Atmos. Chem. Phys. Discuss., 9, 19783–19815, 2009
www.atmos-chem-phys-discuss.net/9/19783/2009/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal *Atmospheric Chemistry and Physics (ACP)*. Please refer to the corresponding final paper in *ACP* if available.

Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers

S. Kundu[1,2], **K. Kawamura**[1], **T. W. Andreae**[3], **A. Hoffer**[4], **and M. O. Andreae**[3]

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan
[2]Graduate School of Environmental Science, Hokkaido University, Sapporo, Japan
[3]Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany
[4]Dept. of Earth and Environmental Sciences, University of Pannonia, Veszprém, Hungary

Received: 15 July 2009 – Accepted: 4 September 2009 – Published: 23 September 2009

Correspondence to: K. Kawamura (kawamura@lowtem.hokudai.ac.jp)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Aerosols in the size class <2.5 µm (6 daytime and 9 nighttime samples) were collected at a pasture site in Rondônia, Brazil, during the intensive biomass burning period of 16–26 September 2002 as part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia – Smoke, Aerosols, Clouds, Rainfall and Climate (LBA-SMOCC). Homologous series of dicarboxylic acids (C_2–C_{11}) and related compounds (ketocarboxylic acids and dicarbonyls) were identified using gas chromatography and GC/mass spectrometry (GC/MS). Among the species detected, oxalic acid was found to be the most abundant, followed by succinic, malonic and glyoxylic acids. Average concentrations of total dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the aerosol samples were 2180, 167 and 56 ngm^{-3}, respectively. These are 2–8, 3–11 and 2–16 times higher, respectively, than those reported in urban aerosols, such as in 14 Chinese megacities. Higher ratios of dicarboxylic acids and related compounds to biomass burning tracers (levoglucosan and K^+) were found in the daytime than in the nighttime, suggesting an importance of photochemical production. On the other hand, higher ratios of oxalic acid to other dicarboxylic acids and related compounds normalized to biomass burning tracers (levoglucosan and K^+) in the daytime provide evidence for the possible degradation of dicarboxylic acids ($\geq C_3$) in this smoke-polluted environment. Assuming that these and related compounds are photochemically oxidized to oxalic acid in the daytime and given their linear relationship, they could account for, on average, 77% of the formation of oxalic acid. The remaining portion of oxalic acid may have been directly emitted from biomass burning as suggested by a good correlation with the biomass burning tracers (K^+, CO and EC_a) and organic carbon (OC). However, photochemical production from other precursors could not be excluded.

ACPD

9, 19783–19815, 2009

1 Introduction

The ubiquity of dicarboxylic acids and related compounds (ketocarboxylic acids and dicarbonyls) is well recognized in atmospheric aerosols from urban (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Limbeck and Puxbaum, 1999; Röhrl and Lammel, 2002; Wang et al., 2002; Fisseha et al., 2006; Ho et al., 2007), rural/suburban (Khwaja, 1995; Limbeck et al., 2001; Legrand et al., 2007), remote marine (Kawamura and Sakaguchi, 1999; Mochida et al., 2003a; Sempéré and Kawamura, 2003; Kawamura et al., 2004; Wang et al., 2006; Legrand et al., 2007), Arctic (Kawamura et al., 1996b; Kerminen et al., 1999; Narukawa et al., 2003) and Antarctic regions (Kawamura et al., 1996a). In contrast, there are relatively few reports on the molecular distributions and concentrations of dicarboxylic acids and ketocarboxylic acids in biomass burning aerosols (Allen and Miguel, 1995; Graham et al., 2002; Mayol-Bracero et al., 2002; Gao et al., 2003; Decesari et al., 2005; Falkovich et al., 2005), or biomass burning haze aerosols (Narukawa et al., 1999).

Although biomass burning is an important source of dicarboxylic acids and related compounds, none of the previous biomass burning aerosol studies has discussed the molecular distributions of dicarboxylic acids and related compounds in the range of C_2–C_{11} along with their formation and degradation pathways in biomass burning plumes. Molecular distributions of dicarboxylic acids and related compounds should provide information on the source and formation mechanisms of water-soluble organic aerosols in the biomass burning aerosols, which are poorly understood (Grosjean et al., 1989; Kawamura and Ikushima, 1993).

Dicarboxylic and ketocarboxylic acids account for 2–9% of water-soluble organic carbon (WSOC) in biomass burning aerosols (Narukawa et al., 1999; Decesari et al., 2005; Falkovich et al., 2005). WSOC in biomass burning aerosols contributes to the CCN activity (Sherwood, 2002; Andreae et al., 2004; Mircea et al., 2005; Andreae and Rosenfeld, 2008), which affects cloud microphysical properties and hence precipitation patterns and cloud albedo (Kaufman and Fraser, 1997; Ramanathan et al., 2001; Kauf-

ACPD
9, 19783–19815, 2009

man et al., 2002). Glutaric acid (C_5 dicarboxylic acid) has been found to increase the CCN activation ability of ammonium sulfate, a major inorganic species in atmospheric aerosols (Cruz and Pandis, 1997, 1998).

In this work we report on the molecular distribution and loadings of dicarboxylic acids and related compounds in the range of C_2–C_{11} in biomass burning aerosol samples collected in Amazonia. The aerosol samples collected both in the day- and nighttime allowed us to address their diurnal variations and hence chemical formation and degradation. The results are used to better understand their possible sources and formation processes in terms of primary versus secondary origin. We also discuss the day/night variations of dicarboxylic acids using biomass burning tracers (K^+, CO, EC_a and levoglucosan) and organic carbon (OC) previously measured in these samples (Hoffer et al., 2006; Fuzzi et al., 2007; Kundu et al., 2009).

2 Experimental

2.1 Site description and aerosol sampling

Aerosol sampling was carried out during an intensive biomass burning period (dry season), 16–26 September 2002, at the FNS (Fazenda Nossa Senhora Aparecida) site (10°45′44″ S, 62°21′27″ W, 315 m a.s.l) located in the western province of Rondônia, Brazil (Andreae et al., 2002). Aerosol sampling procedures have been described in detail elsewhere (Hoffer et al., 2006). Briefly, fine aerosol particles ($PM_{2.5}$) were collected on pre-combusted (~10 h at 600°C) Pallflex quartz fiber filters using a dichotomous virtual impactor (Solomon et al., 1983) mounted on a 10 m high tower. Daytime samples (n=6) were collected from ~7:45 to ~17:45 LT (local time) and nighttime samples (n=9) from ~18:30 to ~7:00 LT. The aerosol filters were placed in pre-baked (~10 h at 600°C) glass jars and stored in a freezer at −20°C at the Max Planck Institute for Chemistry in Mainz, Germany. Small fractions of the filter discs were transported to our laboratory in Sapporo wrapped in pre-baked thick aluminum foil. Filter discs were transferred into

ACPD
9, 19783–19815, 2009

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

2.2 Analytical methods

Filter samples were analyzed for water-soluble dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls (Kawamura and Ikushima, 1993; Kawamura, 1993). Briefly, aliquots of the filter samples were extracted with organics-free pure water (2 ml×3.18 MΩ) by ultrasonic agitation for the isolation of dicarboxylic acids and related compounds. The extracts were passed through a glass column (Pasteur pipette) packed with quartz wool in order to remove filter debris and insoluble particles and then concentrated to almost dryness using a rotary evaporator (~40°C). The concentrates were derivatized with 14% borontrifluoride in n-butanol at 100°C for one hour. The derived dibutyl esters and dibutoxy acetals were separated with n-hexane (~5 ml) after adding pure water (~5 ml). The hexane layer was dried to ca. 50 µl using a rotary evaporator, transferred to small vial (1.5 ml), dried to almost dryness by N_2 blowdown, and dissolved in a known volume of n-hexane (usually 50–100 µl). A 2 µl aliquot of the sample was injected into a capillary GC (Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused silica capillary column (HP-5, 25 m×0.2 mm id×0.5 µm film thickness) and an FID detector. The oven temperature was held at 50°C for 2 min, ramped at 30°C/min to 120°C, then at 6°C/min to 310°C and held for 10 min. Peak identification was carried out by comparison of the GC retention times with those of authentic standards. Authentic dicarboxylic acid dibutyl esters were used as external standards. Identification of esters and acetals was also confirmed by mass spectral analysis using a GC/MS (Thermoquest, Trace MS) with similar GC column conditions.

We spiked pre-combusted quartz fiber filters with free dicarboxylic acids in order to test the recovery. They were extracted and analyzed like the real samples. The recoveries ranged between 80 and 85% for oxalic acid and more than 90% for malonic, glutaric, succinic and adipic acids. Kawamura and Yasui (2005) reported that the recoveries were 88%, 72% and 47% for glyoxylic acid, pyruvic acid and methylglyoxal, respectively, following the same analytical procedure in our laboratory. Repeated anal-

ACPD
9, 19783–19815, 2009

yses of the filter sample showed that the analytical error of this method was less than 10% for major species reported in this study. A field blank showed small peaks of oxalic, succinic, adipic and phthalic acids, and methylglyoxal. However, their levels were very low (0.1–2.6%) compared to those of the real samples. The reported concentrations for the samples are corrected for the field blanks, but not for recoveries.

3 Results and discussions

3.1 Insignificant contribution from anthropogenic sources to biomass burning haze at the FNS site in Rondônia

The LBA-SMOCC campaign at the FNS site in Rondônia was carried out from September to November 2002. Three periods were distinguished based on the concentrations of PM_{10}, carbon monoxide (CO) and total carbon (TC) (Decesari et al., 2006; Fuzzi et al., 2007). The concentrations of PM_{10} measured by a Tapered Element Oscillating Microbalance (TEOM) and different types of cascade impactors during the dry period (7 September–7 October) were higher by a factor of 2.3–3.7 and 4.9–12.4, respectively, than those during the transition (8–30 October) and wet (30 October–14 November) periods. Furthermore, concentrations of CO and TC during the dry period were higher than in other periods by a factor of 2.3–4.3, and 3.6–21.1, respectively. Falkovich et al. (2005) found that in this campaign the mean concentrations of C_2–C_6 dicarboxylic acids during the dry period were 2.3 times higher than during the transition period and 15.3 times higher than in the wet period. Based on the high concentrations of pyrogenic aerosol components, the relatively low levels of fossil fuel components such as sulfate, the presence of a large number of fires, and the lack of substantial urban areas in the upwind region, Fuzzi et al. (2007) concluded that biomass smoke was the dominant aerosol component during the study period in Rondônia. This suggests that the contribution of dicarboxylic acids from other anthropogenic sources during the dry period is not important in our samples.

ACPD
9, 19783–19815, 2009

3.2 Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls

We measured dicarboxylic acids and related compounds in the range of C_2–C_{11} in the aerosol particles collected during the intensive biomass burning period from the FNS site in Rondônia. Figure 1 shows the molecular distributions of dicarboxylic acids and related compounds in the day and night samples.

Among the LMW (low molecular weight) saturated n-dicarboxylic acids (C_2–C_4), oxalic (C_2) acid was the most abundant species followed by succinic (C_4) and malonic (C_3) acids in all samples. The predominance of oxalic (C_2) acid has been reported for biomass burning aerosols (Narukawa et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002; Gao et al., 2003; Decesari et al., 2006; Falkovich et al., 2005), atmospheric aerosols and rain samples from urban areas (Kawamura and Ikushima, 1993; Kawamura et al., 2001; Wang et al., 2002) and remote marine regions (Sempéré and Kawamura, 1996; Kawamura and Sakaguchi, 1999; Mochida et al., 2003b) as well as for Arctic aerosols (Kawamura et al., 1996a), with the exception that a few Antarctic aerosol samples showed a higher abundance for succinic (C_4) acid (Kawamura et al., 1996b). The three species accounted for, on average, 63%, 12% and 9% of the total dicarboxylic acids in the daytime samples, and for 62%, 14% and 8% in the nighttime samples, respectively. Among the HMW (high molecular weight, C_5–C_{11}) saturated n-dicarboxylic acids, adipic (C_6) acid is the most abundant in the daytime while glutaric (C_5) acid is the most abundant in the nighttime followed by azelaic (C_9) acid. These HMW dicarboxylic acids, on average, contributed ~7% of total dicarboxylic acids in both day and night samples.

Among branched, unsaturated aliphatic, unsaturated aromatic and multifunctional dicarboxylic acid groups, major species are methylsuccinic (iC_5), maleic (M), phthalic (Ph) and malic (hC_4) acids, respectively, in all day and night samples. The mean concentration of terephthalic (tPh) acid in both day and night samples is ~36–43% higher than that of isophthalic (iPh) acid. Glyoxylic (ωC_2) acid, ω-oxocarboxylic acid, is the

ACPD
9, 19783–19815, 2009

fourth abundant among all the dicarboxylic acids and related compounds determined. It accounted for 77% of total ketocarboxylic acids in day samples versus 80% in night samples. Its contribution to total dicarboxylic acids plus related compounds was found to be 6% in day samples and 5% in night samples.

A predominance of oxalic (C_2) acid followed by succinic (C_4), malonic (C_3) and glyoxylic (ωC_2) acids was observed throughout the campaign in all day and night samples. The next most abundant species are glutaric (C_5) and phthalic (Ph) acids, whose mean concentrations are almost equal in the day samples, whereas glutaric (C_5) acid is much more abundant than phthalic (Ph) acid in the night samples. This type of molecular distribution is different than that found for 14 Chinese megacities, where for example, phthalic acid is the second most abundant dicarboxylic acid in 11 cities in summertime and in 7 cities in wintertime (Ho et al., 2007). Oxalic (C_2) acid was found to be the dominant species, followed by malonic (C_3) and succinic (C_4) acids, in aerosols of urban Tokyo and Vienna, while the next abundant were glyoxylic (ωC_2), phthalic (Ph) and glutaric (C_5) acids in the case of Tokyo aerosols and were glutaric (C_5), glyoxylic (ωC2) and phthalic (Ph) acids in the case of Vienna aerosols (Sempr et al., 1994; Limbeck and Puxbaum, 1999). Kawamura and Kaplan (1987) have reported the predominance of oxalic (C_2) acid followed by succinic, phthalic (Ph), malonic (C_3) and glutaric (C_5) acids in aerosols of downtown Los Angeles. They have also reported higher abundance of oxalic (C_2) acid followed by succinic (C_4), malonic (C_3), phthalic (Ph) and glutaric (C_5) acids in aerosols of west Los Angeles.

Table 1 presents the concentration ranges and average concentrations of dicarboxylic acids and related compounds determined in day and night samples, as well as their chemical formulas. Although the boundary layer height (average 1690±250 m) in the daytime is ~7.5 times higher than in the nighttime (200–250 m) (Rissler et al., 2006), higher concentrations of all dicarboxylic acids and related compounds except terephthalic and ketomalonic acid were observed in a day sample (see upper limit of the range in Table 1). Probably, this is due to the comparatively thick smoke during this sample collection period. It is of interest that although average concentrations of

ACPD
9, 19783–19815, 2009

most of dicarboxylic acids and related compounds were observed higher by 11–20% in nighttime than in daytime, pimelic (C_7), azelaic (C_9), sebacic (C_{10}), phthalic (Ph), hydroxysuccinic (hC_4), 3-oxopropanoic (ωC_3) and glyoxal (Gly) showed almost equal or higher concentrations in the daytime (Table 1).

Succinic (C_4) acid has been suggested to be a precursor of malonic (C_3) acid (Kawamura et al., 1996b). The mean ratio of C_3/C_4 in this study is 0.81 in the daytime versus 0.59 in the nighttime, which is higher than that for vehicular aerosols (average 0.35, Kawamura and Kaplan, 1987), but similar to that of urban aerosols (0.86 in summer versus 0.61 in winter, Ho et al., 2007). Adipic (C_6) and phthalic (Ph) acids are produced by the oxidation of anthropogenic cyclohexene and aromatic hydrocarbon, whereas azelaic (C_9) acid is from biogenic unsaturated fatty acids (Kawamura and Ikushima, 1993). Consequently, C_6/C_9 and Ph/C_9 ratios can be used as markers to evaluate the source strength of anthropogenic versus biogenic precursors to dicarboxylic acids. The mean value of the C_6/C_9 ratio (2.2 for day and night samples) in our study is about 2–3 times higher than that for urban Chinese and Tokyo aerosols (Kawamura and Yasui, 2005; Ho et al., 2007), suggesting that adipic (C_6) acid is also derived from biomass burning. This finding is in contrast to the study of Narukawa et al. (1999), in which an increase of all dicarboxylic acids in the range of C_2–C_{12} except adipic (C_6) acid during fire-induced haze events in southeast Asia was observed. The mean value of the Ph/C_9 ratio in our study is ~2 times and ~4 times lower than that of aerosols collected from Chinese megacities (Ho et al., 2007) and urban Los Angeles (Kawamura and Kaplan, 1987), respectively. This further supports that the contribution of phthalic (Ph) acid from other anthropogenic sources is less important than from biomass burning. Maleic (M) acid can convert into fumaric (F) acid during photochemical reactions (Kawamura and Ikushima, 1993). M/F ratios in all day and night samples ranged between 0.3–5.6 (average 2.8). This is in contrast to the urban aerosols (0.8–3.9, average 1.5) (Kawamura and Ikushima, 1993) and marine aerosols (0.06–1.3, average 0.26) (Kawamura and Sakaguchi, 1999). This may suggest that biomass burning produces aromatic hydrocarbons, precursors of maleic acid.

ACPD
9, 19783–19815, 2009

3.3 High loadings of dicarboxylic acids and related compounds

The average concentrations of total dicarboxylic acids, total ketocarboxylic acids and α-dicarbonyls along with their concentration ranges are shown in Table 1. Ho et al. (2007) reported dicarboxylic acids and related compounds in the atmospheric aerosols collected from 14 Chinese megacities during summer and winter (Table 2). The mean concentrations of total dicarboxylic acids (2180 ng m^{-3}), total ketocarboxylic acids (167 ng m^{-3}) and total dicarbonyls (56 ng m^{-3}) for all day and night samples in our study were found to be higher by 1.6–7.6, 2.6–10.7 and 2.1–16.3 times, respectively, than those of 14 Chinese megacities. Table 2 compares concentrations of our data of C_2–C_5 dicarboxylic acids with those reported in the atmospheric aerosols collected from urban, semiurban/rural areas and remote marine islands located in different parts of the world as well as oceans and polar regions. The mean concentration of total C_2–C_5 dicarboxylic acids in our study is about 2–10 times higher than those from east Asian, European and North American megacities. Similarly, our mean concentration is about an order of magnitude higher than those of semiurban/rural aerosols, and one to two orders of magnitude higher than the aerosols collected from remote oceans and polar regions. These comparisons clearly suggest that biomass burning is an important source of dicarboxylic acids in the atmosphere.

3.4 Diurnal variations of the concentrations of dicarboxylic acids and related compounds

We have observed a very striking phenomenon, that is, usually the concentrations of dicarboxylic acids and related compounds normalized by the biomass burning tracers (levoglucosan and K^+) are higher in the daytime than in the nighttime (Figs. 2 and 3). For example, the normalized concentrations of oxalic (C_2), malonic (C_3) and succinic (C_4) acids increased in daytime compared to nighttime by a factor of 1.2 to 4.6. Similar daytime enhancement in the normalized concentrations were found for most other acid and aldehyde species (Figs. 2 and 3). On the other hand, the normalized concen-

ACPD
9, 19783–19815, 2009

trations of glutaric (C_5) acid were 0.3 to 0.8 times lower in daytime than in nighttime for the first three pairs of successive day and night samples, but were 1.4 to 3.2 times higher in the remaining daytime samples. Some plausible mechanisms to explain these observations are suggested below.

Biomass burning emits large quantities of non-methane hydrocarbons (NMHC), among which unsaturated alkanes are especially abundant (Andreae and Merlet, 2001; Koppmann et al., 2005). Unsaturated NMHC (e.g., ethene, ethyne, propene, butene, isoprene, cycloalkenes, pinene, etc.) can either be oxidized to dicarboxylic acids and related compounds and subsequently partitioned into the gas and aerosol phase (Gao et al., 2001), or be oxidized to aldehydes and ketones, which dissolve into aerosols and are then oxidized to organic acids in aqueous phase reactions in the daytime (Gao et al., 2001). Alternatively, Gao et al. (2003) suggested that large organic molecules emitted from biomass burning might be oxidized in the daytime to smaller molecules through heterogeneous break-down reactions on the particle surface or by aqueous reactions inside the particles because they found that oxalate, glutarate and succinate increased by an order of magnitude when fresh biomass burning plumes from savanna fires aged for about 40 min.

Limbeck et al. (2001) reported the semivolatile behavior of C_2–C_9 dicarboxylic acids, glyoxylic and phthalic acid on aerosols collected using a low volume sampler equipped with a front/back-up filter tandem system of quartz fiber filters. They found that species detected on the back filter accounted for 13.3 to 38.5% of observed concentrations on the front filter, except for malonic acid. So, it is likely that more dicarboxylic acids and related compounds will be partitioned to the aerosol phase in nighttime when the ambient temperature decreases. However, this condensation process can not be more significant than the possible photoproduction, as we have observed higher carbon-based concentrations of dicarboxylic acids and related compounds in the daytime (Figs. 2 and 3).

The effect of combustion phases may have some effect on the observed diurnal variations of dicarboxylic acids and related compounds. Gao et al. (2003) reported

ACPD
9, 19783–19815, 2009

that the K^+/levoglucosan ratio in aerosols produced from savanna fires was 33.3 for flaming combustion and 0.2–0.6 for smoldering combustion. These results suggest that aerosols produced from flaming phases should have a higher K^+/levoglucosan ratio. Higher K^+/levoglucosan ratios (average 0.78±0.3) for daytime samples and lower ratios (average 0.51±0.2) for nighttime, as well as successive day and nighttime samples have already been reported for the same group of samples used in this study (Kundu et al., 2009).

3.5 Chemical degradation of dicarboxylic acids, ketocarboxylic acids and dicarbonyls

The chemical production of C_2–C_9 dicarboxylic acids from the UV irradiation of the oleic acid-O_3-OH radical system in the laboratory, followed by their chemical degradation after 20 h has been observed (Matsunaga et al., 1999). Kalberer et al. (2000) identified gas phase pentanal as a main product from a smog chamber experiment with the cyclohexene-ozone system, as well as oxalic (C_2), malonic (C_3), succinic (C_4), adipic (C_6) acids, multifunctional dicarboxylic acids (hydroxyglutaric and hydroxyadipic), and oxocarboxylic acids (4-oxobutanoic acid, 5-oxopentanoic acid and 6-oxohexanoic acid) in the aerosol phase. Interestingly, the yield of low-molecular-weight dicarboxylic acids and related compounds (C_2–C_5) was higher than that of high-molecular-weight dicarboxylic acids (C_6), suggesting that C_2–C_5 dicarboxylic acids are likely produced due to the photochemical degradation of adipic (C_6) acid in the cyclohexene-ozone system.

Kawamura et al. (1999) have suggested, based on the higher ratios of C_2/C_4 and C_3/C_4, that C_2 and C_3 dicarboxylic acids were likely produced by the oxidative degradation of C_4 and longer chain dicarboxylic acids in the aerosols of the remote equatorial Pacific more so than in the midlatitudes of the Pacific. Strong anti-correlations between the relative abundance of oxalic acid to total *n*-saturated dicarboxylic acids (C_2–C_{10}) and some high carbon number dicarboxylic acids (methylmalonic (iC_4), maleic (M), methylmaleic (mM), methylsuccinic (iC_5), adipic (C_6) and phthalic (Ph)), ketocarboxylic acids [glyoxylic (ωC_2) and pyruvic (Pyr)], and dicarbonyl [glyoxal (Gly)] have been re-

ported in summer aerosols collected from urban Tokyo (Kawamura and Yasui, 2005). These authors have also suggested that longer-chain (C_5–C_{10}) dicarboxylic acids were produced through the oxidation of semi-volatile fatty acids, which are also the oxidation products of unsaturated fatty acids. They are abundant in leaves of higher terrestrial plants and also are emitted from wood burning (Rogge et al., 1998).

Generally, levoglucosan and K^+ normalized ratios of oxalic acid to other dicarboxylic acids, ketocarboxylic acids and dicarbonyls showed higher values in the daytime than in the nighttime (Figs. 4 and 5). This suggests that oxalic acid is likely produced photochemically from other dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the biomass burning environment.

3.6 Primary versus secondary sources of dicarboxylic acids and related compounds

Primary sources of dicarboxylic acids and related compounds include motor exhausts (Kawamura and Kaplan, 1987; Grosjean, 1989), wood combustion (Rogge et al., 1998; Oros and Simoneit, 2001), forest biomass burning (Narukawa et al., 1999; Falkovich et al., 2005) and the cooking of meat (Rogge et al., 1991). Although it is widely believed that the secondary production of dicarboxylic acids overwhelms the emissions from primary sources, little is known about their secondary production from different precursors, which include ethene and ethyne (Warneck, 2003), toluene and isoprene (Ervens et al., 2004), methylglyoxal (Lim et al., 2005; Carlton et al., 2007), unsaturated fatty acids (Kawamura and Gagosian, 1987; Kawamura and Sakaguchi, 1999; Matsunaga et al., 1999), cycloalkenes (Hatakeyama et al., 1985; Kalberer et al., 2000; Gao et al., 2001), etc.

To better understand the sources and formation mechanisms of dicarboxylic acids and related compounds, we conducted correlation analyses on day and night samples. Tables 3 and 4 show the correlation coefficients among dicarboxylic acids and related compounds for day and night samples, respectively. For day samples, very good correlations were obtained between oxalic (C_2) acid and other normal chain (C_3–C_{11})

ACPD
9, 19783–19815, 2009

and branched chain (iC_4, iC_5 and iC_6) saturated dicarboxylic acids, unsaturated (M, F, mM and Ph) dicarboxylic acids, multifunctional (kC_3, kC_7 except hC_4) dicarboxylic acids, ketocarboxylic acids (ωC_2, ωC_4, ωC_9 and Pyr except ωC_3) and dicarbonyls (Gly and MeGly). Systematically, weaker correlations were observed among oxalic (C_2) acid and other dicarboxylic acid species and related compounds in nighttime samples, which can be interpreted as resulting from the accumulation of dicarboxylic acids and related compounds within the shallow nocturnal boundary layer and the cessation of photo-production and degradation of dicarboxylic acids and related compounds at night.

These correlations suggest a similarity in the sources of dicarboxylic acids and related compounds. The sources are likely either primary emission or secondary production, which are strongly connected to each other by chain reactions transforming other dicarboxylic acids and related compounds to oxalic acid. This is also supported by the higher abundance of oxalic acid relative to other dicarboxylic acids and related compounds in the daytime (Figs. 4 and 5). Assuming that other dicarboxylic acids and related compounds are converted to oxalic (C_2) acid, particularly in the daytime due to photochemical degradation, it can be concluded based on the linear relationship between oxalic acid and other dicarboxylic acids and related compounds (y [other dicarboxylic acid and related compounds]=1.03 [oxalic acid]+243.5) that, on average, 77% of the oxalic (C_2) acid are produced from other dicarboxylic acids and related compounds. The remaining 23% are likely produced from direct emissions, or are chemically produced from other unknown precursors.

Gao et al. (2003) report the emission ratios of oxalic (C_2) acid to succinic (C_4) acid and to glutaric (C_5) acid in the aerosols of savanna plumes to be 0.16 and 2.5, respectively (Gao et al., 2003). In our data, the (C_2/C_4) ratio is 3.5 and 2.9 times higher during day and nighttime, respectively, and the (C_2/C_5) ratio is 35 and 10 times higher during daytime and nighttime, respectively. These findings substantiate the dominant secondary production of oxalic (C_2) acid due to the degradation of succinic (C_4) and glutaric (C_5) acids. The emission ratios of oxalic acid (C_2)/K^+ and succinic acid (C_4)/K^+

ACPD
9, 19783–19815, 2009

as well as oxalic acid (C_2)/levoglucosan and succinic acid (C_4)/levoglucosan can be derived from Gao et al. (2003) for aerosols collected from fresh plumes of savanna fires. Ratios of both dicarboxylic acids to K^+ and levoglucosan are 0.05 and 0.03, respectively. Gao et al. (2003) also showed that dicarboxylic acid ratios with respect to K^+ increased to 0.25 for oxalic (C_2) acid and to 0.15 for succinic (C_4) acid in plumes aged 40 min. A higher average value for oxalic (C_2) acid (0.78) and a similar average value for succinic (C_4) acid (0.14) was obtained for our day and night samples. Sillanpää et al. (2005) reported higher enrichment of oxalate (10) and succinate (5) with respect to K^+ in the case of boreal wildfire smoke transported long-range.

Most of the dicarboxylic acids and related compounds showed moderate to strong correlations with the biomass burning tracers (K^+, CO and EC) and OC except for terephthalic (tPh), malic (hC_4) and 3-oxopropanoic (ωC_3) acids in the daytime, and maleic (M), phthalic (Ph), isophthalic (iPh), ketomalonic (kC_3) and ketopimelic (kC_7) acids, and glyoxal (Gly) in the nighttime (Table 5). It has also been previously reported that dicarboxylic acids and related compounds correlated well with the biomass burning tracers (K^+, BC_e and CO) (Graham et al., 2002; Mayol-Bracero et al., 2002). This suggests that the dicarboxylic acids and related compounds are in part directly emitted from biomass burning. Correlations of dicarboxylic acids and related compounds against biomass burning tracers (K^+, CO and EC_a) and OC are systematically weaker in the nighttime than in the daytime (Table 5).

4 Conclusions

This study demonstrates, for the first time, the molecular distributions of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the full range of C_2–C_{11} in biomass burning aerosols. Oxalic (C_2) acid is the most abundant of these species, followed by succinic (C_4), malonic (C_3) and glyoxylic (ωC_2) acids. Higher loadings of total dicarboxylic acids, total ketocarboxylic acids and total dicarbonyls were found in our biomass burning aerosols than in the aerosols of heavily polluted megacities in East Asia, indicating

ACPD
9, 19783–19815, 2009

that biomass burning is a very important source for dicarboxylic acids and related compounds at the regional and global scale. Evidence for the photochemical formation and degradation of dicarboxylic acids in the smoke layers was obtained in this study. Considering the C_3–C_{11} dicarboxylic acids, ketocarboxylic acids and dicarbonyls as being precursors of oxalic acid, this study has also shown that the secondary formation of oxalic (C_2) acid via photochemical processes overwhelms the primary production. However, these precursor compounds are also derived predominantly from biomass burning emissions and subsequent photochemical oxidations.

Acknowledgements. This research was supported in part by the Japanese Ministry of Education, Science, Sport and Culture (MEXT) through grant-in-aid number 19204055 and also carried out within the framework of the Smoke, Aerosols, Clouds, Rainfall, and Climate (SMOCC) project, a contribution to the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA). The authors gratefully acknowledge financial support by the European Commission (contract No. EVK-CT-2001-00110 SMOCC) and by the Max Planck Society. We are thankful to all members of the LBA-SMOCC and LBA-RACCI Science Teams for their support during the field campaign, in particular J. von Jouanne and A. Camargo for their support in setting up the sampling site and to G. Frank for his help in the preparation of the sampling devices. S. K. acknowledges financial support from MEXT and the cooperation of S. Decesari for supplying additional data gained under the framework of LBA-SMOCC campaign.

References

Allen, A. G. and Miguel, A. H.: Biomass burning in the Amazon-Characterization of the ionic component of aerosols generated from flaming and smoldering rain-forest and savanna, Environ. Sci. Technol., 29(2), 486–493, 1995.

Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochem. Cy., 15, 955–966, 2001.

Andreae, M. O., Artaxo, P., Brandão C., Carswell, F. E., Ciccioli, P., da Costa, A. L., Culf, A. D., et al.: Biogeochemical cycling of carbon, water, energy, trace gases and aerosols in Amazonia: The LBA-EUSTACH experiments, J. Geophys. Res., 107, 8066, doi:10.1029/2001JD000524, 2002.

Andreae, M. O., Rosenfeld, D., Artaxo, P., Costa, A. A., Frank, G. P., Longo, K. M., and Silva-Dias, M. A. F.: Smoking rain clouds over the Amazon, Science, 303(5662), 1337–1342, 2004.

Andreae, M. O. and Rosenfeld, D.: Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols, Earth Sci. Rev., 89, 13–41, 2008.

Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H.-J., and Erven, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmos. Environ., 41, 7588–7602, 2007

Cruz, C. N. and Pandis, S. N.: A study of the ability of secondary organic aerosol to act as cloud condensation nuclei, Atmos. Environ., 31, 2205–2214, 1997.

Cruz, C. N. and Pandis, S. N.: The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol, J. Geophys. Res., 103, 13111–13123, 1998.

Decesari, S., Fuzzi, S., Facchini, M. C., Mircea, M., Emblico, L., Cavalli, F., Maenhaut, W., Chi, X., Schkolnik, G., Falkovich, A., Rudich, Y., Claeys, M., Pashynska, V., Vas, G., Kourtchev, I., Vermeylen, R., Hoffer, A., Andreae, M. O., Tagliavini, E., Moretti, F., and Artaxo, P.: Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds, Atmos. Chem. Phys., 6, 375–402, 2006, http://www.atmos-chem-phys.net/6/375/2006/.

Ervens, B., Feingold, G., Frost, G. J., Kreidenweis, S. M.: A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, J. Geophys. Res., 109, D15205, doi:10.1029/2003JD004387, 2004.

Falkovich, A. H., Graber, E. R., Schkolnik, G., Rudich, Y., Maenhaut, W., and Artaxo, P.: Low molecular weight organic acids in aerosol particles from Rondônia, Brazil, during the biomass-burning, transition and wet periods, Atmos. Chem. Phys., 5, 781–797, 2005, http://www.atmos-chem-phys.net/5/781/2005/.

Fisseha, R., Dommen, J., Gaeggelar, K., Weingartner, E., Samburova, V., Kalberer, M., and Baltensperger, U.: Online gas and aerosol measurement of water soluble carboxylic acids in Zurich, J. Geophys. Res., 111, D12316, doi:10.1029/2005JD006782, 2006.

Fridlind, A. M., Jacobson, M. Z., Kerminen, V.-M., Hillamo, R. E., Ricard, V., and Jaffrezo, J. L.: Analysis of gas-partitioning in the Arctic: comparison of size-resolved equilibrium model results with field data, J. Geophys. Res., 105, 19891–19903, 2000.

Fuzzi, S., Decesari, S., Facchini, M. C., Cavalli, F., Emblico, L., Mircea, M., Andreae, M. O.,

Trebs, I., Hoffer, A., Guyon, P., Artaxo, P., Rizzo, L. V., Lara, L. L., Pauliquevis, T., Maenhaut, W., Raes, N., Chi, X., Mayol-Bracero, O. L., Soto-García, L. L., Clayes, M., Kourtchev, I., Rissler, J., Swietlicki, E., Tagliavini, E., Schkolnik, G., Falkovich, A. H., Rudich, Y., Fisch, G., and Gatti, L. V.: Overview of the inorganic and organic composition of size-segregated aerosol in Rondônia, Brazil, from the biomass burning period to the onset of the wet season, J. Geophys. Res., 112, D01201, doi:10.1029/2005JD006741, 2007.

Gao, S., Hegg, D. A., Frick, G., Caffrey, P. F., Pasternack, L., Cantrell, C., Sullivan, W., Ambrusko, J., Albrechcinski, T., and Kirchstetter, T. W.: Experimental and modeling studies of secondary organic aerosol formation and some applications to the marine boundary layer, J. Geophys. Res., 106(D21), 27619–27634, 2001.

Gao, S., Hegg, D. A., Hobbs, P. V., Kirchstetter, T. W., Magi, B. I., and Sadilek, M.: Water-soluble organic components in aerosols associated with savanna fires in southern Africa: Identification, evolution, and distribution, J. Geophys. Res., 108(D13), 8491, doi:10.1029/2002JD002324, 2003.

Graham, B., Mayol-Bracero, O. L., Guyon, P., Roberts, G. C., Decesari, S., Facchini, M. C., Artaxo, P., Maenhaut, W., Koll, P., and Andreae, M. O.: Water-soluble organic compounds in biomass burning aerosols over Amazonia – 1. Characterization by NMR and GC-MS, J. Geophys. Res., 107(D20), 8047, doi:10.1029/2001JD000336, 2002.

Grosjean, D.: Organic acids in southern California air: Ambient concentrations, mobile source emissions, in situ formation and removal processes, Environ. Sci. Technol., 23, 1506–1514, 1989.

Hatakeyama, S., Tanonaka, T., Weng, J., Bandow, H., Takagi, H., and Akimoto, H.: Ozone-cyclohexene reaction in air: Quantitative analyses of particulate products and the reaction mechanism, Environ. Sci. Technol., 19, 935–942, 1985.

Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., and Watson, J. G.: Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, J. Geophys. Res., 112, D22S27, doi:10.1029/2006JD008011, 2007.

Hoffer, A., Gelencsér, A., Blazsó, M., Guyon, P., Artaxo, P., and Andreae, M. O.: Diel and seasonal variations in the chemical composition of biomass burning aerosol, Atmos. Chem. Phys., 6, 3505–3515, 2006, http://www.atmos-chem-phys.net/6/3505/2006/.

Kalberer, M., Yu, J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: Aerosol formation in the cyclohexene-ozone system, Environ. Sci. Technol., 34, 4894–4901, 2000.

Kaufman, Y. J. and Fraser, R. S.: The effect of smoke particles on clouds and climate forcing, Science, 277(5332), 1636–1639, 1997.
Kaufman, Y. J., Tanre, D., and Boucher, O.: A satellite view of aerosols in the climate system, Nature, 419(6903), 215–223, 2002.
Kawamura, K. and Gagosian, R. B.: Implications of ω-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids, Nature, 325, 330–332, 1987.
Kawamura, K. and Kaplan, I. R.: Motor exhaust emission as a primary source of dicarboxylic acids in Los Angeles ambient air, Environ. Sci. Technol., 21, 105–110, 1987.
Kawamura, K.: Identification of C_2–C_{10} ω-oxocarboxylic acids, pyruvic acid and C_2–C_3 α-dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC-MS, Anal. Chem., 65, 3505–3511, 1993.
Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, Environ. Sci. Technol., 27, 2227–2235, 1993.
Kawamura, K. and Usukura, K.: Distribution of low molecular weight dicarboxylic acids in the North Pacific aerosol samples, J. Oceanogr., 49, 271–283, 1993.
Kawamura, K., Sempéré, R., Imai, Y., Fujii, Y., and Hayashi, M.: Water soluble dicarboxylic acids and related compounds in Antarctic aerosols, J. Geophys. Res., 101, 18721–18728, 1996a.
Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of dicarboxylic acids, ketoacids, and dicarbonyls in arctic aerosols at polar sunrise, Atmos. Environ., 30, 1709–1722, 1996b.
Kawamura, K. and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropic, J. Geophys. Res., 104, 3501–3509, 1999.
Kawamura, K., Steinberg, S., Ng, L., and Kaplan, I. R.: Wet deposition of low molecular weight mono- and dicarboxylic acids, aldehydes and inorganic species in Los Angeles, Atmos. Environ., 35, 3917–3926, 2001.
Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T., and Lee, M.: Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in: Geochemical Investigation in Earth and Space Science: A Tribute to Issac R. Kaplan, edited by: Hill, R. J., Leventhal, J., Aizenshtat, Z., Baedecker, M. J., Claypool, G., Eganhouse, R., Goldhaber, M., and Peters, K., The Geochemical Society,

Publications Series No. 9, Elsevier, 243–265, 2004.
Kawamura, K. and Yasui, O.: Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, Atmos. Environ., 39, 1945–1960, 2005.
Kerminen, V. M., Teinila, K., Hillamo, R., and Makela, T.: Size segregated chemistry of particulate dicarboxylic acids in the Arctic atmosphere, Atmos. Environ., 33, 2089–2100, 1999.
Khwaja, H. A.: Atmospheric concentrations of carboxylic acids and related compounds at a semiurban site, Atmos. Environ., 29, 127–139, 1995.
Koppmann, R., von Czapiewski, K., and Reid, J. S.: A review of biomass burning emissions, part I: gaseous emissions of carbon monoxide, methane, volatile organic compounds, and nitrogen containing compounds, Atmos. Chem. Phys. Discuss., 5, 10455–10516, 2005, http://www.atmos-chem-phys-discuss.net/5/10455/2005/.
Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: 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, J. Aerosol. Sci., in press, 2009.
Legrand, M., Preunkert, S., Oliveira, T., Pio, C. A., Hammer, S., Gelencśer, A., Kasper-Giebl, A., and Laj, P.: Origin of C_2–C_5 dicarboxylic acids in the European atmosphere inferred from year-round aerosol study conducted at a west-east transect, J. Geophys. Res., 112, D23S07, doi:10.1029/2006JD008019, 2007.
Lim, H.-J., Carlton, A. G., and Turpin, B. J.: Isoprene forms secondary organic aerosol through cloud processing: Model simulations, Environ. Sci. Technol., 39, 4441–4446, doi:10.1021/es048039h, 2005.
Limbeck, A. and Puxbaum, H.: Organic acids in continental background aerosol, Atmos. Environ., 33, 1847–1852, 1999.
Limbeck, A., Puxbaum, H., Otter, L., and Scholes, M. C.: Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA), Atmos. Environ., 35(10), 1853–1862, 2001.
Matsunaga, S., Kawamura, K., Nakatsuka, T., and Ohkouchi, N.: Preliminary study on laboratory photochemical formation of low molecular weight dicarboxylic acids from unsaturated fatty acid (oleic acid), Res. Org. Geochem., 14, 19–25, 1999.
Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S., Facchini, M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds in biomass burning

aerosols over Amazonia – 2. Apportionment of the chemical composition and importance of the polyacidic fraction, J. Geophys. Res., 107(D20), 8091, doi:10.1029/2001JD000522, 2002.

Mircea, M., Facchini, M. C., Decesari, S., Cavalli, F., Emblico, L., Fuzzi, S., Vestin, A., Rissler, J., Swietlicki, E., Frank, G., Andreae, M. O., Maenhaut, W., Rudich, Y., and Artaxo, P.: Importance of the organic aerosol fraction for modeling aerosol hygroscopic growth and activation: a case study in the Amazon Basin, Atmos. Chem. Phys., 5, 3111–3126, 2005, http://www.atmos-chem-phys.net/5/3111/2005/.

Mochida, M., Kawabata, A., Kawamura, K., Hatsushika, H., and Yamazaki, K.: Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific, J. Geophys. Res., 108, 4193, doi:10.1029/2002JD002355, 2003a.

Mochida, M., Kawamura, K., Umemoto, N., Kobayashi, M., Matsunaga, S., Lim, H.-J., Turpin, B. J., Bates, T. S., and Simoneit, B. R. T.: Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: Continental outflow of organic aerosols during the ACE-Asia campaign, J. Geophys. Res., 108(D23), 8638, doi:10.1029/2002JD003249, 2003b.

Narukawa, M., Kawamura, K., Takeuchi, N., and Nakajima, T.: Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, Geophys. Res. Lett., 26(20), 3101–3104, 1999.

Narukawa, M., Kawamura, K., Li, S.-M., and Bottenheim, J. W.: Dicarboxylic acids in the Arctic aerosols and snowpacks collected during ALERT 2000, Atmos. Environ., 36, 2491–2499, 2002.

Narukawa, M., Kawamura, K., Anlauf, K. G., and Barrie, L. A.: Fine and coarse modes of dicarboxylic acids in the Arctic aerosols collected during the Polar Sunrise Experiment 1997, J. Geophys. Res., 108(D18), 4575, doi:10.1029/2003JD003646, 2003.

Oros, D. R. and Simoneit, B. R. T.: Identification and emission factors of molecular tracers in organic aerosols from biomass burning, part 2, Deciduous trees, Appl. Geochem., 16, 1545–1565, 2001.

Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D.: Atmosphere – Aerosols, climate, and the hydrological cycle, Science, 294(5549), 2119–2124, 2001.

Rissler, J., Vestin, A., Swietlicki, E., Fisch, G., Zhou, J., Artaxo, P., and Andreae, M. O.: Size distribution and hygroscopic properties of aerosol particles from dry-season biomass burning

in Amazonia, Atmos. Chem. Phys., 6, 471–491, 2006, http://www.atmos-chem-phys.net/6/471/2006/.
Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.: Sources of fine organic aerosol. 1. Charbroillers and meat cooking operations, Environ. Sci. Technol., 25, 1112–1125, 1991.
Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.: Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces, Environ. Sci. Technol., 32, 13–22, 1998.
Röhrl, A. and Lammel, G.: Determination of malic acid and other C_4 dicarboxylic acids in atmospheric aerosol samples, Chemosphere, 46, 1195–1199, 2002.
Sempéré, R. and Kawamura, K.: Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosol from urban atmosphere, Atmos. Environ., 28, 449–459, 1994.
Sempéré, R. and Kawamura, K.: Low molecular weight dicarboxylic acids and related polar compounds in the remote marine rain samples collected from western Pacific, Atmos. Environ., 30, 1609–1619, 1996.
Sempéré, R. and Kawamura, K.: Trans-hemispheric contribution of C_2–C_{10} α, ω-dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions, Global Biogeochem. Cy., 17, 1069, doi:10.1029/2002GB001980, 2003.
Sherwood, S.: A microphysical connection among biomass burning, cumulus clouds, and stratospheric moisture, Science, 295, 1272–1275, 2002.
Sillanpää, S., Saarrikoski, S., Hillamo, R., Pennanen, A., Makkonen, U., Spolnik, Z., Grieken, R. V., Koskentalo, T., and Salonen, R.: Chemical composition, mass size distribution and sources analysis of long-range transported wildfire smokes in Helsinki, Sci. Total Environ., 350, 119–135, 2005.
Solomon, P. A., Moyers, J. L., and Fletcher, R.: High-volume dichotomous virtual impactor for the fractionation and collection of particles according to aerodynamic size, Aerosol Sci. Technol., 2, 455, doi:10.1080/02786828308958649, 1983.
Wang, G., Liu, N. C., and Wang, L.: Identification of dicarboxylic acids and aldehydes of PM_{10} and $PM_{2.5}$ aerosols in Nanjing, China, Atmos. Environ., 36, 1941–1950, 2002.
Wang, H., Kawamura, K., and Yamazaki, K.: Water soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the southern Ocean and western Pacific Ocean,

J. Atmos. Chem., 53, 43–61, 2006.
Warneck, P.: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, Atmos. Environ., 37, 2423–2427, 2003.

Table 1. Concentrations of dicarboxylic acids, ketocarboxylic acids and dicarbonyls detected in biomass burning aerosols collected during the LBA-SMOCC campaign at the FNS site in Rondônia, Brazil.

			Concentration ($ng\,m^{-3}$)					
			Daytime samples (n=6)			Nighttime samples (n=9)		
Name of compounds	Chemical formula	Abbreviation	Minimum	Maximum	Average	Minimum	Maximum	Average
Saturated *n*-dicarboxylic acids								
Oxalic	HOOC-COOH	C_2	695	2059	1161	1156	1897	1551
Malonic	HOOC-CH_2-COOH	C_3	95	345	173	145	296	203
Succinic	HOOC-$(CH_2)_2$-COOH	C_4	124	414	213	229	428	341
Glutaric	HOOC-$(CH_2)_3$-COOH	C_5	3	88	31	45	78	62
Adipic	HOOC-$(CH_2)_4$-COOH	C_6	22	101	43	35	65	51
Pimelic	HOOC-$(CH_2)_5$-COOH	C_7	8	28	15	6	26	15
Suberic	HOOC-$(CH_2)_6$-COOH	C_8	0.07	23	7	2	16	9
Azelaic	HOOC-$(CH_2)_7$-COOH	C_9	9	46	24	13	28	20
Sebacic	HOOC-$(CH_2)_8$-COOH	C_{10}	1	8	4	1	7	3
Undecanedioic	HOOC-$(CH_2)_9$-COOH	C_{11}	0.19	7	2	2	5	3
Branched dicarboxylic acids								
Methylmalonic	HOOC-CH(CH_3)-COOH	iC_4	3	16	8	9	15	12
Methylsuccinic	HOOC-CH(CH_3)-CH_2-COOH	iC_5	15	65	29	33	71	54
Methylglutaric	HOOC-CH(CH_3)-$(CH_2)_2$-COOH	iC_6	2	9	4	4	11	7
Unsaturated dicarboxylic acids								
Maleic	HOOC-CH=CH-COOH (cis)	M	10	40	16	3	56	30
Fumaric	HOOC-CH=CH-COOH (trans)	F	3	15	6	7	14	11
Methylmaleic	HOOC-C(CH_3)=CH-COOH (cis)	mM	3	30	9	14	27	19
Phthalic	HOOC-(C_6H_4)-COOH (ortho)	Ph	25	66	42	31	56	42
Isophthalic	HOOC-(C_6H_4)-COOH (meta)	iPh	1	5	3	2	5	3
Terephthalic	HOOC-(C_6H_4)-COOH (para)	tPh	5	26	13	2	18	11
Multifunctional dicarboxylic acids								
Hydroxysuccinic	HOOC-CH(OH)-CH_2-COOH	hC_4	10	44	23	15	27	21
Ketomalonic	HOOC-HC(O)-COOH	kC_3	0.14	33	10	12	36	23
Ketopimelic	HOOC-CH_2-CH_2-HC(O)$(CH_2)_2$-COOH	kC_7	5	13	10	5	11	8
Subtotal (Total dicarboxylic acids)			**1039**	**3480**	**1849**	**1773**	**3193**	**2500**
Ketocarboxylic acids								
Glyoxylic	OHC-COOH	ωC_2	65	225	119	100	224	143
3-Oxopropanoic	OHC-CH_2-COOH	ωC_3	BDL	23	5	1	3	1
4-Oxobutanoic	OHC-$(CH_2)_2$-COOH	ωC_4	BDL	7	3	2	8	5
9-Oxononanoic	OHC-$(CH_2)_7$-COOH	ωC_9	2	4	3	1	3	2
Pyruvic acid	CH_3-(O)C-COOH	Pyr	12	50	26	20	40	29
Subtotal (Ketocarboxylic acids)			**78**	**309**	**155**	**124**	**277**	**179**
α-Dicarbonyls								
Glyoxal	OHC-CHO	Gly	19	54	30	9	40	31
Methylglyoxal	CH_3-(O)C-CHO	MeGly	13	38	23	19	43	28
Subtotal (α-dicarbonyls)			**31**	**93**	**53**	**29**	**83**	**59**
Total (All detected species)			**1137**	**3831**	**2030**	**1906**	**3513**	**2709**

ACPD
9, 19783–19815, 2009

Table 2. Comparison between the results of this study and other study results for the average concentrations of C_2–C_5 (ng m^{-3}) dicarboxylic acids in atmospheric aerosols.

Name of site	Oxalic	Malonic	Succinic	Glutaric	Total	References
Urban						
Hong Kong, China	618	92	68	16	794	Ho et al. (2007)
Guangzhou, China	948	66	81	23	1118	Ho et al. (2007)
Xiamen, China	648	47	61	17	773	Ho et al. (2007)
Chongqing, China	639	41	109	29	818	Ho et al. (2007)
Hangzhou, China	723	52	79	26	880	Ho et al. (2007)
Wuhan, China	628	49	80	21	778	Ho et al. (2007)
Shanghai, China	537	63	87	28	715	Ho et al. (2007)
Xi'an, China	802	61	148	62	1073	Ho et al. (2007)
Qingdao, China	283	18	43	13	357	Ho et al. (2007)
Yulin, China	267	39	43	14	363	Ho et al. (2007)
Jinchang, China	155	13	20	9	197	Ho et al. (2007)
Tianjin, China	400	42	78	34	554	Ho et al. (2007)
Beijing, China	553	47	77	35	712	Ho et al. (2007)
Changchun, China	345	40	82	29	496	Ho et al. (2007)
Nanjing, China	660	89	113	48	910	Wang et al. (2002)
Tokyo, Japan	270	55	37	11	373	Kawamura and Ikushima (1993)
Zurich, Switzerland	122	21	9	4	156	Fisseha et al. (2006)
Viena, Austria	340	244	117	26	727	Limbeck and Puxbaum (1999)
Leipzig, Germany	229	66	35		330	Röhrl and Lammel (2002)
Los Angeles, USA	513	80	172	59	824	Kawamura and Kaplan (1987)
Semiurban/rural						
Puy de Dôme, France	137	29	12	9	187	Legrand et al. (2007)
K-puszta, Hungary	282	29	29	20	360	Legrand et al. (2007)
New York, USA	231	119	84		434	Khwaja (1995)
Nylsvley Nature Reserve (S. Africa)	79	52	13	1.9	146	Limbeck et al. (2001)
Remote marine Islands						
Gosan, South Korea	473	67	52	11	603	Kawamura et al. (2004)
Chichi-jima Island, Japan	91	13	8	1.6	114	Mochida et al. (2003a)
Azores, Portugal	54	6	2	1.3	63	Legrand et al. (2007)
Coastal site/Open Ocean						
Aveiro, Portugal	265	25	20	13	323	Legrand et al. (2007)
Southern Ocean (>50° S, 130–150° E)	2.4	0.8	0.4	0.1	4	Wang et al. (2006)
Western Pacific (35° N–50° S)	38	12	5	1.2	56	Wang et al. (2006)
Western Pacific (5° N–40° S)	2.8	1	0.8	0.3	5	Sempéré and Kawamura (2003)
Tropical to Western North Pacific	40	11	2.8	0.6	54	Kawamura and Sakaguchi (1999)
Polar regions						
Alert, Canada	9.5	2.9	4.1	1.3	18	Narukawa et al. (2003)
Alert, Canada	21	6.5	7.5	1.5	37	Narukawa et al. (2002)
Alert, Canada	14	2	4	1	21	Kawamura et al. (1996b)
Alert, Canada	14	4	4.1	1.6	24	Kawamura et al. (2005)
Sevettijarvi, Finland	21	16	23	6	66	Kerminen et al. (1999)
Sevettijarvi, Finland	63		45	16	124	Fridlind et al. (2000)
Syowa Station, Antarctic	4.6	0.9	17	0.9	23	Kawamura et al. (1996a)
Biomass burning aerosols						
Rondônia, Brazil	1356	188	277	47	1868	This study

ACPD
9, 19783–19815, 2009

Table 3. Correlation co-efficients (r^2) analysis among dicarboxylic acids, ketocarboxylic acids and dicarbonyls for day samples (n=6).

Species	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	iC_4	iC_5	iC_6	M	F	mM	Ph	iPh	tPh	hC_4	kC_3	kC_7	ωC_2	ωC_3	ωC_4	ωC_9	Pyr	Gly	MeGly
C_2	1																												
C_3	0.99	1																											
C_4	0.99	0.99	1																										
C_5	0.99	0.99	0.98	1																									
C_6	0.96	0.98	0.99	0.94	1																								
C_7	0.96	0.96	0.97	0.91	0.97	1																							
C_8	0.94	0.97	0.98	0.95	0.97	0.94	1																						
C_9	0.88	0.86	0.88	0.80	0.91	0.95	0.84	1																					
C_{10}	0.84	0.86	0.88	0.82	0.87	0.92	0.93	0.83	1																				
C_{11}	0.98	0.99	0.98	0.99	0.95	0.92	0.97	0.82	0.87	1																			
iC_4	0.97	0.99	0.99	0.97	0.98	0.95	0.98	0.84	0.89	0.98	1																		
iC_5	0.97	0.99	0.99	0.96	0.99	0.96	0.99	0.87	0.89	0.98	0.99	1																	
iC_6	0.93	0.94	0.95	0.90	0.97	0.95	0.97	0.92	0.91	0.94	0.94	0.97	1																
M	0.90	0.92	0.93	0.88	0.96	0.88	0.88	0.87	0.70	0.88	0.91	0.93	0.91	1															
F	0.97	0.98	0.98	0.96	0.99	0.94	0.95	0.88	0.80	0.96	0.97	0.98	0.95	0.98	1														
mM	0.95	0.96	0.97	0.93	0.98	0.91	0.93	0.87	0.76	0.94	0.95	0.97	0.94	0.99	0.99	1													
Ph	0.82	0.80	0.82	0.72	0.86	0.92	0.76	0.97	0.76	0.73	0.78	0.80	0.83	0.83	0.83	0.81	1												
iPh	0.64	0.64	0.67	0.53	0.72	0.83	0.65	0.87	0.76	0.55	0.66	0.67	0.71	0.64	0.65	0.62	0.93	1											
tPh	−0.20	−0.20	−0.20	−0.20	−0.18	−0.03	0.00	−0.13	0.32	−0.13	−0.10	−0.13	−0.08	−0.44	−0.30	−0.36	−0.15	0.16	1										
hC_4	0.01	0.04	0.07	−0.07	0.16	0.19	0.02	0.16	0.02	−0.09	0.11	0.08	−0.01	0.20	0.11	0.13	0.38	0.52	−0.07	1									
kC_3	0.89	0.92	0.93	0.91	0.91	0.89	0.98	0.77	0.96	0.95	0.94	0.94	0.94	0.78	0.87	0.84	0.67	0.60	0.16	−0.09	1								
kC_7	0.60	0.57	0.60	0.46	0.67	0.78	0.62	0.85	0.78	0.50	0.59	0.61	0.70	0.57	0.58	0.55	0.89	0.98	0.26	0.42	0.59	1							
ωC_2	0.97	0.99	0.99	0.96	0.99	0.97	0.99	0.87	0.90	0.97	0.98	0.99	0.95	0.91	0.97	0.95	0.82	0.70	−0.07	0.13	0.94	0.64	1						
ωC_3	0.02	−0.05	−0.10	0.07	−0.24	−0.21	−0.23	−0.30	−0.33	−0.03	−0.14	−0.20	−0.31	−0.22	−0.14	−0.17	−0.31	−0.51	−0.29	−0.41	−0.24	−0.59	−0.17	1					
ωC_4	0.60	0.60	0.61	0.56	0.66	0.60	0.63	0.75	0.58	0.64	0.55	0.64	0.79	0.71	0.66	0.68	0.60	0.43	−0.24	−0.32	0.62	0.50	0.57	−0.37	1				
ωC_9	0.64	0.60	0.59	0.63	0.58	0.51	0.52	0.63	0.36	0.64	0.51	0.57	0.65	0.68	0.65	0.67	0.49	0.18	−0.56	−0.46	0.47	0.19	0.51	0.14	0.85	1			
Pyr	0.98	0.99	0.98	0.99	0.94	0.91	0.95	0.78	0.83	0.99	0.98	0.97	0.89	0.86	0.94	0.93	0.71	0.54	−0.15	−0.01	0.91	0.46	0.97	0.06	0.51	0.55	1		
Gly	0.98	0.97	0.97	0.95	0.96	0.96	0.91	0.89	0.79	0.93	0.96	0.95	0.90	0.93	0.97	0.96	0.87	0.70	−0.28	0.19	0.82	0.61	0.96	−0.02	0.55	0.59	0.95	1	
MeGly	0.96	0.97	0.98	0.96	0.96	0.95	0.98	0.82	0.92	0.96	0.99	0.98	0.92	0.85	0.93	0.90	0.77	0.68	0.02	0.11	0.95	0.62	0.99	−0.13	0.49	0.43	0.97	0.93	1

Note: See Table 1 for abbreviations.

ACPD
9, 19783–19815, 2009

Table 4. Correlation co-efficients (r^2) analysis among dicarboxylic acids, ketocarboxylic acids and dicarbonyls for night samples (n=9).

Species	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	iC_4	iC_5	iC_6	M	F	mM	Ph	iPh	tPh	hC_4	kC_3	kC_7	ωC_2	ωC_3	ωC_4	ωC_9	Pyr	Gly	MeGly
C_2	1																												
C_3	0.93	1																											
C_4	0.84	0.67	1																										
C_5	0.74	0.48	0.98	1																									
C_6	0.66	0.41	0.91	0.96	1																								
C_7	0.14	−0.20	0.51	0.69	0.79	1																							
C_8	0.77	0.72	0.87	0.73	0.79	0.40	1																						
C_9	0.59	0.47	0.83	0.80	0.86	0.59	0.86	1																					
C_{10}	0.26	0.21	0.46	0.47	0.63	0.54	0.61	0.76	1																				
C_{11}	0.60	0.39	0.84	0.88	0.88	0.65	0.71	0.94	0.59	1																			
iC_4	0.97	0.95	0.78	0.63	0.58	0.07	0.83	0.59	0.30	0.54	1																		
iC_5	0.60	0.41	0.90	0.93	0.93	0.66	0.72	0.81	0.61	0.80	0.50	1																	
iC_6	0.60	0.28	0.79	0.90	0.84	0.67	0.54	0.68	0.19	0.84	0.43	0.75	1																
M	−0.23	−0.23	−0.22	−0.20	−0.28	−0.28	−0.60	−0.35	−0.31	−0.12	−0.36	−0.12	−0.10	1															
F	0.42	0.20	0.67	0.78	0.70	0.59	0.27	0.38	0.21	0.54	0.26	0.78	0.65	0.33	1														
mM	0.28	0.01	0.41	0.64	0.47	0.47	0.02	0.33	−0.04	0.61	0.09	0.46	0.75	0.30	0.65	1													
Ph	−0.30	−0.14	−0.72	−0.65	−0.67	−0.57	−0.64	−0.63	−0.28	−0.62	−0.30	−0.69	−0.61	0.27	−0.54	−0.24	1												
iPh	0.51	0.62	0.35	0.17	0.30	0.02	0.67	0.46	0.67	0.21	0.65	0.22	−0.17	−0.52	−0.16	−0.48	−0.05	1											
tPh	0.63	0.58	0.66	0.64	0.65	0.41	0.83	0.76	0.63	0.63	0.68	0.60	0.40	−0.68	0.19	0.17	−0.45	0.64	1										
hC_4	0.73	0.49	0.95	0.99	0.96	0.67	0.76	0.83	0.46	0.89	0.62	0.94	0.92	−0.18	0.73	0.59	−0.69	0.15	0.61	1									
kC_3	0.59	0.79	0.25	0.00	−0.03	−0.50	0.38	−0.03	0.02	−0.19	0.68	0.04	−0.27	−0.14	−0.06	−0.47	0.12	0.65	0.25	0.00	1								
kC_7	0.33	0.31	0.42	0.38	0.54	0.41	0.68	0.81	0.87	0.64	0.42	0.40	0.23	−0.49	−0.10	−0.07	−0.23	0.70	0.66	0.39	−0.01	1							
ωC_2	0.66	0.82	0.48	0.26	0.30	−0.21	0.64	0.36	0.46	0.15	0.73	0.40	−0.08	−0.22	0.09	−0.39	−0.07	0.80	0.49	0.28	0.88	0.36	1						
ωC_3	0.37	0.07	0.53	0.67	0.61	0.54	0.20	0.33	−0.10	0.56	0.19	0.51	0.89	0.16	0.60	0.71	−0.36	−0.44	−0.04	0.69	−0.35	−0.07	−0.29	1					
ωC_4	−0.02	−0.20	0.35	0.37	0.30	0.44	0.18	0.24	−0.17	0.36	−0.04	0.30	0.48	−0.10	0.41	0.41	−0.82	−0.38	0.16	0.37	−0.41	−0.15	−0.42	0.34	1				
ωC_9	0.63	0.56	0.56	0.56	0.45	0.15	0.55	0.65	0.16	0.73	0.62	0.35	0.62	−0.28	0.08	0.55	−0.28	0.16	0.63	0.56	−0.01	0.46	0.08	0.35	0.25	1			
Pyr	0.28	0.06	0.49	0.55	0.68	0.67	0.38	0.30	0.45	0.28	0.21	0.63	0.40	−0.08	0.65	0.04	−0.38	0.22	0.14	0.53	0.08	0.15	0.27	0.41	0.03	−0.32	1		
Gly	0.64	0.74	0.28	0.05	−0.06	−0.51	0.26	−0.12	−0.43	−0.10	0.67	−0.10	0.03	−0.03	−0.04	−0.15	0.05	0.24	0.03	0.07	0.77	−0.24	0.48	0.06	−0.09	0.26	−0.12	1	
MeGly	0.75	0.84	0.59	0.45	0.42	−0.12	0.61	0.38	0.39	0.25	0.74	0.55	0.13	−0.09	0.32	−0.09	−0.09	0.62	0.50	0.46	0.80	0.22	0.94	−0.06	−0.36	0.16	0.34	0.46	1

Note: See Table 1 for abbreviations.

ACPD

9, 19783–19815, 2009

Table 5. Correlation coefficients (R^2) for the concentrations of dicarboxylic acids, ketocarboxylic acids and dicarbonyls against potassium (K^+), carbon monoxide (CO), organic (OC) and elemental carbon (EC) in the atmospheric aerosols collected in day- and night-time during the intensive burning period (16–26 September 2002) from Rondônia, Brazil under the framework of LBA-SMOCC campaign.

	K^+		CO		OC		EC	
Compound	Day	Night	Day	Night	Day	Night	Day	Night
Saturated *n*-dicarboxylic acids								
Oxalic, C_2	0.95	0.49	0.92	0.33	0.95	0.57	0.68	0.07
Malonic, C_3	0.98	0.33	0.94	0.08	0.98	0.39	0.72	0.09
Succinic, C_4	0.98	0.82	0.94	0.59	0.98	0.79	0.72	0.31
Glutaric, C_5	0.96	0.82	0.89	0.77	0.96	0.85	0.73	0.34
Adipic, C_6	0.98	0.72	0.97	0.63	0.98	0.72	0.67	0.23
Pimelic, C_7	0.94	0.45	0.90	0.59	0.93	0.48	0.67	0.11
Suberic, C_8	0.99	0.54	0.90	0.24	0.99	0.55	0.79	0.19
Azelaic, C_9	0.86	0.68	0.86	0.39	0.83	0.59	0.42	0.21
Sebacic, C_{10}	0.92	0.28	0.73	0.12	0.88	0.23	0.80	0.11
Undecanedioic, C_{11}	0.98	0.77	0.89	0.56	0.98	0.68	0.74	0.18
Branched dicarboxylic acids								
Isomalonic, iC_4	0.98	0.39	0.94	0.17	0.99	0.46	0.78	0.01
Isosuccinic, iC_5	0.99	0.86	0.95	0.73	0.99	0.84	0.73	0.52
Isoglutaric, iC_6	0.98	0.75	0.91	0.73	0.96	0.74	0.62	0.21
Unsaturated dicarboxylic acids								
Maleic, M	0.89	0.12	0.99	0.11	0.92	−0.08	0.46	−0.02
Fumaric, F	0.96	0.77	0.98	0.84	0.97	0.76	0.61	0.41
Methylmaleic, Mm	0.94	0.62	0.99	0.83	0.96	0.66	0.57	0.30
Phthalic, Ph	0.76	−0.79	0.83	−0.52	0.75	−0.69	0.37	−0.43
Isophthalic, iPh	0.64	−0.09	0.66	−0.31	0.67	−0.05	0.40	−0.16
Terephthalic, tPh	−0.05	0.44	−0.38	0.37	−0.11	0.60	0.39	0.37
Multifunctional dicarboxylic acids								
Hydroxysuccinic, hC_4	−0.02	0.84	0.25	0.73	0.06	0.84	0.05	0.35
Ketomalonic, kC_3	0.97	−0.08	0.80	−0.27	0.96	0.00	0.84	0.00
Ketopimelic, kC_7	0.61	0.14	0.58	−0.11	0.57	0.07	0.35	−0.17
Ketocarboxylic acids								
Glyoxylic, ωC_2	0.98	0.16	0.94	−0.12	0.99	0.19	0.77	0.15
3-Oxopropanoic, ωC_3	−0.21	0.52	−0.22	0.59	−0.22	0.48	−0.06	0.01
4-Oxobutanoic, ωC_4	0.68	0.61	0.63	0.52	0.63	0.55	0.09	0.36
9-Oxononanoic, ωC_9	0.59	0.47	0.59	0.33	0.55	0.50	−0.01	0.09
Pyruvic acid, Pyr	0.95	0.28	0.89	0.35	0.96	0.28	0.78	0.01
α-dicarbonyls								
Glyoxal, Gly	0.92	0.00	0.95	−0.19	0.93	0.04	0.62	−0.21
Methylglyoxal, MeGly	0.97	0.35	0.89	0.19	0.97	0.43	0.84	0.35

ACPD
9, 19783–19815, 2009

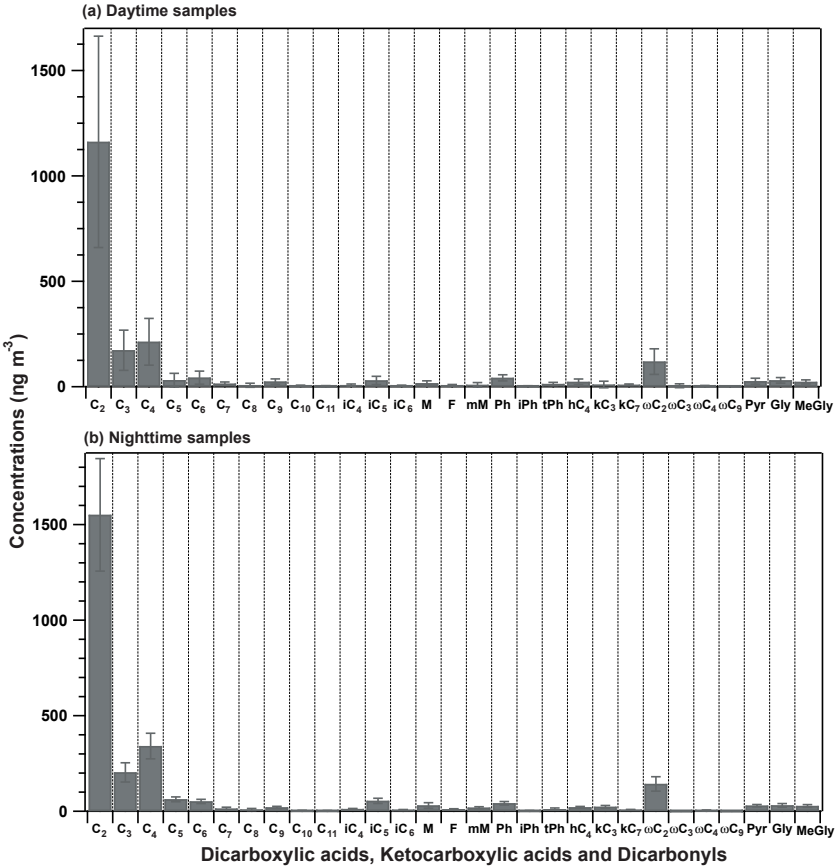

Fig. 1. Averaged molecular distributions of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in **(a)** daytime and **(b)** nighttime samples collected during the intensive biomass burning period from the FNS site in Rondônia, Brazil. See Table 1 for abbreviations. The error bars represent one standard deviation.

ACPD
9, 19783–19815, 2009

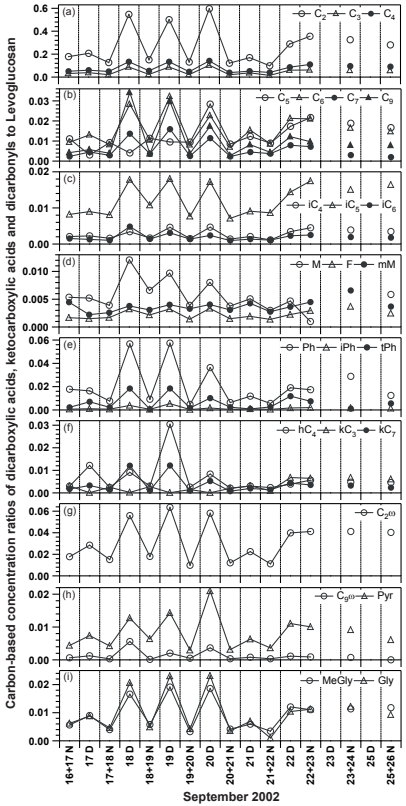

Fig. 2. Diurnal variations in the carbon-based concentration ratios of **(a)** low molecular weight (C_2, C_3 and C_4), **(b)** high molecular weight (C_5, C_6, C_7 and C_9), **(c)** branched (iC_4, iC_5 and iC_6), **(d)** aliphatic unsaturated (M, F and mM), **(e)** aromatic unsaturated (Ph, iPh and tPh) and **(f)** multifunctional (hC_4, kC_3 and kC_7) dicarboxylic acids, **(g–h)** ketocarboxylic acids ($C_2\omega$, $C_9\omega$ and Pyr) and **(i)** dicarbonyls (MeGly and Gly) to levoglucosan in biomass burning aerosols. See Table 1 for abbreviations.

ACPD
9, 19783–19815, 2009

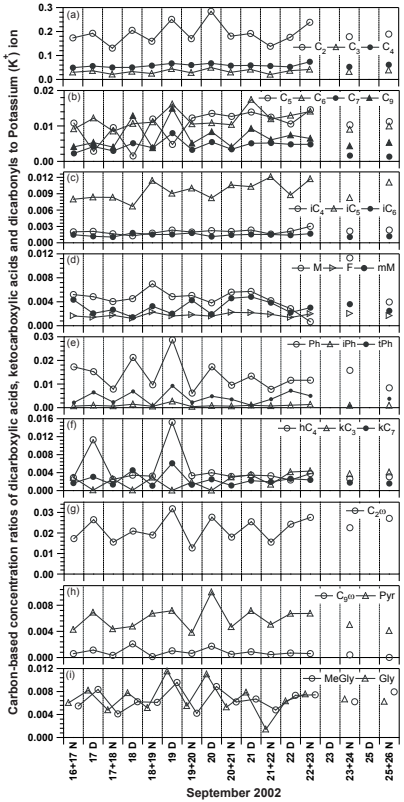

Fig. 3. Diurnal variations in the carbon-based concentration ratios of **(a)** low molecular weight (C_2, C_3 and C_4), **(b)** high molecular weight (C_5, C_6, C_7 and C_9), **(c)** branched (iC_4, iC_5 and iC_6), **(d)** aliphatic unsaturated (M, F and mM), **(e)** aromatic unsaturated (Ph, iPh and tPh) and **(f)** multifunctional (hC_4, kC_3 and kC_7) dicarboxylic acids, **(g–h)** ketocarboxylic acids ($C_2\omega$, $C_9\omega$ and Pyr) and **(i)** dicarbonyls (MeGly and Gly) to potassium ion in biomass burning aerosols. See Table 1 for abbreviations.

ACPD
9, 19783–19815, 2009

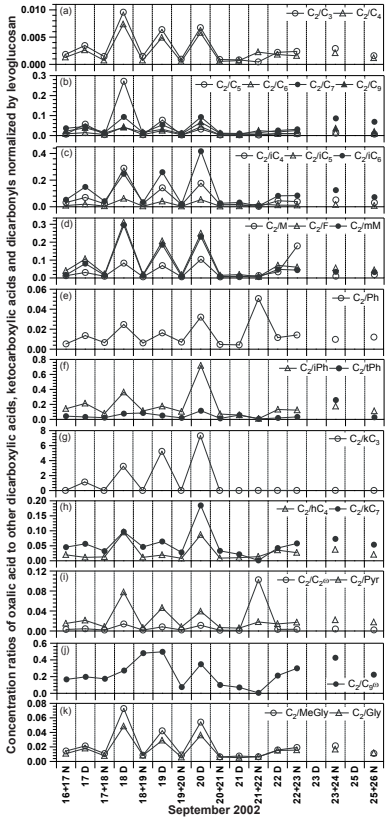

Fig. 4. Diurnal variations of the concentration ratios of oxalic acid to **(a)** low molecular weight (C_3 and C_4), **(b)** high molecular weight (C_5, C_6, C_7 and C_9), **(c)** branched (iC_4, iC_5 and iC_6), **(d)** aliphatic unsaturated (M, F and mM), **(e–f)** aromatic unsaturated (Ph, iPh and tPh) and **(g–h)** multifunctional (kC_3, hC_4 and kC_7) dicarboxylic acids, **(i–j)** ketocarboxylic acids ($C_2\omega$, Pyr and $C_9\omega$) and **(k)** dicarbonyls (MeGly and Gly) normalized by levoglucosan in biomass burning aerosols. See Table 1 for abbreviations.

ACPD
9, 19783–19815, 2009

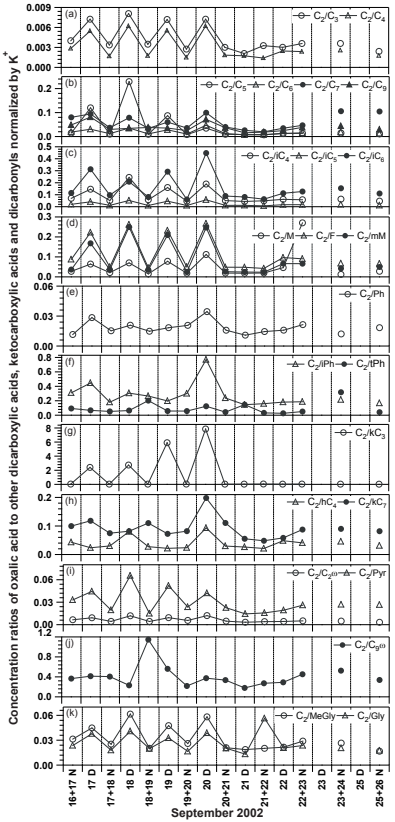

Fig. 5. Diurnal variations of the concentration ratios of oxalic acid to **(a)** low molecular weight (C_3 and C_4), **(b)** high molecular weight (C_5, C_6, C_7 and C_9), **(c)** branched (iC_4, iC_5 and iC_6), **(d)** aliphatic unsaturated (M, F and mM), **(e–f)** aromatic unsaturated (Ph, iPh and tPh) and **(g–h)** multifunctional (kC_3, hC_4 and kC_7) dicarboxylic acids, **(i–j)** ketocarboxylic acids ($C_2\omega$, Pyr and $C_9\omega$) and **(k)** dicarbonyls (MeGly and Gly) normalized by potassium ion in biomass burning aerosols. See Table 1 for abbreviations.

ACPD
9, 19783–19815, 2009