**Atmospheric
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Organic molecular markers and signature from wood combustion particles in winter ambient aerosols: aerosol mass spectrometer (AMS) and high time-resolved GC-MS measurements in Augsburg, Germany

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Organic molecular markers and signature from wood combustion particles

M. Elsasser et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

| ◄◄ | ►► |
| ◄ | ► |

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

| ◄◄ | ►► |
| ◄ | ► |

| Back | Close |

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

⏮ | ⏭

◀ | ▶

Back | Close

Full Screen / Esc

Abstract

The impact of wood combustion on ambient aerosols was investigated in Augsburg, Germany during a winter measurement campaign of a six-week period. Special attention was paid to the high time resolution observations of wood combustion with different mass spectrometric methods. Here we present and compare the results from an Aerodyne aerosol mass spectrometer (AMS) and gas chromatographic – mass spectrometric (GC-MS) analysed PM_1 filters on an hourly basis. This includes source apportionment of the AMS derived organic mass by using positive matrix factorisation (PMF) and analysis of levoglucosan as wood combustion marker, respectively.

In the measurement period nitrate and organics are the main contributors to the defined submicron particle mass with 28 % and 35 %, respectively. To the latter wood combustion organic aerosol (WCOA) contributes 23 % on average and 27 % in the evening and night-time. Conclusively, wood combustion has a strong influence on the organics and overall aerosol composition. Levoglucosan accounts for 14 % of WCOA mass with a higher percentage in comparison to other studies. The ratio between the mass of levoglucosan and organic carbon amounts to 0.06.

This study is unique in the one-hour time resolution comparison between the wood combustion results of the AMS and the GC-MS analysed filter method at a PM_1 particle size range. This comparison of the concentration courses of the PMF WCOA factor, levoglucosan estimated by the AMS data and the levoglucosan measured by GC-MS is highly correlated, and a detailed discussion on the contributors to the wood combustion marker ion at mass-to-charge ratio 60 will be given. This offers a suitable application possibility for the description of the wood combustion course by the WCOA factor and the levoglucosan concentration estimated by AMS data. However, quantitative description of the levoglucosan concentration estimated by the AMS data is difficult due to the offset of latter compared to measured levoglucosan by the GC-MS.

1 Introduction

Ambient organic aerosol is of high interest due to its effect on climate and human health. (IPCC, 2007; Lohmann et al., 2005; Pope and Dockery, 2006). During winter season, wood combustion (WC) is one of the major sources of organic aerosol in Europe (Puxbaum et al., 2007). Besides primary particles consisting of a complex mixture of soot, inorganic and organic matter, WC additionally emits a considerable amount of volatile organic compounds (VOCs), some of which are known to be secondary organic aerosol (SOA) precursors (Grieshop et al., 2009; Heringa et al., 2011). WC has an important influence on aerosol composition. Nevertheless, its significance may grow with the anticipated increase in use of renewable energy sources. Therefore, it is important to develop tools to quantify the contribution of WC to air pollution.

Nowadays, several novel offline and online measurement systems make the observation of the highly dynamic process of WC emission events and their contribution to the ambient aerosol possible. The offline methods limited by time resolution, for instance, the analysis of filter samples with gas chromatography (GC), provide quantifications and qualifications of WC markers such as levoglucosan, potassium and retene (Sandradewi et al., 2008a; Svane et al., 2009; Simoneit et al., 2002; Cass et al., 1998). Some of these WC markers and several statistical source apportionment methods (Viana et al., 2008) like positive matrix factorisation (PMF) are also the basis for the online WC emission analysis. Recently, some online high-time resolution instruments became available, for instance the aerosol mass spectrometer with subsequent statistical analyses (e.g. Lanz et al., 2008; Ulbrich et al., 2009). In addition, multi-wavelength light-absorption measurements were used to determine the contribution of wood combustion particles (Sandradewi et al., 2008a, b). Consequently, it is of high interest to know how well these methods agree. Other studies have compared source apportionment (Favez et al., 2010; Kim et al., 2004).

The present work is primarily focused on the Aerodyne aerosol mass spectrometer (AMS) data gathered during a winter measurement campaign of 2010 in the city of

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Augsburg, Germany. This campaign was designed to determine the WC influence on the ambient aerosol with different highly time-resolved online and offline mass spectrometric methods in a medium sized Central European city during wintertime.

We specifically compare WC organic mass derived from PMF analysis of AMS data and levoglucosan concentrations from GC-MS measurements. The signal of mass-to-charge ratio (*m/z*) 60 is of major interest due to its function as a WC marker ion in electron ionisation mass spectrometry, like the AMS (e.g. Alfarra et al., 2007; Schneider et al., 2006). The novelty of the presented approach is the comparison of AMS data and PMF analysis with results from offline PM_1 filter measurements under ambient conditions on a one-hour basis. Recently, other ambient studies (Aiken et al., 2009; Favez et al., 2010) compared the GC-MS and AMS methods in a time resolution range of 12–24 h and on a $PM_{2.5}$ filter measurement basis. In an emission study by Lee et al. (2010) wood burning results of these methods were compared on an approximately one-hour resolution $PM_{2.5}$ filter measurement basis. The concurrent filter and AMS data will be analysed to carry out the comparison in a similar particle size range with a high time resolution; this offers the opportunity to study the dynamic impact of WC on the organic aerosol composition (for example, diurnal variation and levoglucosan to organic carbon (OC) ratio).

Additional online mass spectrometers were run during this campaign. They include an Alkali AMS (Svane et al., 2004, 2009) for online potassium and sodium determination, a single-particle thermal-desorption laser mass spectrometer (TD-REMPI-SP-ToF-MS) (Bente et al., 2006) for polycyclic aromatic hydrocarbon (PAH) detection on single particles (Oster el al., 2011) and an AMS for local source apportionment set up in a mobile atmospheric pollution laboratory "measurements of spatial quantitative imissions of trace gases and aerosols" called MOSQUITA (Bukowiecki et al., 2002; Mohr et al., 2011). These data will be presented in following studies (e.g. Oster el al., 2011).

2 Methods

2.1 General

The campaign was carried out in the city of Augsburg, Germany for a six-week winter period from 31 January to 12 March 2010. Augsburg is located in the southwest of Bavaria, Germany and has about 260 000 inhabitants. The city and the surrounding terrain are flat and covered with mainly multi-storey buildings with chimneys. Augsburg was subject to a number of ambient (Gu et al., 2011) and health studies (Löwel et al., 2005). The measurement site for the data collection includes two measurement containers for long-term PM and PM composition observation (Cyrys et al., 2006) and is located at the University of Applied Sciences in Augsburg (48 3581 latitude; 10 9070 longitude), around 1 km south southeast of the city centre. Significant traffic hotspots next to this site are the city circle motorway (approx. 120 m) and the tram headquarter (approx. 50 m).

2.2 AMS

The Aerodyne AMS is a real-time measurement instrument for submicron non-refractory (NR) aerosol components such as organics, sulphates, nitrates, and ammonium (Allan et al., 2004) with a 100 % transmission efficiency in the AMS system for 70–500 nm sized particles and considerable transmission for particles in the 30–70 nm and 500 nm–2.5 µm ranges (Jayne et al., 2000; Zhang et al., 2002). The AMS system and data analysis software have already been described in detail in several publications (DeCarlo et al., 2006; Canagaratna et al., 2007; Zhang et al., 2004). A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) was used in this campaign.

The AMS was run alternatively between V-(single stage reflectron) and W-mode (double stage reflectron), with 2 min of measuring time for each mode. In this paper the V-mode data are presented. The V-mode alternates between the mass spectrum (MS)

mode for the total non-refractory PM$_1$ particle mass chemical composition (4 times 15 s chopper open and closed per 2 min of measuring time) and the particle time-of-flight (PToF) mode for the particle size distribution (4 times 15 s per 2 min of measuring time). The heater for the aerosol thermal desorption was run at 600 °C and the tung-

5   sten filament for electron ionisation at an accelerating voltage of 70 eV, respectively. A collection efficiency (CE) of 0.5 was used for this instrument (for detail see Sect. SI-1 of the Supplement) and applied to all AMS data.

The servo position check and the lens alignment were made in the beginning of the campaign. Flow and size calibrations were performed before and after the campaign.

10 Routine calibrations of the ionisation efficiency (IE), baseline, *m/z* and single ion, as well as a gas phase correction that was carried out using a high efficiency particulate air (HEPA) filter in front of the sampling inlet, were performed every four to five days (Aiken et al., 2008).

The software package Igor Pro 6.12A (Wavemetrics, Lake Oswego, OR) was used as

15 a basis for the standard AMS data analysis tools (SQUIRREL v1.49 and PIKA v.1.08, Sueper, 2010). The fragmentation table (Allan el al., 2004) was modified according to gas phase composition.

2.3   PMF

Positive matrix factorisation (PMF) is a bilinear unmixing model used to describe the

20 measurements as a linear combination of factors. PMF was applied here to reconstruct the measured AMS organic mass spectra as a linear combination of factors character-ized by a constant mass spectrum (factor profile) and a variable contribution over time (strength of the factor). Both, the source profiles and the factors contributions are un-known. Strength and profile of the sources are constrained to be positive, representing

25 physically meaningful positive concentrations and contributions in the model (Ulbrich et al., 2009; Lanz et al., 2007). Equation (1) models the observed matrix **X** as linear combination of the chemical composition of several sources (sources profile) and their

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

contribution to the total mass over time (source strength or time series) (Paatero et al., 1997):

$$\mathbf{X}_{ij} = \sum_{k=1}^{p} \left(\mathbf{F}_{ik} \cdot \mathbf{G}_{kj} \right) + \mathbf{E}_{ij} \qquad (1)$$

where $\mathbf{X}$ is $m \times m$ matrix of the measurements, with m number of rows (time series) and n number of columns (m/z in the MS), $\mathbf{G}$ is the $m \times p$ matrix of the strengths (time series) of the p sources, $\mathbf{F}$ is the $p \times n$ matrix of p profiles, $\mathbf{E}$ is the $m \times n$ matrix of residuals between the measurements and the fit for each data point. The indices j, i and k are associated to the time series, the m/z in the measurements matrix, and a discrete factor, respectively. The model is solved by minimizing the quantity Q with a least-square method (Supplement; Fig. SI-2.1); Q represents the sum of the residuals E normalized by the uncertainty matrix of the measurements

$$Q = \sum_i \sum_j \left(\mathbf{E}_{ij} / \boldsymbol{\sigma}_{ij} \right)^2 \qquad (2)$$

The PMF analysis for the organics source apportionment was performed using the AMS PMF Toolkit version 2.03 developed by Ulbrich et al. (2009) together with the Igor Pro software. Organic concentrations and error matrix were obtained following the procedure described by Ulbrich et al. (2009). The final matrix was formed by 14 285 time points and 268 mass-to-charge ratios from m/z 12 to 300. PMF was applied to the unit mass resolution AMS V-mode data recorded with a time resolution of 4 min due to the 2 min of measuring time for the V- and W-mode.

2.4 GC-MS

PM_1 filter samples were collected on quartz fibre filters with a one-hour time resolution from 15 to 19 February in order to determine the organic composition with in situ derivatisation thermal desorption gas chromatography time of flight mass spectrometry

(IDTD-GC-ToFMS) (Orasche et al., 2011). Additionally, $PM_{2.5}$ filters were sampled daily and analysed by the same method.

The PM_1 samples were collected with a sequential low volume sampler (LVS3/SEQ 47/50, Leckel GmbH, Berlin, Germany) on quartz fiber filters (T293, Munktell, Grycksbo, Sweden) at a flow rate of $38.3 \, l \, min^{-1}$. Sampling time was one hour, yielding a collected air volume of $2.3 \, m^3$. The $PM_{2.5}$ samples were collected with a low volume sampler (Partisol-Plus Model 2025, Rupprecht & Patashnick, NY, USA) using a flow rate of $16.7 \, l \, min^{-1}$; within 24 h sampling time airborne particulate matter of $24 \, m^3$ air was collected.

Prior to sampling, the quartz fiber filters were tempered for at least eight hours at $550 \, ^\circ C$ to remove all organic matter. After sampling, the filters were cut into strips of $2 \, mm \times 13.5 \, mm$ ($27 \, mm^2$) representing a volume of $0.047 \, m^3$ of ambient air for PM_1 and $0.550 \, m^3$ for $PM_{2.5}$. The filter strips were stored in glass containers at $-18 \, ^\circ C$ until analysis by thermal desorption GC-MS.

The principle of the analysis is to conduct an automatic *in situ* derivatisation with N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) before thermal desorption, GC-MS separation and detection. As no manual extraction and derivatisation step is necessary before GC-MS analysis, this method is time saving (Orasche et al., 2011). It allows the analysis of non-polar and polar organic compounds in one measurement. Due to thermal desorption low limits of quantification (LOQ) were possible.

The filter strips in a GC liner were spiked with an internal standard mixture of standard isotope labelled reference compounds, for instance, levoglucosan for quantification. MSTFA was added directly onto the filter punches (autosampler, Combi PAL, CTC Analytics AG, Zwingen, CH) for derivatisation. The GC liners were put directly into the injector, which increased its temperature to $300 \, ^\circ C$ from room temperature and kept the temperature for 16 min (injection port: Optic III with LINEX-TD system, ATAS-GL, Veldhoven, NL). During the high temperatures of thermal desorption, the carrier gas (helium) was enriched with gaseous MSTFA to ensure ongoing of silylation reaction. The derivatised and desorbed analytes were focused on a retention gap of deactivated

fused silica with an oven temperature of 70 °C (Retention gap: SGE, Ringwood, AUS; column: BPX5, SGE, Ringwood, AUS; and GC: Agilent 6890, Agilent, Palo Alto, CA, USA). After both procedures (thermal desorption and derivatisation reaction) were finished, no more MSTFA was added to the carrier gas and detection by GC-MS was started. Standard electron ionisation (EI) and ToF-MS equipment (Pegasus III, LECO Ltd., St. Joseph, MI, USA) was used for detection.

2.5 Other instruments

An additional instrument used during this campaign was a scanning mobility particle sizer (SMPS) (TSI, model 3080, 3022A). The SMPS was running continuously in parallel with the AMS to obtain particle number size distributions in the size range from 14.33 to 673.17 nm. Furthermore, a twin differential mobility particle sizer (TDMPS) system combined with an aerodynamic particle sizer (APS, model 3321, TSI Inc., USA) was used to measure the particle size distribution in the range from 3 nm to 10 μm; the total used size range was from 50 nm to 1000 nm. To convert the APS (aerodynamic) to TDMPS (mobility) diameter an effective density of $1.7 \, \mathrm{g \, cm^{-3}}$ was assumed in the overlap range of 800 to 900 nm (Pitz et al., 2008). In addition, a condensation particle counter (CPC) (TSI, model 3025 A) was used for total particle number concentration measurements.

An Aethalometer (Thermo Fisher Scientific Inc., USA, series 8100) was used to measure black carbon (BC). The $PM_{2.5}$ mass concentration was measured using a tapered element oscillating microbalance (TEOM, model 1400ab, Thermo Fisher Scientific Inc., USA) equipped with a filter dynamics measurement system (FDMS model 8500b, Thermo Fisher Scientific Inc., USA). A sulfate particulate monitor (SPA, model 5020, Thermo Fisher Scientific Inc., USA) was used to measure $PM_{2.5}$ particle-bound sulfate concentrations (cf. Supplement Fig. SI-3.2). Meteorological data including wind velocity and direction, temperature, relative humidity and global radiation were measured with an ultrasonic anemometer, resistance thermometer, capacitive humidity element and pyranometer, respectively (Adolf Thies GmbH & Co. KG, Germany).

3 Results and discussion

3.1 General

During the campaign, the temperature ranged from -9.9 to $14.4\,^\circ$C under typical seasonal weather conditions. $PM_{2.5}$ mass concentration ranged from 1.1 to $110.7\,\mu g\,m^{-3}$.
Beside the weather condition and $PM_{2.5}$ mass concentration Fig. 1 shows the hourly mean time series of the main submicron aerosol components from the AMS data, such as organics, nitrate, sulphate, ammonium and the $PM_{2.5}$ BC Aethalometer data during the whole campaign. A high variation in particulate matter (PM) concentration and composition could be observed with higher $PM_{2.5}$ concentrations during cold and snowy periods, while lower concentrations were observed during warm and rainy periods. In a high PM phase from 5 to 20 February (average temperature of $-2.4\,^\circ$C) the low wind speeds (WS) (on average $1.2\,m\,s^{-1}$) are accompanied with little vertical air exchange and an increase of secondary inorganic aerosol. It is somehow surprising in this case that the global radiation is low, on average $36\,W\,m^{-2}$ (over the whole campaign $61\,W\,m^{-2}$). The low PM phase, e.g. from 25 February to 2 March (average temperature: $6.4\,^\circ$C) has a higher average WS of $2.1\,m\,s^{-1}$ and in extremely low PM phase a WS of up to $6\,m\,s^{-1}$. Normally, the visually observed snow falls had no impact on the PM concentration as measured by AMS, but two special events could be observed with abrupt increases in PM in the morning hours of 11 February and 3 March 2010, concurrent with humid snow fall events.

3.2 Source apportionment results

The PMF analysis of the AMS data provides a three-factor solution for the source apportionment of the organics. This three-factor solution was chosen to describe the major sources of organics due to the structure of their mass spectra, time series and high correlation coefficient by comparing the factor time series with results from other measurements of source related species. The largest contribution to the

total organic mass is represented mostly by the oxygenated fraction (oxidised organic aerosol, OOA) typically interpreted to be mainly of secondary origin. The second factor is hydrocarbon-like and attributed to freshly emitted organic aerosol (HOA) from fossil fuel combustion, and the third factor is identified as wood combustion organic aerosol (WCOA). Source interpretations are based on the MS comparison of these estimated PMF factors (Fig. 2a) with representative source MS from previous studies (http:cires.colorado.edu/jimenez-group/AMSsd, July 2011). A high similarity is given with the MS factor from a PMF solution during a winter measurement campaign in Grenoble (Favez et al., 2010). The European Alp city Grenoble has a similar population size like Augsburg. The comparison of the Augsburg and Grenoble factors for OOA, HOA and WCOA show a correlation coefficient of $R^2 = 0.47$, 0.84 and 0.66, respectively. In addition to the three-factor PMF solution, a four-factor solution was also evaluated. In the four-factors PMF analysis the new factor shows parts from the OOA and WCOA components. However, this four-factor solution provides less correlation with the measured data set compared to the three-factor solution, for instance, HOA with m/z 57. Additionally in this four-factor solution HOA shows a high correlation with m/z 44 in contrast to OOA. More information about the four-factor PMF solution are provided in Sect. SI-2.2 and in Table SI-1 of the Supplement.

The average relative contribution of the OOA, HOA and WCOA factors is 42 % (range 2–69 %), 34 % (range 19–78 %) and 23 % (range 6–62 %), respectively. The contribution of OOA to total organics is approximately 55 % in the high PM periods and approximately 25 % in the warm and humid periods. During the latter periods, HOA has a maximum contribution of around 60 % to the total organics. Hence freshly emitted aerosol has the biggest influence in warm and rainy periods. The daily mean contribution of WCOA to total organics is constant at about 20 % of the total organics during the whole campaign. Nevertheless, peak values during the daily variations can be observed especially in the evening and at night.

Matrix rotation was explored in the 3-factor solution using the "FPEAK" parameter of the PMF. The mass spectra and time series variations in the FPEAK range from

−1 up to +1 with a step of 0.1 were analysed and are summarised in Fig. SI-2.2 of the Supplement. The *Q/Q* expected ratio is constant for various FPEAKs. FPEAK equal to 0.2 showed good correlation between reference mass spectra (Favez et al., 2010), marker ions (Fig. 3) and source related species data (Fig. 4). Negative FPEAK

5 values greatly reduced the correlation of factor time series with source the related tracer species while the positive FPEAK values showed similar correlations with tracer species as the FPEAK = 0. However the FPEAK 0 solution is between the negative and positive FPEAK and shows a step in the factor contribution. Due to this the FPEAK 0.2 is chosen for the subsequent analysis as a more stable PMF solution. Some variation

10 of the factor mass spectra in FPEAK dependency over all FPEAKs is observed in the mass spectra from WCOA and OOA, whereas only the time series of the HOA and OOA are changed (Figs. SI-2.2 and SI-2.3).

To support the interpretation of the PMF factors, time series of the marker ions *m/z* 44, 57 and 60 (Zhang et al., 2005; Aiken et al., 2009; Alfarra et al., 2005 and 2007) and

15 the source associated species (SO_4^{2-}, NH_4^+, BC and levoglucosan) were correlated with the factors time series and showed a correlation coefficient $R^2 > 0.77$ (Figs. 3 and 4). The correlation is $R^2 = 0.95$ for OOA with the secondary marker ion *m/z* 44 and 0.97 for HOA with the primary marker ion *m/z* 57 (Fig. 3). Chirico et al. (2010) showed that aged diesel emissions contain high amounts of oxygenated *m/z* 57 which is produced trough

20 oxidative processes. However, the high course correlation in this case is not surprising, because both the oxygenated fragment ($C_3H_5O^+$) and the non-oxygenated fragment ($C_4H_9^+$), which is with approximately 47 % the main contributor to *m/z* 57, show a high correlation with HOA ($R^2 = 0.85$ and 0.88, respectively) and additionally the courses of HOA and OOA correlate with $R^2 = 0.58$. WCOA and OOA provide a good correlation

25 with $R^2 = 0.80$ and 0.72, respectively, only with the oxygenated fragment ($C_3H_5O^+$). The WCOA factor correlates well with *m/z* 60 with an $R^2 = 0.77$. The main differences between the temporal variations of OOA and *m/z* 44 data are observed during the time when the HOA concentration is notably high.

A high correlation is found as well between the source related species data and the results from the PMF analysis (Fig. 4). The time series of OOA and the three main inorganic components sulphate, nitrate and ammonium used as markers for oxygenated aerosol result in correlations of $R^2 = 0.82$, 0.68 and 0.83, respectively. Additionally,
5 the AMS sulphate data show a good correlation ($R^2 = 0.85$) with data from the sulphate monitor (Supplement; Fig. SI-3.2). Primary aerosol mass HOA correlate well ($R^2 = 0.81$) with Aethalometer BC data. BC is mainly attributed to traffic and combustion exhaust (Szidat et al., 2007). The WCOA factor is in good correlation ($R^2 = 0.84$) with the levoglucosan measurements from the PM_1 and also ($R^2 = 0.92$) with the $PM_{2.5}$
10 GC-MS filters.

3.3 Wood combustion results

The following section focuses on the diurnal variation of the organic aerosol composition, especially on the WC results from levoglucosan and WCOA. In Fig. 5, the diurnal variation of AMS levoglucosan equivalent concentration data is displayed as hourly av-
15 erages of the whole campaign. The AMS levoglucosan equivalent concentration was calculated from the organic fraction of m/z 60 by subtracting the organic background which has been found to be approximately 0.3 % of the total organic aerosol signal in several field campaigns (DeCarlo et al., 2008; Docherty et al., 2008) and multiplied by an instrument-specific levoglucosan standard factor (11.24 for our instrument)
20 consisting of the ratio of m/z 60 to total organic signal from a levoglucosan standard mass spectrum (Aiken el al., 2009). The WC contribution strongly increases during the evening period from 06:00 to 09:00 p.m. after the end of regular working time and rush hour, i.e. people arrive at home and start domestic heating by wood combustion. During the night, the concentration remains approximately constant with a small decrease
25 indicating low emissions and stable atmospheric conditions with low wind speed and low mixing layer height. In contrast, a minor increase of levoglucosan is observed in the morning from 07:00 to 10:00 a.m. with a maximum from 08:00 to 09:00 a.m. Previous studies by Sandradewi et al. (2008b) have also shown a maximum for WC in

the evening and night period, and Krecl et al. (2008) have observed the evening increase for traffic and WC related BC. The daily minimum in the afternoon was probably produced by a decreased WC activity together with an increase in mixing layer height during the day. The GC-MS levoglucosan daily variation of PM_1 filters shows the similar profile except for the high morning peak and some spikes due to the low number of GC-MS data points (Supplement; Fig. SI-3.3). The AMS levoglucosan equivalent concentration to organic mass ratio indicates a longer emission period on the weekend from the morning hours until noon compared to working days, which is expected due to normal weekend activity where people are more likely to spend the morning at home.

The PMF factor diurnal variations are plotted in Fig. 6. Similarly to the AMS levoglucosan equivalent concentration variation, the WCOA variation shows a strong increase in the evening hours from 04:00 to 09:00 p.m. and a maximum followed by a constant level at night from 09:00 p.m. to 01:00 a.m. The WCOA fraction contributes with approximately 27 % to the total organic mass in the latter period. The morning peak is smaller compared to the AMS levoglucosan equivalent concentration. Except for the less pronounced morning peak the WCOA diurnal variation matches well with the GC-MS levoglucosan variation (Supplement; Fig. SI-3.3). The HOA morning and evening maxima were obtained during the traffic rush hours. The HOA variation additionally shows a small increase around noon and a decrease after the rush hours in the night. The OOA is the biggest fraction of the organics at any time. However, OOA shows higher values during the day, especially from 01:00 to 04:00 p.m. when OOA contributes 50 % to the total organics. This afternoon maximum is likely caused by photochemical processing of primary emissions, which partly compensate the dilution due to an increase in mixing layer height in contrast to the directly emitted components which decrease upon mixing.

For a discussion of the aerosol chemistry and the wood combustion impact on the aerosol the view of ratios are often considered, e.g. organic mass (OM) to organic carbon (OC) ratio. However, these ratios, as discussed below for the different levoglucosan to OC ratios and ranges, are strongly linked to external circumstances and influences.

The organic mass (OM) to organic carbon (OC) ratio calculated from the AMS high resolution data of this study amounts to an average of 1.7. Favez et al. (2010) found a similar ratio of 1.78 in Grenoble (French Alps) in the wintertime. The OM to OC ratios for hydrocarbon like and oxygenated organic aerosols have been previously found to be in the range of 1.2 to 1.4 and 1.8 to 2.4, respectively (e.g. Turpin and Lim, 2001; Aiken et al., 2008).

The following ratios from this study represent the estimated slope of the linear orthogonal regression from data comparisons over 87 data points. The PM_1 levoglucosan analyzed by the GC-MS represents 3.4 % of the total organic mass and 14.3 % of the PMF WCOA mass in this study. The GC-MS levoglucosan to WCOA ratio compared to other studies is relatively high. For example, Lanz et al. (2008) found a ratio of 8 %. The levoglucosan to OC ratio amounts 0.06 (ratio of the quotient ranged from 0.02–0.16). The OC concentrations were calculated from the OM to OC ratio and OM of the AMS high resolution data. The diurnal variation of levoglucosan to OC ratio of the quotient (range 0.03–0.9) provides a similar variation as the GC-MS levoglucosan variation (Supplement; Fig. SI-3.3), only with stronger increases and decreases. Several studies (Puxbaum et al., 2007; Sullivan et al., 2008) pointed out that the used fuel type has a strong impact on this ratio (for instance, hardwood or softwood and even the wood species in those groups themselves). Additionally, the burning conditions and the use of wood or pellet boilers have an impact on this ratio (Johansson et al., 2004; Schmidl et al., 2008; Hedberg et al., 2006). Considering the range of variability of the levoglucosan to OC ratio due to these influences on the ratio, Table 1 shows that the observed ratio in this study is within a similar range as compared to the above-mentioned emission and ambient studies. The Augsburg ratio is similar to the results obtained in the French Alpine city Grenoble (around 157 000 inhabitants), and higher than results measured in Beijing, where a major OC contribution may be related to traffic.

3.4 Correlation of AMS and one-hour PM$_1$ filter WC results

The wood combustion measurement data of the AMS are compared with hourly PM$_1$ filter GC-MS measurements of levoglucosan and additional anhydrosugars in this section. The signal of *m/z* 60 or rather the ion C$_2$H$_4$O$_2^+$ is the main marker of WCOA and
5 is mainly formed from levoglucosan (C$_6$H$_{10}$O$_5$). During this Augsburg campaign the main contributor to signal of *m/z* 60 in the ambient aerosol is the ion fragment C$_2$H$_4$O$_2^+$ (93 % of *m/z* 60) as in other campaigns (Aiken et al., 2009; Mohr et al., 2009; Lee et al., 2010).

    The time series of levoglucosan from GC-MS and AMS measurements show a good
10 correlation with $R^2 = 0.84$ (Fig. 7b) and the daily variations of the GC-MS data are well reflected by the AMS data (Fig. 7a). The AMS levoglucosan equivalent concentration is about 2.7 times higher than the levoglucosan concentration from the GC-MS measurements. Aiken et al. (2009) also found a higher factor of 3.2. This offset can be explained due to other compounds that contribute to *m/z* 60 and raise the AMS levoglucosan
15 equivalent concentration results. The other anhydro sugars like the WC compounds mannosan and galactosan contribute as well to *m/z* 60, the GC-MS data additionally include these compounds to the levoglucosan concentration (Fig. 7a). This addition increases the levoglucosan concentration of around 10 %. The ratio of levoglucosan and mannosan is 11.4, which is close to the typical ratios for beech wood (14.8) and oak
20 wood (14.2) combustion (Schmidl et al., 2008). Thus the AMS equivalent levoglucosan offset is still too high and cannot be explained by the inclusion of these anhydrosugars. However, the AMS anhydrosugar equivalent concentration used by Lee et al. (2011) may be a more convenient expression. There must be other compounds co-emitted with the anhydrosugars sustaining the high correlation $R^2 = 0.84$. Various carboxylic
25 acids are emitted from wood combustion e.g. (Fine et al., 2004). These acids also produce the fragment due to a McLafferty rearrangement over a six membered transition state after EI (McLafferty, 1959) and thus contribute to the *m/z* 60 signal from wood combustion. Additionally one may speculate that cellulose from incomplete combustion

is pyrolysed by the AMS heater, forming levoglucosan and therefore contributing to the *m/z* 60 signal (Lee et al., 2011). Another study (Mohr et al., 2009) reported a contribution to *m/z* 60 from food cooking aerosols. For this and for other sources additional important contributors to *m/z* 60 could be as shown above long-chain carboxylic acids,

5 e.g. fatty acids like dodecanoic acid and octadecanoic acid. Long-chain carboxylic acids with chain-lengths from C_{12}–C_{20} play an important role for ambient aerosols as shown in several studies, cited in Mirivel et al. (2009). Our GC analyses provide qualitative and quantitative information of these acids. Dodecanoic acid for example shows high concentrations with an average of $60 \, \text{ng m}^{-3}$. It could be possible that not all

10 of these compounds are completely covered by the subtracted background (0.3 % of organics).

A detailed view at the *m/z* 60 signal with the PMF factor of OOA (Fig. 2a) shows that the contribution of the secondary aerosol source factor OOA to the *m/z* 60 signal match with the subtracted background (0.3 % of organics) from *m/z* 60 signal of the

15 calculation of the AMS levoglucosan equivalent concentration (course correlation $R^2 =$ 0.83 and OOA represent 70 % of the background during the whole campaign, except in low PM periods, the OOA roughly provides a two times lower value than the organic background). Note that the PMF analysis is a statistical calculation with variability opportunities; this detailed view at signal of *m/z* 60 can only show that the subtracted

20 organic background is in a reasonable range for the SOA.

Similar to the diurnal courses, the time series of the PMF WCOA factor and the PM_1 GC-MS levoglucosan data show a high correlation of $R^2 = 0.84$ during the PM_1 filter sampling period (Fig. 8). The main disagreement in the temporal variations is analogue to the comparison of the AMS anhydrosugar equivalent concentration in the

25 period from 03:00 to 06:00 a.m. on 17 February. Both, the WCOA and the AMS anhydrosugar equivalent concentration show a suitable application possibility for qualitative WC emission observation. The AMS anhydrosugar equivalent concentration and the WCOA variations correlate with $R^2 = 0.71$ during the whole campaign period and with $R^2 = 0.97$ over the PM_1 filter period.

4   Conclusions

The present study gives an overview of the Augsburg winter campaign 2010 including a detailed view of the WC results obtained by two different mass spectrometer methods. The first comparison of hourly PM_1 filter GC-MS measurements with AMS data under ambient conditions represents the particular novelty of this study. Additionally, it includes a detailed view of the dynamic changes of the aerosol composition over the day, which confirms that WC has an important influence on aerosol composition.

The main submicron aerosol fractions obtained by the AMS are organics and nitrate in Augsburg during winter. This is typical for winter in Central Europe (Lanz et al., 2010). PMF analysis of the organic data reveals the secondary process associated OOA to be the biggest with 42 % and WCOA to be with 23 % one of the main contributors to organic aerosol. The influence of WC is particularly important for the aerosol composition in the evening and the night hours, while the primary HOA emission factor is of higher concern during the morning rush hours. The levoglucosan to OC ratio is with an average of 0.06 in this study in a typical range for ambient WC.

The comparison of GC-MS levoglucosan measurements from the high time resolved PM_1 filters with AMS data shows that either AMS WCOA or alternatively AMS levoglucosan equivalent concentration analysis have a high course correlation and are therefore suitable for WC observation. Similar to Aiken et al. (2009), we identified the AMS levoglucosan equivalent concentration or better the AMS anhydrosugar equivalent concentration (Lee et al., 2010) to be higher than the GC-MS levoglucosan concentration. Therefore, it is suggested that not only levoglucosan contributes to the WC marker ion at m/z 60, or rather to the fragment ion $C_2H_4O_2^+$, but also other components from WC emissions like mannosan or galactosan or as shown in other studies from cellulose (Lee et al., 2010). Different analysis of additional GC-MS data and PMF results reveal that long-chain carboxylic acids could additionally increase the m/z 60 signal and that the subtracted organic background is comparable to the OOA fraction of m/z 60 signal. The analysis of the diurnal variation of the PMF factors appears to be important in

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the interpretation of the organic sources, especially for WC. The PMF WCOA diurnal variation presents a similar profile as the hourly PM_1 GC-MS levoglucosan results.

Supplementary material related to this article is available online at:
http://www.atmos-chem-phys-discuss.net/12/4831/2012/
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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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M. Elsasser et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Table 1. Literature data of levoglucosan to OC ratios from emission and ambient studies. The OC content was mainly analysed by using a thermal/optical transmission (TOT) method (Birch and Cary, 1996) with a Sunset Lab analyzer and is referred to OC from BB in the emission studies and total OC in the ambient studies. The OC content in this study is calculated from the organic mass of AMS data and the high resolution data (OM to OC ratio).

source place	fuel type	levoglucosan/OC	reference
fire place	hardwood	0.14	Fine et al. (2002)
fire place	softwood	0.04	Fine et al. (2002)
wood stove	beech	0.08	Puxbaum et al. (2007)
wood stove	spruce	0.21	Puxbaum et al. (2007)
stack burn	oak	0.06	Sullivan et al. (2008)
Beijing, China (July 2002 to July 2003; monthly mean)	ambient	0.012 to 0.035	Zhang et al. (2008)
Grenoble, France (14 to 29 January 2009; median)	ambient	0.09	Favez et al. (2010)
Augsburg, Germany (13 February to 12 March 2008; orthogonal fit)	ambient	0.10	unpublished study
Augsburg, Germany (15 to 19 February 2011; orthogonal fit)	ambient	0.06	this study
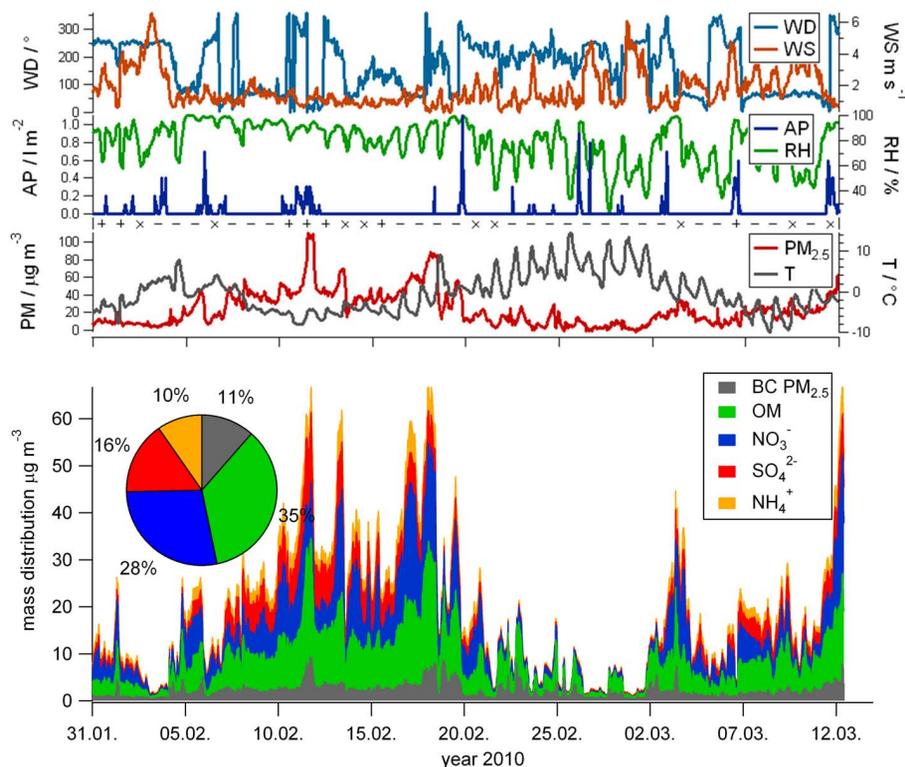
Fig. 1. (above) time series of meteorological and PM data: particulate matter (PM$_{2.5}$/red), temperature (T/grey), atmospheric precipitation (AP/dark blue), relative humidity (RH/green), wind direction (WD/grey blue), wind speed (WS/brown) and daily observation of snow fall events (+ = snow fall, − = no snow fall and x = light snow fall); (below) hourly mean time series of submicron aerosol components with the AMS organic (green), nitrate (blue), sulphate (red), ammonium (orange) and the PM$_{2.5}$ BC (grey) from the Aethalometer data. An individual overview of components is given in the supplemental material (Supplement; Fig. SI-3.1).
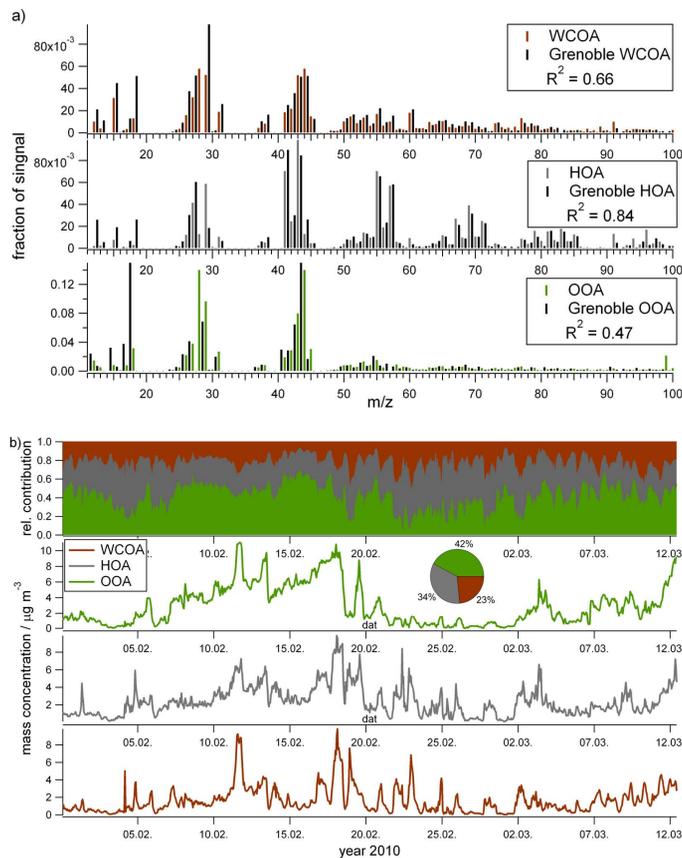
Fig. 2. AMS PMF results of the period from 31 January to 12 March, with FPEAK = 0.2. **(a)** Campaign calculated mass spectra of the PMF factors compared with reference mass spectra from Grenoble, January 2009 (Favez et al., 2010) and **(b)** time series of the hourly mean PMF factors and their averaged and relatively contribution to total organic matter.
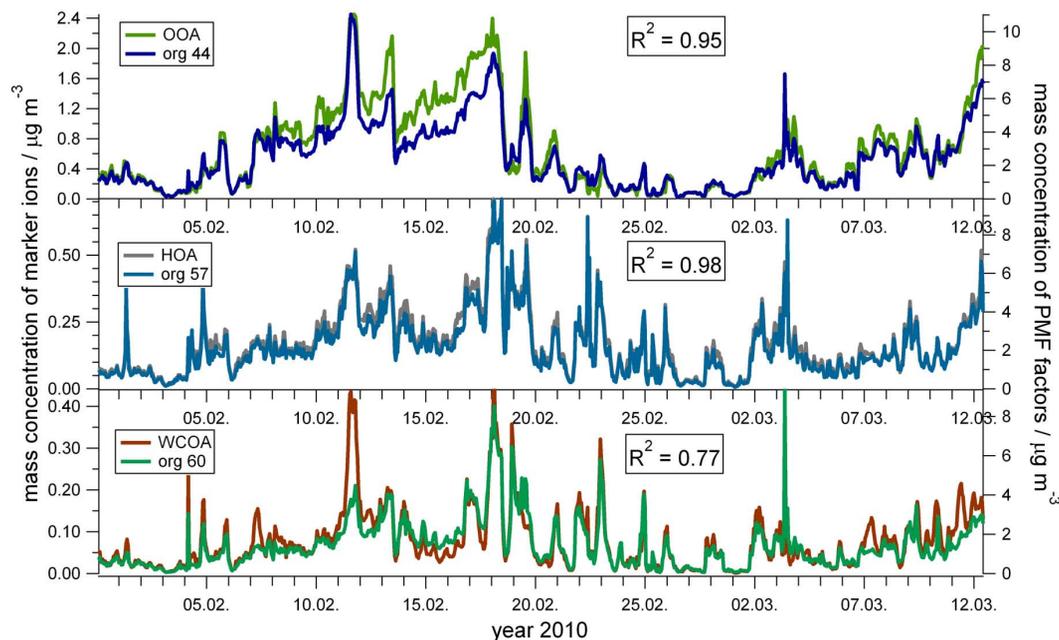
Fig. 3. Hourly averaged time series of WCOA (brown), HOA (grey) and OOA (green) PMF factors mass concentrations on the right axis correlated with hourly averaged mass concentrations of the marker ions *m/z* 60 (turquoise), *m/z* 57 (blue) and *m/z* 44 (light blue) from the AMS on the left axis.
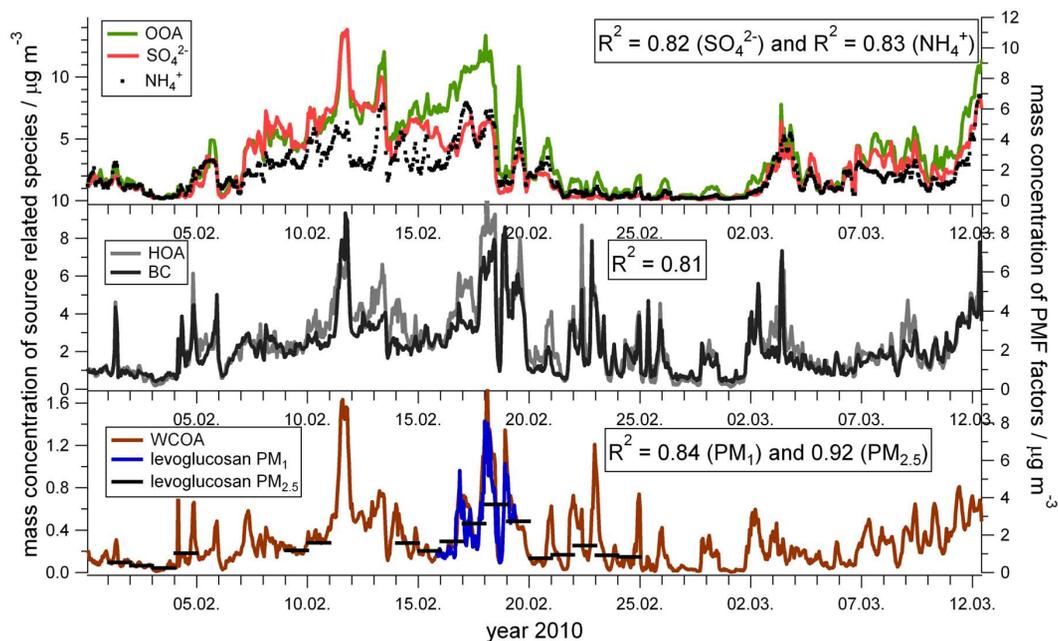
Fig. 4. Hourly averaged time series of OOA (green), HOA (grey) and WCOA (brown) PMF factors correlate with AMS sulphate (red), ammonium (black dots), $PM_{2.5}$ Aethalometer BC (black line) and hourly PM_1 (blue) and daily $PM_{2.5}$ (black line) levoglucosan GC-MS data.
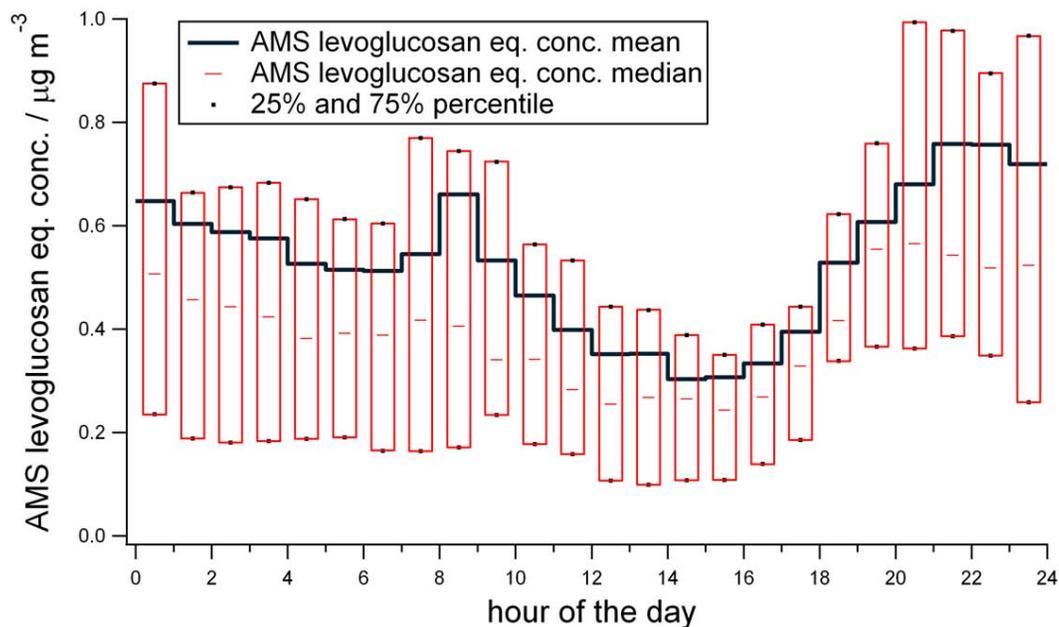
Fig. 5. Diurnal variation of AMS levoglucosan equivalent concentration displayed as a box plot during the whole campaign calculated from 14 285 data points.
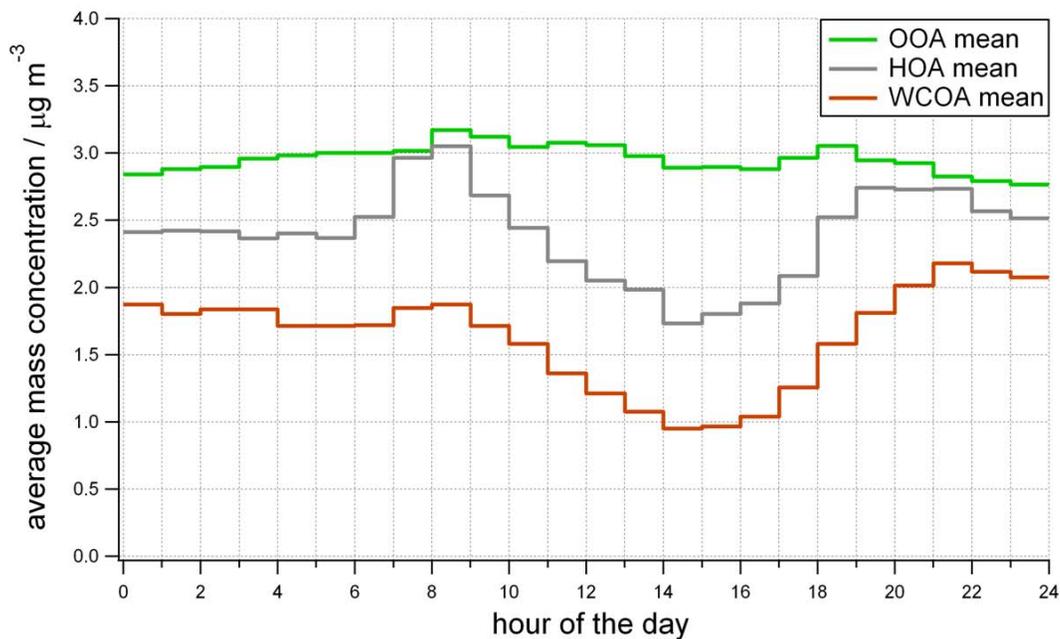
Fig. 6. Diurnal variation of the AMS PMF factor OOA (green), HOA (grey) and WCOA (brown) during the whole measurement period of the campaign.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►◄

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
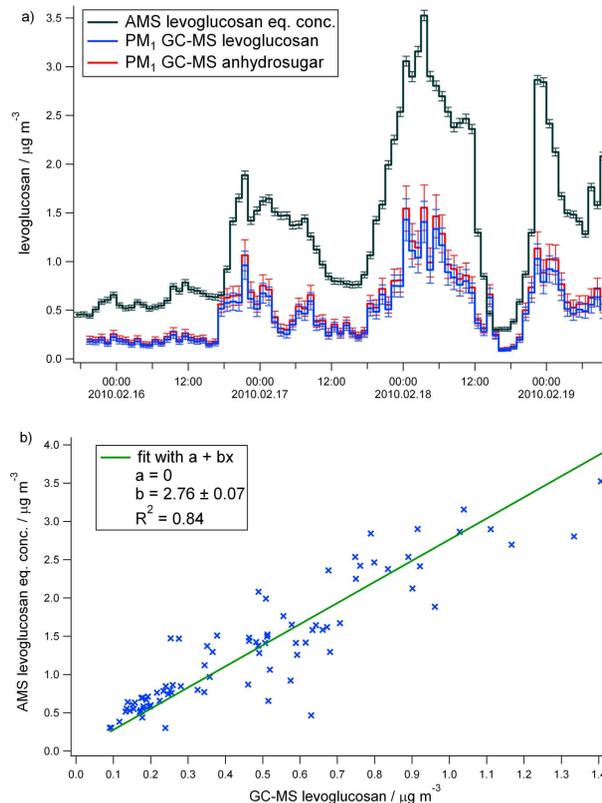
Fig. 7. (a) Time series of hourly mean AMS levoglucosan equivalent concentration (dark blue), PM_1 GC-MS levoglucosan (light blue) and sum of anhydrosugar (red) results in the week of 15 to 19 February. The error bars of the GC-MS data reflect the 15 % uncertainty associated with the method; the AMS levoglucosan equivalent concentration error bars were calculated with the SQUIRREL software for each species. **(b)** Scatter plot of hourly mean AMS levoglucosan equivalent concentration versus PM_1 GC-MS levoglucosan. Regression values are calculated with the orthogonal distance regression.

Fig. 8. (a) Time series of the hourly mean PMF WCOA factor (brown) and the hourly PM$_1$ GC-MS levoglucosan data (blue) during the week of 15 to 19 February. **(b)** Scatter plot of hourly mean PMF WCOA factor versus PM$_1$ GC-MS levoglucosan. Regression values are calculated with the orthogonal distance regression.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion