Atmos. Chem. Phys. Discuss., 5, 8027–8054, 2005
www.atmos-chem-phys.org/acpd/5/8027/
SRef-ID: 1680-7375/acpd/2005-5-8027
European Geosciences Union

Atmospheric
Chemistry
and Physics
Discussions

Chemical transformations in organic aerosol from biomass burning

A. Hoffer[1], **A. Gelencsér**[2], **M. Blazsó**[3], **P. Guyon**[1], **P. Artaxo**[4], **and M. O. Andreae**[1]

[1]Max Planck Institute for Chemistry, Mainz, Germany
[2]Air Chemistry Group of the Hungarian Academy of Sciences, Veszprém, Hungary
[3]Institute of Materials and Environmental Chemistry CRC, Hungarian Academy of Sciences, Budapest, Hungary
[4]Instituto de Fisica, Universidade de Sao Paulo, Sao Paulo, Brazil

Received: 1 July 2005 – Accepted: 31 July 2005 – Published: 5 September 2005

Correspondence to: A. Hoffer (ahoffer@mpch-mainz.mpg.de)

Abstract

Fine aerosol particles were collected separately during daytime and nighttime at a tropical pasture site in Rondônia, Brazil, during the burning and dry-to-wet transition period in 2002. Total carbon (TC) and water-soluble organic carbon (WSOC) were measured by evolved gas analysis (EGA). Based on the thermochemical properties of the fine aerosol, the relative amounts of the low and higher molecular weight compounds were estimated. It was found that the thermally refractory (possibly higher molecular weight) compounds dominated the TC composition. Their contribution to TC was higher in the daytime samples than in the nighttime ones. The relative share of WSOC also showed a statistically significant diel variation and so did its refractory fraction. Anhydrosugars and phenolic acids were determined by GC-MS and their diel variation was studied. Based on the decrease of their relative concentrations between the biomass burning and transition periods and their distinctly different diel variations, we suggest that the phenolic acids may undergo chemical transformations in the aerosol phase, possibly towards more refractory compounds (humic-like substances, HULIS), as has been suggested previously. These conclusions are supported by the results of the thermally assisted hydrolysis and methylation gas chromatography-mass spectrometry of the same filter samples.

1. Introduction

Biomass burning emits – beside gaseous compounds – vast amounts of carbonaceous particles into the atmosphere (Andreae, 1993). These particles scatter and absorb solar radiation and may act as cloud condensation nuclei (CCN) (Roberts et al., 2002), (Andreae et al., 2004). As a result of the increase in CCN concentration, the average size of the cloud droplets decreases, suppressing the ability to form precipitation (Rosenfeld, 1999) and increasing the cloud albedo. These effects can influence vast areas in the tropics, since smoke haze covers large regions that can frequently rise to high altitudes (Andreae et al., 2004) and undergo long range transport (Pickering et al., 1996; Andreae et al., 2001). Since one of the key factors governing the CCN-ability of smoke particles is their chemical composition, studying possible chemical transformations that may affect the aerosol composition during transport is particularly important.

The chemical composition of biomass burning aerosols can be approached from the molecular level by organic speciation (Oros and Simoneit, 2001a, b; Simoneit, 2002; Graham et al., 2002), but useful complementary information can be obtained by non-specific bulk carbon analysis methods that can also address high molecular weight carbon compounds such as soot and humic-like substances (HULIS) (Simoneit 2002 and references therein; Mayol-Bracero et al., 2002). Recently, strong evidence has been presented that some organic species and HULIS are closely related (Gelencsér et al., 2003; Hoffer et al., 2004).

Among the pyrogenic (biomass-burning derived) low molecular weight polar compounds, several sugar derivatives were identified (Simoneit et al., 1999; Graham et al., 2002; Gao et al., 2003) that are major products of plant cellulose and hemicellulose pyrolysis. Among them, levoglucosan (1,6-anhydroglucose) – which forms upon cellulose pyrolysis – is clearly predominant. Galactosan and mannosan are isomers of levoglucosan, and are released from the combustion of hemicellulose (Nolte et al., 2001). The anhydrosugars are considered as good tracers of biomass burning as these compounds are thought to be largely non-reactive in the atmosphere (Fraser and Lakshmanan, 2000).

The same may not hold for lignin pyrolysis products, which can undergo chemical transformation in the atmosphere. Lignin is an important constituent of plants, which – together with cellulose – provides their mechanical strength (Simoneit, 2002). From lignin, depending on its composition, mainly semi-volatile aromatic compounds are released during the burning process. The aromatic ring may contain hydroxy, methoxy and aliphatic groups (Simoneit, 2002), but these compounds usually convert to phenolic acids during atmospheric transport (Simoneit, 2001).

The lignin pyrolysis products carry the imprints of major plant classes. For example, in the smoke from the burning of grass lignin, 4-hydroxybenzoic compounds can be found in addition to wood lignin components (Simoneit, 1993). High amount of guaiacyl derivatives (e.g. vanillic acid, vanillin) can be found in smoke of softwood burning (Simoneit, 2002; Oros and Simoneit, 2001a; Simoneit et al., 1993). The derivatives of the syringyl components (e.g. syringic acid, syringyl aldehyde) are considered as tracers for burning of hardwood (Simoneit et al., 1993, 2002). Albeit the relative amounts of various phenolic compounds can be used as tracers for the type of biomass burned, the long-range stability of the individual pyrolysis products is questionable in the atmosphere (Simoneit, 2002; Lanzalunga and Betti, 2000; Kjällstrand et al., 2001a).

Besides carbohydrate derivatives and phenolic compounds, other low molecular weight (LMW) compounds were also identified in biomass burning aerosols, but their total concentration was less than 10% of the total carbon (Mayol-Bracero et al., 2002). The composition of the aerosol from biomass burning depends not only on the biomass burned but also on the type of the combustion. From the early pyrolysis stage of combustion and from smoldering fires mainly LMW pyrolysis products are released, in contrast to flaming fires in which soot and inorganic ash components are major components of the pyrogenic aerosol (Andreae, 1998).

On a mass basis, high molecular weight carbonaceous compounds are important constituents of biomass burning aerosol. Among them, primary soot measured by thermal methods can make up of 5–25% of the total carbon in biomass burning aerosol (Mayol-Bracero et al., 2002; Artaxo et al., 2002). Considerable fraction of biomass-burning aerosol has been shown to consist of humic-like substances (HULIS). These compounds can derive either from primary or secondary sources. Mayol-Bracero et al. (2002) hypothesized that the high molecular weight polymeric matter could derive from the incomplete breakdown of polymeric carbohydrates and lignin as primary component, which can be further modified in the process of combustion. The second possible route for the formation of HULIS can be the transformation of the pyrogenic semi-volatile organic compounds through condensation reactions with other molecules (Mayol-Bracero et al., 2002).

Recently, Gelencsér et al. (2003) have shown that colored and refractory organic matter, with properties and composition similar to those of HULIS found in atmospheric aerosol (Hoffer et al., 2004), may form from a single phenolic precursor in OH-induced free radical polymerization. This finding implies that secondary processes can be particularly important in HULIS formation in biomass burning regions in the tropics, where high amounts of semi-volatile phenolic precursors are released and the photochemical activity is high.

During the Large Scale Biosphere-Atmosphere Experiment in Amazonia – Smoke Aerosols, Clouds, Rainfall and Climate (LBA-SMOCC) campaign, daytime and night-time aerosol samples were collected in the Amazon Basin during the polluted dry and the cleaner transition and semi-clean periods, which allowed us to study the diel differences in aerosol compositions, with possible implications for photochemical processes in the smoke layers.

2. Sampling

Aerosol sampling was performed during September–November 2002 at Fazenda Nossa Senhora Aparecida (10°45′44″ S, 62°21′27″ W, 315 m above sea level). The site is located about 8 km southwest from the town Ouro Preto do Oeste in Rondônia, Brazil. The site was first deforested in 1977 for crops and is now used as pasture (Kirkman, 2002). In September, the atmosphere at the site was affected by heavy biomass burning across the region (hereafter referred as the biomass burning period), whereas in November the aerosol mass concentration decreased considerably, indicating the onset of the wet season (semi-clean period). The samples from October 2002 represent the transition period. Fine and coarse aerosols were collected on Pallflex quartz fiber filters (pre-baked for at least 10 h at 600°C) by a dichotomous virtual impactor (Solomon et al., 1983), which was mounted on a 10 m high tower. The air was sampled with a total flow of 16.33 $m^3 h^{-1}$, and split inside the instrument at a 9:1 ratio in order to separate fine and coarse particles respectively, with a 50% aerodynamic diameter (D_p) cutpoint of 2.5 μm (Solomon et al., 1983). The aerosol collection was performed separately during day and night, with sampling times ranging 10–48 h. For the ~24 and ~48 h sampling, the aerosol was collected in 2 and 3 consecutive days and nights, respectively. The loaded filters were placed in pre-baked (at least 10 h at 600°C) glass jars and stored in a freezer at −20°C until analysis.

3. Methods

Since during sampling about 10% of the fine aerosol mass deposit on the coarse filter due to the design of the sampler (Solomon et al., 1983), this contribution from the very large fine mode to the much less abundant coarse mode during the burning season makes an analysis of the "coarse fraction" of the dichotomous sampler meaningless, and therefore only the fine aerosol was analyzed. The total carbon (TC) and the water soluble organic carbon (WSOC) were measured by EGA (Mayol-Bracero et al., 2002). For the TC measurements 1.5–3.0 cm^2 of the filter (depending on the filter loading) was placed into the oven of the instrument. The temperature was increased linearly from 50°C to 780°C at a rate of 20°C/min and the carbonaceous compounds were converted to CO_2 in an oxygen atmosphere. The conversion was completed over a MnO_2 catalyst bed held at 800°C. The concentration of CO_2 formed was measured by a non-dispersive IR detector and recorded on a computer. Thus, a thermogram is obtained in which the area under the plot of the CO_2 concentration vs. temperature is proportional to the carbon content of the sample. The volatile and reactive compounds are found in the first part of the thermogram, whereas the more refractory compounds start to oxidize at higher temperatures. For the WSOC measurements, the same amount of sample as for the TC measurement was placed in 7 ml of high purity (MilliQ) water and soaked without shaking for 1 h. After the extraction, the filters were removed and dried in a desiccator for 12 h. The dried filters were measured in the same way as the untreated samples. The amount of the WSOC was obtained by subtracting the amount of carbon found on a filter after water extraction from that found on the nonextracted filters (TC). In some cases the water fraction was analyzed by a Shimadzu TOC 500A instrument. The amount of the WSOC (DOC) measured from the liquid fraction agreed well with the amount of WSOC determined from the filter measurements (R^2=0.9769, the equation of the regression line is DOC (μg m^{-3})=1.029×WSOC (μg m^{-3})−1.1745 μg m^{-3}).

Individual polar compounds were analyzed by gas chromatography-mass spectrometry (Hewlett Packard 6890 GC-MSD) after derivatization. The method was adapted from Graham et al. (2002). The extraction of the sample was performed in acetonitrile. Depending on the filter loading, 3.5–5.3 cm^2 of the filter was put into 4–6 ml acetonitrile and shaken until the filter broke apart. The extraction time was 1 h, and the solution was agitated once every 15 min. The sample was then filtered through a 0.45 μm pore size PTFE syringe filter (Pall). An internal standard (3,3-dimethylglutaric acid) was added to 3 ml of filtered sample solution, which was then brought to dryness under a gentle stream of N_2. After this process, 50 μl pyridine and 50 μl bis(trimethylsilyl)trifluoroacetamide (BSTFA), containing 1% trimethylchlorosilane (TMCS) as a catalyst (Supelco), were added to the samples. To accelerate the derivatization reaction, the samples were put into an oven at 70°C for 30 min. The samples were allowed to cool down to room temperature and were analyzed immediately afterwards. 1 μl of sample was injected in the GC-MS operating in splitless mode at 280°C. The separation was performed on a HP 5-MS column (30 m×250 μm×0.2 μm) equipped with a Supelco guard column (deactivated methylsiloxane, 1 m×0.32 mm). The oven temperature was held for 10 minutes at 65°C and ramped at 10°C/min to 310°C and held for 10 min. The temperature of the interface was 280°C. The detector was operated both in SIM and SCAN mode, and it was calibrated with aliquots of a stock solution of authentic standards. Repeated analysis of the samples showed that the precision of the method was about 20%.

Thermally assisted hydrolysis methylation gas chromatography-mass spectrometry (THM-GC/MS) was used to investigate the composition of the bulk organic constituents of the aerosols. 0.8 cm^2 of the filter was placed in a quartz tube and 10 μl of TMAH (tetramethylammonium hydroxide (15 wt.% in water, Fluka, Switzerland) was poured onto the quartz filter. The samples were dried at room temperature for 1 h prior to analysis. The thermally assisted hydrolysis and methylation took place in a Pyroprobe 2000 pyrolyzer (Chemical Data System), coupled to an Agilent 6890 GC–5973 MSD. The temperature in the pyrolyzer was held at 250°C and the sample was heated to 400°C for 20 s. The GC inlet was used in splitless mode, and a HP 5MS fused silica capillary column ($30\,\text{m}\times250\,\mu\text{m}\times0.25\,\mu\text{m}$) was applied temperature programmed from 50 to 300°C at 10°C/min with an isothermal period of 1 min at 50°C and of 4 min at 300°C. The interface of the GC-MS system was held at 280°C, and the MSD operated in scan mode using electron impact ionisation (EI).

4. Results and discussion

4.1. Total carbon

Figure 1 shows a thermogram of the fine aerosol from the burning period, together with one of pure levoglucosan. The thermograms of the aerosol samples contain 3 peaks. The shape of the thermogram is similar to those obtained from previous campaigns (Mayol-Bracero et al., 2002). The compounds responsible for the first peak of the thermogram volatilize and/or oxidize below about 280°C. It is worth noting that the levoglucosan peak also appears in this temperature region. Since levoglucosan is a LMW, non-volatile compound (MW=162.14), it is reasonable to assume that the first peak of the thermograms contains LMW compounds, whereas above 280°C the higher molecular weight compounds (HMW) predominate.

It should be noted that the decarboxylation of the higher molecular weight acidic compounds does not contribute to the area of the first peak, since this process was not observed at temperatures below 280°C from measurements of a model humic acid (Aldrich), using the same instrument and parameters (Andreae et al., 2002[1]). On the

---

[1] Andreae, M. O., Andreae, T. W., Artaxo, P., Gelencser, A., Graham, B., Guyon, P., Helas, G.,

other hand, in spite of the oxygen atmosphere and the low heating rate applied during the measurements, charring of organic species might take place in the oven, which could cause a positive bias in the concentration of HMW compounds.

Figure 2 summarizes the relative amounts of the high molecular weight, refractory compounds and the absolute concentration of total carbon (TC) for the three different periods. The total carbon concentration decreased by ca. two orders of magnitude from the biomass burning to the semi-clean period, indicating that the intensity and extent of burning decreased significantly in the transition and semi-clean periods. In the majority of the samples from the biomass burning and transition period, the total carbon concentration is higher during the night than during the day. This can be explained by the combined effect of ongoing burning overnight, accompanied by the significantly lower mixing heights during nights (Rissler et al., 2005). In the semi-clean period, the diel variation of the TC mass concentrations cannot be followed because of the averaging effects of the longer residence time of the collected aerosol. This is probably because burning activity almost completely ceased in the direct vicinity of the measurement site during this period, and the aerosols were not influenced by local, fresh pyrogenic emissions. Nevertheless, the refractory fraction remains the predominant form of carbon, since the valley point of thermograms changes little between the different periods.

The relative share of the more refractory compounds (Fig. 2) shows a statistically significant diel variation in the biomass burning and transition period. During the day, the relative amount of refractory compounds is higher than during the night. This difference between the bulk composition of the day and night samples can be attributed to the change of the fire characteristics between day and night. Flaming fires produce more soot and more refractory primary organic compounds, which are expected to appear above 280°C in the thermogram. On the other hand, during smoldering combustion more LMW polar compounds are released by pyrolysis. The burning process

---

Maenhaut, W., and Mayol-Bracero, O.: Brown and black carbon: Light absorbing carbonaceous matter in atmospheric aerosols, oral presentation, International Global Atmospheric Chemistry (IGAC), Crete, Greece, 18–25 September, 2002.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀▌ | ▶▌
◀ | ▶
Back | Close
Full Screen / Esc
Print Version
Interactive Discussion
EGU

is described in detail by Simoneit (2002). Additionally, the nighttime condensation of semi-volatile compounds may also contribute to the enhanced share of the LMW compounds during the night.

Since the source strength diminished towards the end of the campaign, and the average residence time of the collected aerosol particles got longer, the diel differences gradually disappeared after the biomass burning period. These changes were accompanied by a noticeable increase in the relative contribution of the refractory compounds. The higher share of these compounds cannot be explained by the different fire properties between the biomass burning and semi-clean period, because there were more and more rain episodes, and the fuel was getting moister toward the end of the campaign. The higher humidity of the fuel would have resulted in more smoldering fires in the transition period, which would decrease the relative amount of the HMW compounds, therefore less refractory compounds would have been expected to form. Instead, this increase might be related to chemical transformations, which could be more significant as more aged plumes were sampled.

4.2. Water soluble organic carbon

The relative share and thermal properties of WSOC – although being non-specific – may also shed light on the evolution of the aerosol chemical properties. As was pointed out above, WSOC was determined indirectly as a carbon content difference before and after water extraction. Assuming that the thermochemical characteristics of the aerosol constituents are preserved during the extraction, and that the catalysis by potassium only affects the thermochemical properties of soot and carbonaceous compounds that oxidize at higher temperatures (Novakov and Corrigan, 1995), the same temperature boundary marker was used as above (280°C) to distinguish between low and high molecular weight carbon species. However, due to the high solubility of the LMW compounds, the valley separating the two subsets in the thermogram becomes indiscernible in some cases. Example thermograms before and after water extraction are shown in Fig. 3. Table 1 shows the ratio of WSOC to TC and the water-soluble fraction of the low and higher molecular weight refractory compounds.

The relative share of the WSOC also displayed a statistically significant diel variation (probability, that the two data set are different ($P>95\%$) during the biomass-burning season. Similar to the total WSOC, the fractional amount of the water-soluble refractory compounds is higher during day than during night. Interestingly, its variation between the biomass burning and the cleaner period (transition and semi-clean period) is also statistically considerable. It should be noted that the relative amount of the LMW compounds is also higher during the day than during the night.

The evaluation of carbon thermograms suggested that the composition of biomass burning aerosols might be affected by photochemical transformations in addition to the influence of the combustion stage (smoldering/flaming). The WSOC data corroborates this conclusion. If only the fire properties had affected the chemical composition of the biomass burning aerosol, the relative amount of the WSOC would have been lower during day due to the elevated amount of soot and refractory compounds released by flaming fires. Preliminary results from laboratory burns showed that the relative amount of WSOC is higher in aerosol samples collected under controlled conditions from smoldering combustion than in aerosol from flaming combustion. For this preliminary experiment oak wood was burned and the freshly formed particles were collected on quartz filters by a Hi-Vol sampler. Consequently it can be assumed that the amount of water-soluble refractory matter (soluble fraction of HULIS) observed during daytime may be significantly affected by photochemical processes. It is important to see that in the transition period (as the biomass-burning source strength decreases and the aerosols become more aged) the relative share of WSOC also increases, implying the possible importance of photochemical transformations during aging.

4.3. Speciation of aerosol WSOC by gas chromatography-mass spectrometry

In order to shed some light on the possible chemical transformations, we determined the concentrations of some selected water-soluble organic tracers and evaluated their diel variations.

4.3.1. Anhydrosugars

Among the anhydrosugars, the mass concentrations of levoglucosan, galactosan, and mannosan were measured. Figure 4 shows the concentrations of these anhydrosugars (expressed as carbon content in anhydrosugars) related to TC, which was measured by EGA.

Similar to previous studies, the concentrations of levoglucosan were by far the highest among the individually identified compounds (e.g. Graham et al., 2002). The relative amount of the anhydrosugars fluctuates between day and night, with more anhydrosugars found in the night samples than in the daytime ones. Apart from the hydrolysis of these species under acidic conditions, these compounds are considered to be non-reactive and non-volatile (Fraser and Lakshanan, 2000; Simoneit, 1999). Therefore, they can be used as molecular indicators for the combustion type. Despite the possible nighttime condensation of semivolatile compounds on the aerosols, the amount of TC did not increase (thereby decreasing the relative contribution of levoglucosan) to a degree that would suppress the diel variation of the anhydrosugars. Consequently, the effect of the condensation process on the diel variation of the investigated compounds is less significant than the prevalence of the different fire types between day and night.

4.3.2. Lignin pyrolysis products

Among the lignin pyrolysis products, the acidic forms of the three most important phenolic compounds formed during biomass burning were measured: p-salicylic acid, vanillic acid, and syringic acid. Figure 5 shows the relative concentration of these phenolic acids separately for the biomass burning and transition period.

On average, syringic acid has the highest concentration in both periods. Similar to the anhydrosugars, the concentrations of the phenolic acids also varied between day and night, their concentrations relative to TC being higher during the night. This difference is statistically significant in the biomass burning period and noticeable in the transition period (P=94.5%).

The volatility of the investigated aromatic acids is low, similar to levoglucosan, consequently the effect of the nighttime condensation on their diel variation can be neglected as for the anhydrosugars. The diel variations in the concentration of phenolic compounds can result from the change of combustion types between day and night, but photochemical transformations in the aerosol phase cannot be excluded either. Kjällstrand and Olsson (2004) have observed an enrichment in methoxyphenolic compounds from incomplete, low temperature, combustion (smoldering fires), whereas at higher temperature (above 800°C), methoxyphenols are thermally decomposed and carcinogenic polycyclic aromatic compounds are formed. This may explain the elevated concentrations of phenolic compounds during the night, when smoldering fires predominate.

The overall reactivity of these compounds was also taken into account by Kjällstrand and Petterson (2001a). From the phenolic compounds, phenoxy radicals can be formed via hydrogen abstraction of the phenolic OH group. The kinetics of radical formation depends on the type and number of functional groups on the aromatic ring. Phenoxy radical formation requires less energy in syringyl compounds than in guaiacyl compounds (vanillyl compounds) as a result of the radical stabilizing effect of the methoxy groups (Kjällstrand and Peterson, 2001a, b). The 4-hydroxybenzoic compounds do not contain methoxy groups, consequently the formation of the phenoxy radical is energetically not favored.

In light of the above it is interesting to see the diel variation of the concentrations of phenolic acids. The concentrations of syringic acid (most reactive) vary with the highest amplitude between day and night, whereas the less reactive vanillic acid varies with somewhat lesser amplitude (except in the transition period). The more stable 4-hydroxybenzoic acid shows the least variation between day and night in the biomass burning season, whereas its variation is comparable to that of vanillic acid in the transition period, when the aerosol was more aged. These variations are in good agreement with the reactivity of the compounds. It should also be noted that lignin formation in plants takes place by non-enzymatic (random) radical-radical coupling of phenoxy radicals, yielding a three-dimensional amorphous polymer (Argyropoulos and Menachem, 1997), a mechanism that could be similar to that occurring in the aerosol phase. Very recently, polymeric compounds have been produced in both aqueous and gas-phase from aromatic precursors under conditions close to those prevalent in the atmosphere (Hoffer et al., 2004; Kalberer et al., 2004).

In order to reveal the effects of photochemical reactions and the different reactivity of the phenolic compounds, the amounts of the less reactive anhydrosugars and that of the more reactive phenolic compounds were compared. Figure 6 shows the concentrations of the measured phenolic acids normalized to those of levoglucosan.

Among the phenolic acids the ratio of syringic acid to levoglucosan showed a clear diel variation. This diel variation could hardly be observed for vanillic acid (only in the second half of biomass burning period). The ratio of 4-hydroxybenzoic acid to levoglucosan did not show any diel variation. During the day, the normalized concentrations of syringic acid were lower than during the night. As both methoxyphenols and levoglucosan are primarily emitted from the smoldering stage of combustion, these differences indicate the atmospheric reactivity of the phenolic compounds.

The effects of the photochemical processes are more explicit when the change in the ratio of phenolic compounds to levoglucosan during biomass burning is compared to that in transition period. In all cases, this ratio is lower in the transition period, when the conditions were more favorable for low-temperature combustion. Since the average residence time of the aerosol is longer (reduced influence of fresh local combustion sources) and therefore the aerosol is more aged in this period, the lower amount of the phenolic compounds relative to that of levoglucosan indicates that the former compounds probably participate in photochemical reactions. The difference between the biomass burning and transition period can not be attributed to the changing fire properties because both levoglucosan evolution from the cellulose part (Mészáros, 2004) and that of methoxyphenols from the lignin component of biomass (Jakab, 1997) occur in the temperature range of smoldering between 300 and 500°C (Bilbao, 2002), thus no drastic changes in the product ratios are expected.

The effects of the photochemical processes on the composition of the aerosols can be further evaluated on the basis of the results of THM-GC/MS measurements. Figure 7 shows the ratio of the total ion intensity of the coumaryl, guaiacyl and syringyl compounds determined by thermally assisted hydrolysis and methylation gas chromatography-mass spectrometry to the amount of the TC on the filter.

The relative abundances of the major phenolic compounds are distinctly different from the results of organic speciation by derivatization-GC/MS, moreover, the diel variation of the abundance of phenolic compounds is much less apparent in Fig. 7 than in Fig. 5. The reason for these differences could be related to the different capability of the two analysis methods. By analytical pyrolysis, oligomers or other associated materials of higher molecular mass formed from LMW primary pyrogenic products are broken down into their precursors, and thus the phenolic compounds liberated from the refractory material are added to the “free” phenolic acids that are measured in the aerosol extracts. Our proposal of photochemical oligomerisation of phenolic acids on the aerosol surfaces in daytime is able to explain the disappearance of a substantial fraction of them. However, it is surprising that coumaryl compounds were predominant among the pyrolysis products. Previous investigations showed that these compounds may not be derived from grass lignin but from a more easily volatilisable moiety of the aerosol particles (Blazsó et al., 2003). Another observation has to be also interpreted, namely that the relative amount of the phenolic compounds decreases considerably in the transition period. We may assume that in the more mature aerosols the phenolic compounds participate in photochemical reactions forming higher molecular weight compounds of more complex structures, from which the phenolic acids cannot be released by analytical pyrolysis in their original form. Unfortunately, the underlying processes are very poorly understood and much remains to be done to better characterize the chemical evolution of biomass burning particles.

5. Conclusions

In this study, we investigated the diel variation in the composition of tropical aerosols affected by varying contributions from biomass burning (different periods). The chemical properties of the pyrogenic aerosol are affected by a number of factors, including photochemical processes. In the aerosols, the effects of all factors are superimposed in the different seasons, making an assessment of the importance of the single processes more difficult. Nevertheless, the differences observed in the chemical properties of the aerosol collected in different seasons outline the potential importance of photochemical processes in both the gas- and the aerosol phase. Although no direct evidence can be obtained in support of such processes, the combination of non-specific bulk carbon analysis methods and organic speciation techniques supports these statements. The results presented here are among the very first field observations supporting the chemical transformations that have been recently suggested in laboratory and smog chamber experiments. The chemical evolution of biomass burning aerosol, which greatly affects the atmospheric fate and impact of biomass burning emissions, is a very important yet poorly characterized process, which deserves special attention and further laboratory and field experiments.

Acknowledgements. This work was carried out within the frame work of the Smoke, Aerosols, Clouds, Rainfall, and Climate (SMOCC) project, a European contribution to the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA). The authors gratefully acknowledge financial support by the European Commission (contract No. EVK2-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 paricular J. von Jouanne and A. Camargo for their support in setting up the sampling location and to G. Frank for his help in the preparation of the sampling devices.

References

Andreae, M. O., Andreae, T. W., Annegarn, H., Beer, J., Cachier, H., le Canut, P., Elbert, W., Maenhaut, W., Salma, I., Wienhold, F. G., and Zenker, T.: Airborne studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical composition, J. Geophys. Res.-Atmos., 103, 32 119–32 128, 1998.

Andreae, M. O., Artaxo, P., Fischer, H., Freitas, S. R., Gregoire, J. M., Hansel, A., Hoor, P., Kormann, R., Krejci, R., Lange, L., Lelieveld, J., Lindinger, W., Longo, K., Peters, W., de Reus, M., Scheeren, B., Dias, M., Strom, J., van Velthoven, P. F. J., and Williams, J.: Transport of biomass burning smoke to the upper troposphere by deep convection in the equatorial region, Geophys. Res. Lett., 28, 951–954, 2001.

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, 1337–1342, 2004.

Andreae, M. O.: The influence of tropical biomass burning on climate and the atmospheric environment, in Biogeochemistry of Global Change: Radiatively Active Trace Gases, Chapman and Hall, New York, 113–150, 1993.

Argyropoulos, D. S. and Menachem, S. B.: Lignin, in: Biotechnology in the Pulp and Paper Industry, edited by: Eriksson, K.-E. L., Springer Verlag, Berlin Heidelberg, 127–158, 1997.

Artaxo, P., Martins, J. V., Yamasoe, M. A., Procopio, A. S., Pauliquevis, T. M., Andreae, M. O., Guyon, P., Gatti, L. V., and Leal, A. M. C.: Physical and chemical properties of aerosols in the wet and dry seasons in Rondonia, Amazonia, J. Geophys. Res.-Atmos., 107, 8081, doi:10.1029/2001JD000666, 2002.

Bilbao, R., Mastral, J. F., Aldea, M. E., Ceamanos, J., Betran, M., and Lana, J. A.: Experimental and theoretical study of the ignition and smoldering of wood including convective effects, Combust. Flame, 126, 1363–1372, 2001.

Blazsó, M., Janitsek, S., Gelencsér, A., Artaxo, P., Graham, B., and Andreae, M. O.: Study of tropical organic aerosol by thermally assisted alkylation-gas chromatography mass spectrometry, J. Anal. Appl. Pyrolysis, 68-9, 351–369, 2003.

Fraser, M. P. and Lakshmanan, K.: Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols, Environ. Sci. Technol., 34, 4560–4564, 2000.

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.-Atmos., 108, 8491, doi:10.1029/2002JD002324, 2003.

Gelencsér, A., Hoffer, A., Kiss, G., Tombácz, E., Kurdi, R., and Bencze, L.: In-situ formation of light-absorbing organic matter in cloud water, J. Atmos. Chem., 45, 25–33, 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.-Atmos., 107, D20, 8047, doi:10.1029/2001JD000336, 2002.

Hoffer, A., Kiss, G., Blazsó, M., and Gelencsér, A.: Chemical characterization of humic-like substances (HULIS) formed from a lignin-type precursor in model cloud water, Geophys. Res. Lett., 31, L06115, doi:10.1029/2003GL018962, 2004.

Jakab, E., Faix, O., and Till, F.: Thermal decomposition of milled wood lignins studied by thermogravimetry mass spectrometry, J. Anal. Appl. Pyrolysis, 40-1, 171–186, 1997.

Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A. S. H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., and Baltensperger, U.: Identification of polymers as major components of atmospheric organic aerosols, Science, 303, 1659–1662, 2004.

Kirkman, G. A., Gut, A., Ammann, C., Gatti, L. V., Cordova, A. M., Moura, M. A. L., Andreae, M. O., and Meixner, F. X.: Surface exchange of nitric oxide, nitrogen dioxide, and ozone at a cattle pasture in Rondonia, Brazil, J. Geophys. Res.-Atmos., 107, 8083, doi:10.1029/2001JD000523, 2002.

Kjällstrand, J. and Petersson, G.: Phenolic antioxidants in wood smoke, Sci. Total Environ., 277, 69–75, 2001a.

Kjällstrand, J. and Petersson, G.: Phenolic antioxidants in alder smoke during industrial meat curing, Food Chem., 74, 85–89, 2001b.

Kjällstrand, J. and Olsson, M.: Chimney emissions from small-scale burning of pellets and fuelwood-examples referring to different combustion appliances, Biomass and Bioenergy, 27, 557–561, 2004.

Lanzalunga, O. and Bietti, M.: Photo- and radiation chemical induced degradation of lignin model compounds, J. Photochem. Photobiol. B-Biol., 56, 85–108, 2000.

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.-Atmos., 107, 8091, doi:10.1029/2001JD000522, 2002.

Mészáros, E., Jakab, E., Várhegyi, G., Szepesváry, P., and Marosvölgyi, B.: Comparative study of the thermal behavior of wood and bark of young shoots obtained from an energy plantation, J. Anal. Appl. Pyrolysis, 72, 317–328, 2004.

Nolte, C. G., Schauer, J. J., Cass, G. R., and Simoneit, B. R. T.: Highly polar organic compounds present in wood smoke and in the ambient atmosphere, Environ. Sci. Technol., 35, 1912–1919, 2001.

Novakov, T. and Corrigan, C.: Thermal Characterization of biomass smoke particles, Mikrochimica Acta, 119, 157–166, 1995.

Oros, D. R. and Simoneit, B. R. T.: Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 1. Temperate climate conifers, Appl. Geochem., 16, 1513–1544, 2001a.

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, 2001b.

Pickering, K. E., Thompson, A. M., Wang, Y. S., Tao, W. K., McNamara, D. P., Kirchhoff, V., Heikes, B. G., Sachse, G. W., Bradshaw, J. D., Gregory, G. L., and Blake, D. R.: Convective transport of biomass burning emissions over Brazil during TRACE A, J. Geophys. Res.-Atmos., 101, 23 993–24 012, 1996.

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. Discuss., in press, 2005.

Roberts, G. C., Artaxo, P., Zhou, J. C., Swietlicki, E., and Andreae, M. O.: Sensitivity of CCN spectra on chemical and physical properties of aerosol: A case study from the Amazon Basin, J. Geophys. Res.-Atmos., 107, 8070, doi:10.1029/2001JD000583, 2002.

Rosenfeld, D.: TRMM observed first direct evidence of smoke from forest fires inhibiting rainfall, Geophys. Res. Lett., 26, 3105–3108, 1999.

Simoneit, B. R. T.: Biomass burning – A review of organic tracers for smoke from incomplete combustion, Appl. Geochem., 17, 129–162, 2002.

Simoneit, B. R. T. and Elias, V. O.: Detecting organic tracers from biomass burning in the atmosphere, Mar. Pollut. Bull., 42, 805–810, 2001.

Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, Atmos. Environ., 33, 173–182, 1999.

Simoneit, B. R. T., Rogge, W. F., Mazurek, M. A., Standley, L. J., Hildemann, L. M., and Cass, G. R.: Lignin Pyrolysis Products, Lignans, and Resin Acids as Specific Tracers of Plant Classes in Emissions from Biomass Combustion, Environ. Sci. Technol., 27, 2533–2541, 1993.

Solomon, P. A., Moyers, J. L., and Fletcher, R. A.: High-Volume Dichotomous Virtual Impactor for the Fractionation and Collection of Particles According to Aerodynamic Size, Aerosol Sci. Technol., 2, 455–464, 1983.

Table 1. Water soluble carbon content of the aerosol particles collected during the three periods.

Period	Sample	WSOC (in % of TC)	$WSOC^{*}_{LMW}$ (% of LMW)	$WSOC_{HMW}$ (% of HMW)
Biomass burning	18 Sept. day	77.6	92.1	74.1
	18 Sept. night	60.5	72.9	54.4
	19 Sept. day	82.4	95.1	79.2
	19 Sept. night	56.0	65.0	51.6
	20 Sept. day	77.6	92.3	73.3
	20 Sept. night	55.1	65.9	50.0
	21 Sept. day	59.8	73.9	54.5
	21 Sept. night	53.9	64.2	49.3
	22 Sept. day	74.0	89.4	69.5
	22 Sept. night	69.6	80.9	65.6
Transition	20, 21 Oct. day	–	–	–
	21, 22 Oct. night	67.2	87.6	61.6
	23, 24 Oct. day	84.4	91.3	82.9
	24, 25 Oct. night	80.7	95.3	76.2
	26, 27 Oct. day	82.9	96.2	79.4
	27, 28 Oct. night	67.5	83.3	61.9
	29, 30 Oct. day	79.7	94.3	76.4
Semi-clean	30, 31 Oct. night	74.7	68.4	75.8
	01, 02, 03, 04 Nov. day	85.3	95.0	83.1
	01, 02, 03, 04 Nov. night	83.9	97.3	81.0
	05, 06, 07, 08 Nov. day	82.0	–	79.2
	05, 06, 07, 08 Nov. night	78.2	91.0	75.7

(* LMW=low molecular weight compounds)

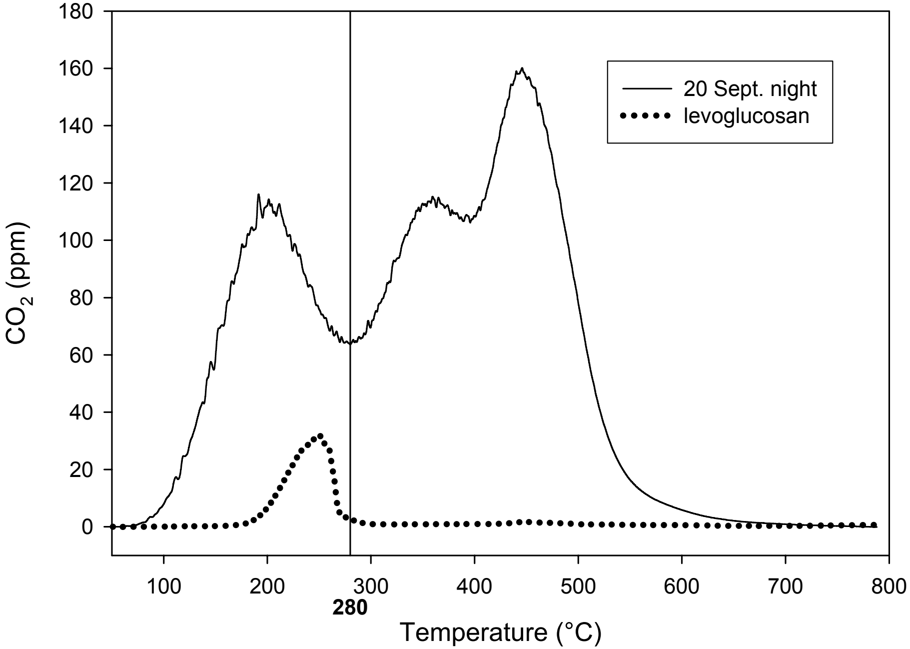

Fig. 1. Thermogram of the levoglucosan (dotted line) and that of an aerosol sample from the biomass burning period (solid line).

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀
▶
Back
Close
Full Screen / Esc
Print Version
Interactive Discussion
EGU

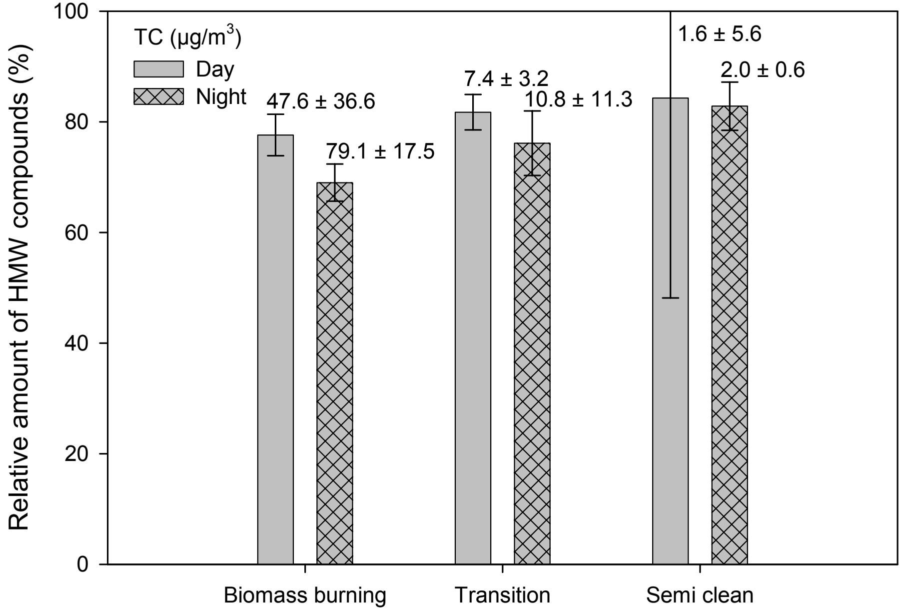

Fig. 2. Relative amount of HMW compounds to TC for day (gray bars) and nighttime samples (shaded bars) of the biomass burning, transition, and semi-clean periods. The respective average TC concentrations (μg/m^3) are indicated above the columns. The error bars show the variability (confidence interval) of the data.

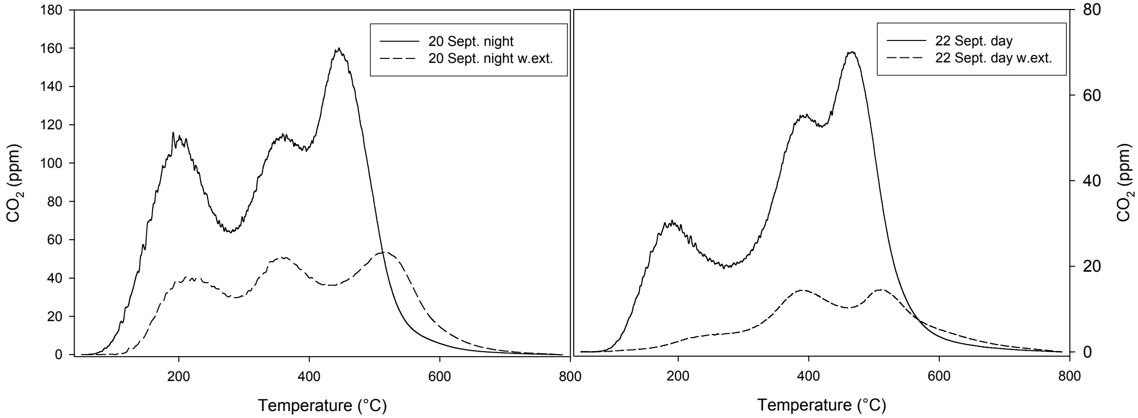

Fig. 3. Thermograms of fine aerosol before and after water extraction.

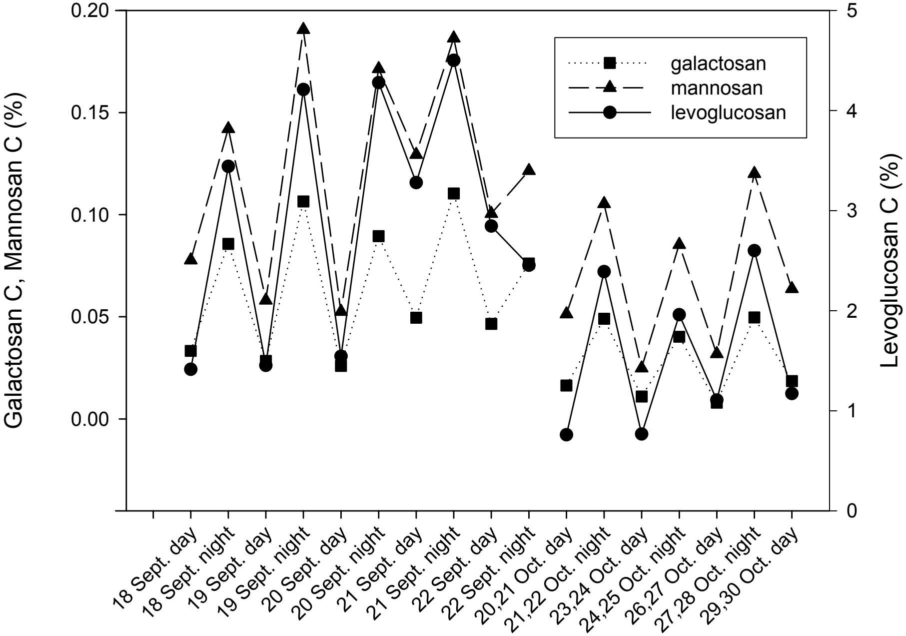

Fig. 4. Relative amount of the anhydrosugars-C to the total carbon.

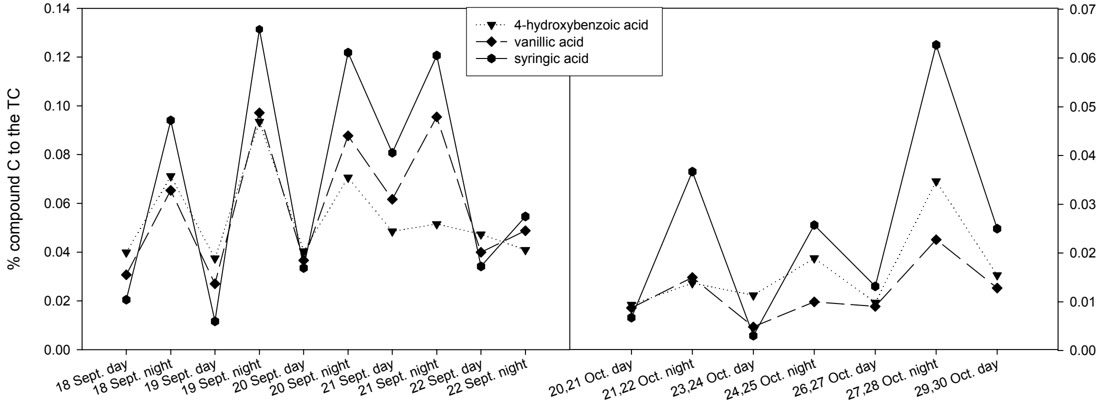

Fig. 5. Relative amount of the phenolic acids to the total carbon.

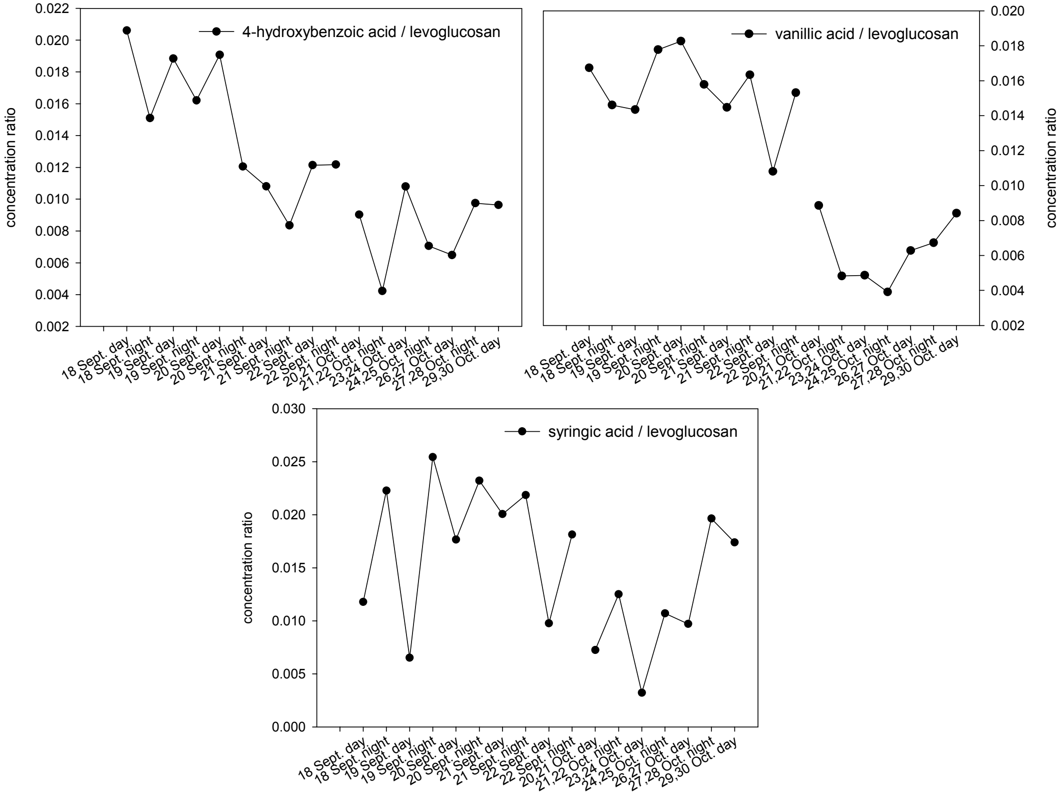

Fig. 6. Variation of the concentration ratio of the phenolic acids to levoglucosan.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Print Version
Interactive Discussion
EGU

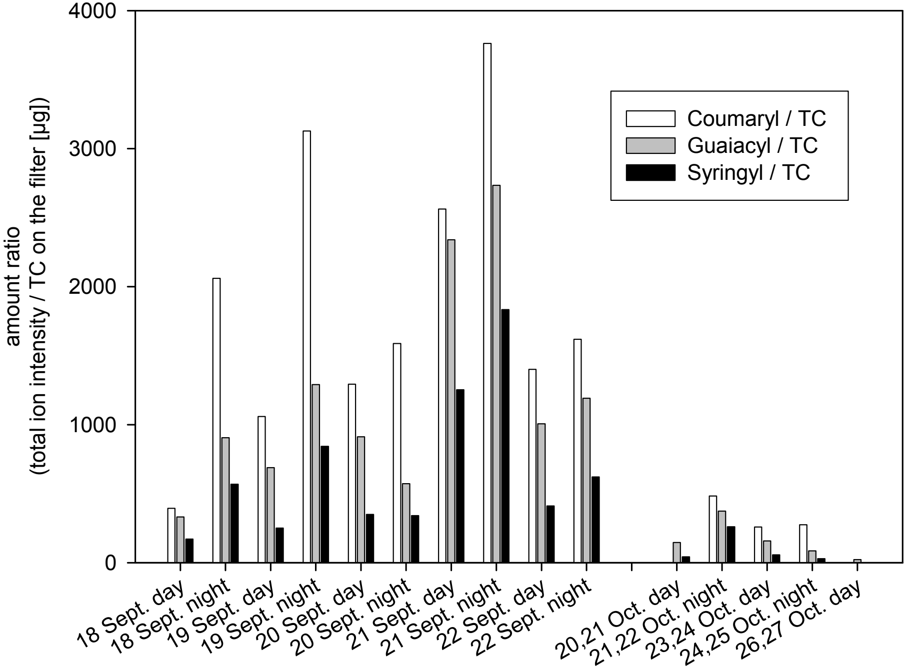

Fig. 7. Ratio of the total ion intensity of the coumaryl, guaiacyl, and syringyl compounds measured by THM-GC-MS relative to the amount of the TC on the filter.