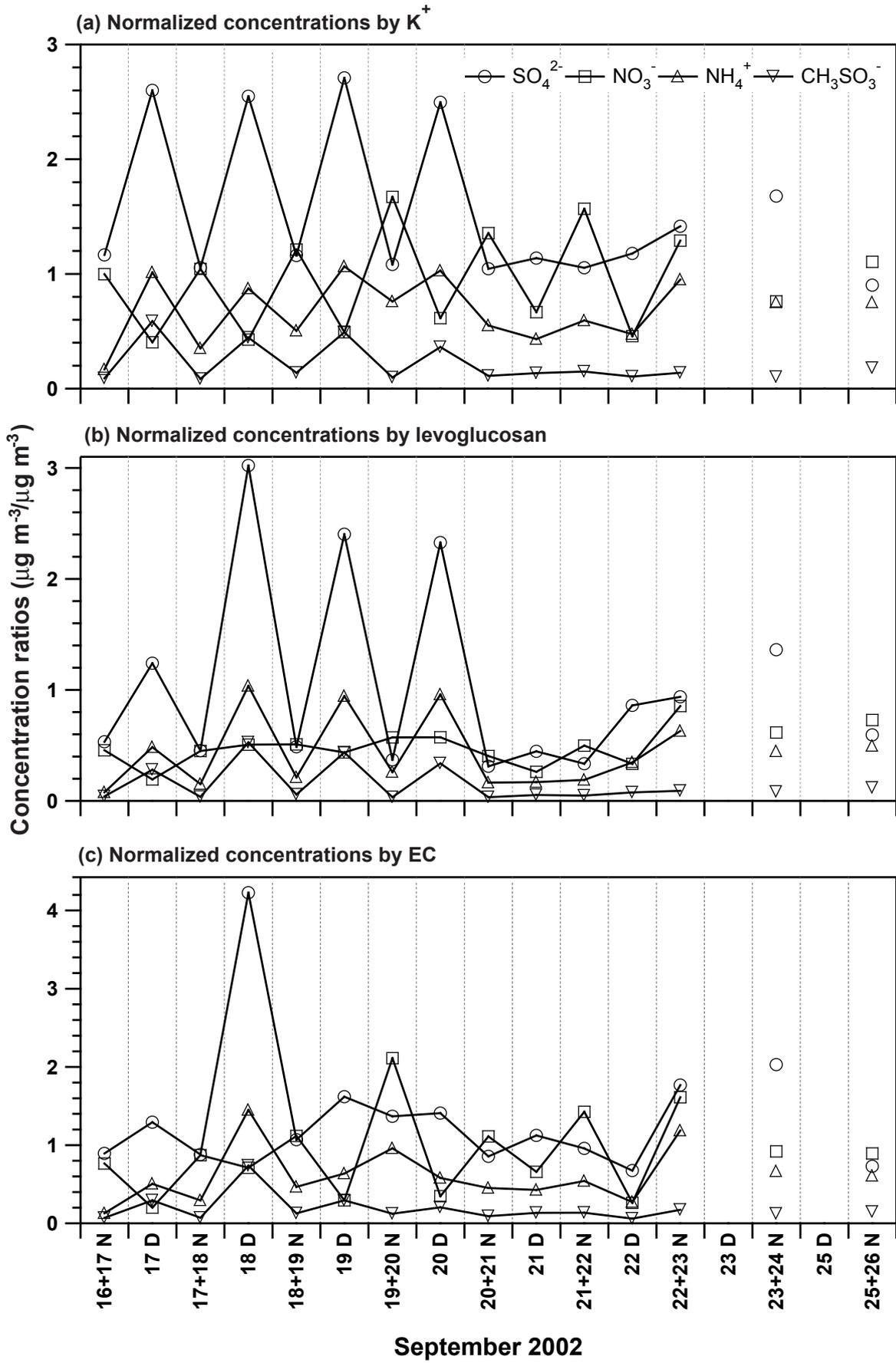
Figure 1.

Figure 2.

(a) Anions (Day)

F⁻ MSA⁻ Cl⁻ NO₂⁻ NO₃⁻ SO₄²⁻

(b) Anions (Night)

(c) Cations (Day)

Na⁺ NH₄⁺ K⁺ Mg²⁺ Ca²⁺

(d) Cations (Night)

Figure 3.

(a) Normalized concentrations by K$^+$

(b) Normalized concentrations by levoglucosan

(c) Normalized concentrations by EC

Concentration ratios (μg m^{-3}/μg m^{-3})

SO$_4^{2-}$ NO$_3^-$ NH$_4^+$ CH$_3$SO$_3^-$

September 2002

Figure 4.

(a) MSA$^-$/SO$_4^{2-}$

(b) K$^+$/Levoglucosan

Concentration ratios (μg m^{-3}/μg m^{-3})

September 2002

Figure 5.

Figure

Figure 6.

(a) Day samples

- 48% Anhydrosugars
- 3% Sugars/sugar alcohols
- 41% Diacids
- 3% Oxoacids
- 1% Dicarbonyls
- 4% Aromatics

(b) Night samples

- 62% Anhydrosugars
- 2% Sugars/sugar alcohols
- 28% Diacids
- 2% Oxoacids
- 1% Dicarbonyls
- 5% Aromatics

Legend:
- Anhydrosugars
- Sugars/sugar alcohols
- Diacids
- Oxoacids
- Dicarbonyls
- Aromatics

Figure 7.

Figure

Figure 8.

Figure 9.

Figure 10.

September 2002