



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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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 PM₁ filters on an hourly basis. This includes source apportionment of the AMS derived organic matter (OM) using positive matrix factorisation (PMF) and analysis of levoglucosan as wood combustion marker, respectively.

During the measurement period nitrate and OM mass are the main contributors to the defined submicron particle mass of AMS and Aethalometer with 28 % and 35 %, respectively. Wood combustion organic aerosol (WCOA) contributes to OM with 23 % on average and 27 % in the evening and night time. Conclusively, wood combustion has a strong influence on the organic matter 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 that it provides a one-hour time resolution comparison between the wood combustion results of the AMS and the GC-MS analysed filter method at a PM₁ particle size range. The comparison of the concentration variation with time of the PMF WCOA factor, levoglucosan estimated by the AMS data and the levoglucosan measured by GC-MS is highly correlated ($R^2 = 0.84$), and a detailed discussion on the contributors to the wood combustion marker ion at mass-to-charge ratio 60 is given. At the end, both estimations, the WCOA factor and the levoglucosan concentration estimated by AMS data, allow to observe the variation with time of wood combustion emissions (gradient correlation with GC-MS levoglucosan of $R^2 = 0.84$). In the case of WCOA, it provides the estimated magnitude of wood combustion emission. Quantitative estimation of the

levoglucosan concentration from the AMS data is problematic due to its overestimation in comparison to the levoglucosan measured 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 and Feichter, 2005; Pope and Dockery, 2006). During the 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 (OM), 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 the 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, for instance the analysis of filter samples with gas chromatography (GC), provide quantitative and qualitative results of WC markers such as levoglucosan, potassium and phenolic compounds (Sandradewi et al., 2008a; Svane et al., 2009; Simoneit, 2002; Cass, 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 methodologies (Favez et al., 2010; Kim and Hopke, 2004).

The present work is primarily focused on the measurements performed in Augsburg, Germany, using an Aerodyne aerosol mass spectrometer (AMS) during a winter measurement campaign in 2010. 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 matter 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 potential as a WC marker ion in electron ionisation mass spectrometry, like the AMS (e.g. Alfarra et al., 2007 and Schneider et al., 2006). The novelty of the presented approach is the comparison of AMS data and PMF analysis with results from offline PM₁ 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 obtained with these methods were compared on an approximately one-hour resolution PM_{2.5} filter measurement basis. In this work, 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 et al., 2011) and an AMS for local source apportionment set up in the mobile atmospheric pollution laboratory “MOSQUITA” (“Measurements Of Spatial QUantitative Imissions of Trace gases and Aerosols”, Bukowiecki et al., 2002; Mohr et al., 2011). These data are presented in other studies (e.g. Oster et 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), 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. The city centre is surrounded by compact residential areas and some industrial districts. Significant impact of traffic next to this site may be caused by 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., Billerica, MA, USA) was used in this campaign.

In this study 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_{10} particle mass chemical composition (four 15-s intervals for chopper opened and closed every two minutes of measuring time) and the particle time-of-flight (PToF) mode for the particle size distribution (four 15-s intervals every two minutes of measuring time). The heater for the aerosol thermal desorption was run at 600 °C and the tungsten filament for electron ionisation at an accelerating voltage of 70 eV, respectively. A collection efficiency (CE) of 0.5 was used for this instrument and applied to all AMS data. In a detailed discussion provided in the Sect. SI-1 of the Supplement it is shown that an acidity balance and nitrate dependence is given. However, a novel calculation of an alternated CE (Middlebrook et al., 2012) shows that the nitrate dependence does not affect the obtained results with a constant CE of 0.5. According to Bahreini et al. (2009) this CE could vary by around 20 %.

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. 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 a basis for the standard AMS data analysis tools (SQUIRREL v1.49 and PIKA v1.08, Sueper, 2010). The fragmentation table (Allan et 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 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 characterized 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 unknown. Strength and profile of the sources are constrained to be positive, representing physically meaningful positive concentrations and contributions in the model (Ulbrich et al., 2009; Lanz et al., 2007; Paatero and Tappert, 1994; Paatero, 1997). A detailed description of the PMF analysis is provided in Sect. SI-2 of the Supplement. 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_{10} 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, 17 daily $\text{PM}_{2.5}$ samples were collected during the period of 1 to 24 February and analysed using the same method.

The PM_{10} 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 38.31 min^{-1} . Sampling time was one hour, yielding a collected air volume of 2.3 m^3 . The $\text{PM}_{2.5}$ samples were collected with a low volume sampler (Partisol-Plus Model 2025, Rupprecht & Patashnick, NY, USA) using a flow rate of 16.71 min^{-1} ; within 24 h of 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 °C to remove all organic matter. After sampling, the filters were cut into strips of 2 \times 13.5 mm (27 mm^2) representing a volume of 0.047 m^3 of ambient air for PM_{10} and 0.550 m^3 for $\text{PM}_{2.5}$. The filter strips were stored in glass containers at -18 °C until analysis by thermal desorption GC-MS. No significant difference between the analyte masses of PM_{10} (hourly filters) and $\text{PM}_{2.5}$ (daily filters) were found.

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 reached (levoglucosan, mannosan, galactosan, and dodecanoic acid reached LOQs of 0.06, 0.05, 0.02, and 0.06 ng, respectively).

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. For analysis an autosampler decapped the liners, added MSTFA directly onto the filter punches and put the GC liners directly into the injector (autosampler, Combi PAL, CTC Analytics AG, Zwingen, CH; LINEX-TD system, ATAS-GL, Veldhoven, NL). The injector increased its temperature from room temperature to 300 °C and kept the temperature for 16 min (injection port: Optic III, ATAS-GL, Veldhoven, NL). During the high temperatures of thermal desorption, the carrier gas (helium) was enriched with gaseous MSTFA to ensure the ongoing 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

Another 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 to 673 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 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 3025A) 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. 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 ambient temperature ranged from -9.9 °C to 14.4 °C under typical seasonal weather conditions. PM_{2.5} mass concentration ranged from 1.17 µg m⁻³ to 110.7 µg 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 organic matter, 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 phase of high PM concentrations (above 20 µg m⁻³) from 5 to 20 February (average temperature of -2.4 °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. The phase of low PM concentrations (below 8 µg m⁻³), e.g. from 25 February to 2 March (average temperature: 6.4 °C), has a higher average WS of 2.1 m s⁻¹ and in phases with extremely low PM (below 3 µg m⁻³) 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 organic matter. This three-factor solution was chosen to describe the major sources of organic matter 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 OM mass is represented mostly by the oxygenated fraction (oxygenated 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

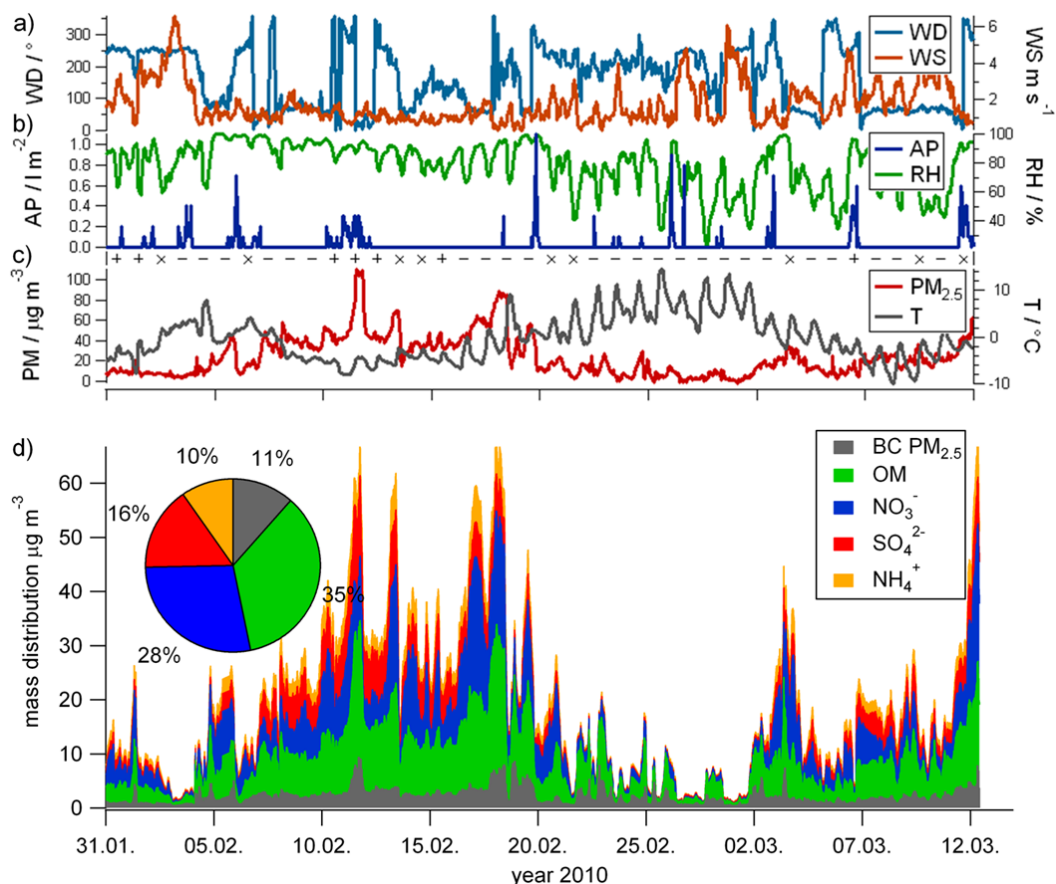


Fig. 1. Time series of meteorological and PM data: (a) wind direction (WD/grey blue) and wind speed (WS/brown); (b) atmospheric precipitation (AP/dark blue), relative humidity (RH/green) and daily observation of snow fall events (+ = snow fall, – = no snow fall and × = light snow fall); (c) particulate matter (PM_{2.5}/red) and temperature (T/grey) and (d) hourly mean time series of submicron aerosol components with the AMS organic matter (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 (Fig. SI-3.1).

factors (Fig. 2a) with representative source MS from previous studies (<http://cires.colorado.edu/jimenez-group/AMSsd>, July 2011). A high similarity is obtained with the MS factor from a PMF solution during a winter measurement campaign in Grenoble (Favez et al., 2010). The European Alp city of Grenoble has a population size similar to that of Augsburg. The comparison of the Augsburg and Grenoble factors for OOA, HOA and WCOA over 246 data points is in good agreement with the 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-factor PMF analysis the new factor shows parts from the OOA and WCOA components. However, this four-factor PMF solution, in comparison to the three-factor solution, provides inferior correlations with the measured data set. For instance, HOA and the signal of m/z 57 correlate with just a R^2 of 0.43. Additionally in this four-factor solution HOA shows a high correlation with m/z 44 ($R^2 = 0.93$) in contrast to OOA ($R^2 = 0.43$). More information about the four-factor

PMF solution is provided in Sect SI-2.2 and in Table SI-1 of the Supplement. A possible food cooking factor has not been found in PMF analysis. Additionally, the AMS does not provide a high ratio of the m/z 55 and 57, which would be a robust marker for food cooking (Mohr et al., 2012).

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. The Q/Q_{expected} ratio (Sect. SI-2.2 of the Supplement; Paatero, 1997) is constant for various FPEAKs. FPEAK equal to 0.2 showed good correlations between reference mass spectra (Favez et al., 2010), marker ions (Fig. 3) and source-related species data (Fig. 4). PMF solution with negative FPEAK values provide weaker correlations of calculated factor with temporal variation of the source-related tracer species, while the PMF solution of positive FPEAK values showed similar correlations with tracer species as the FPEAK = 0. However, the FPEAK 0 solution

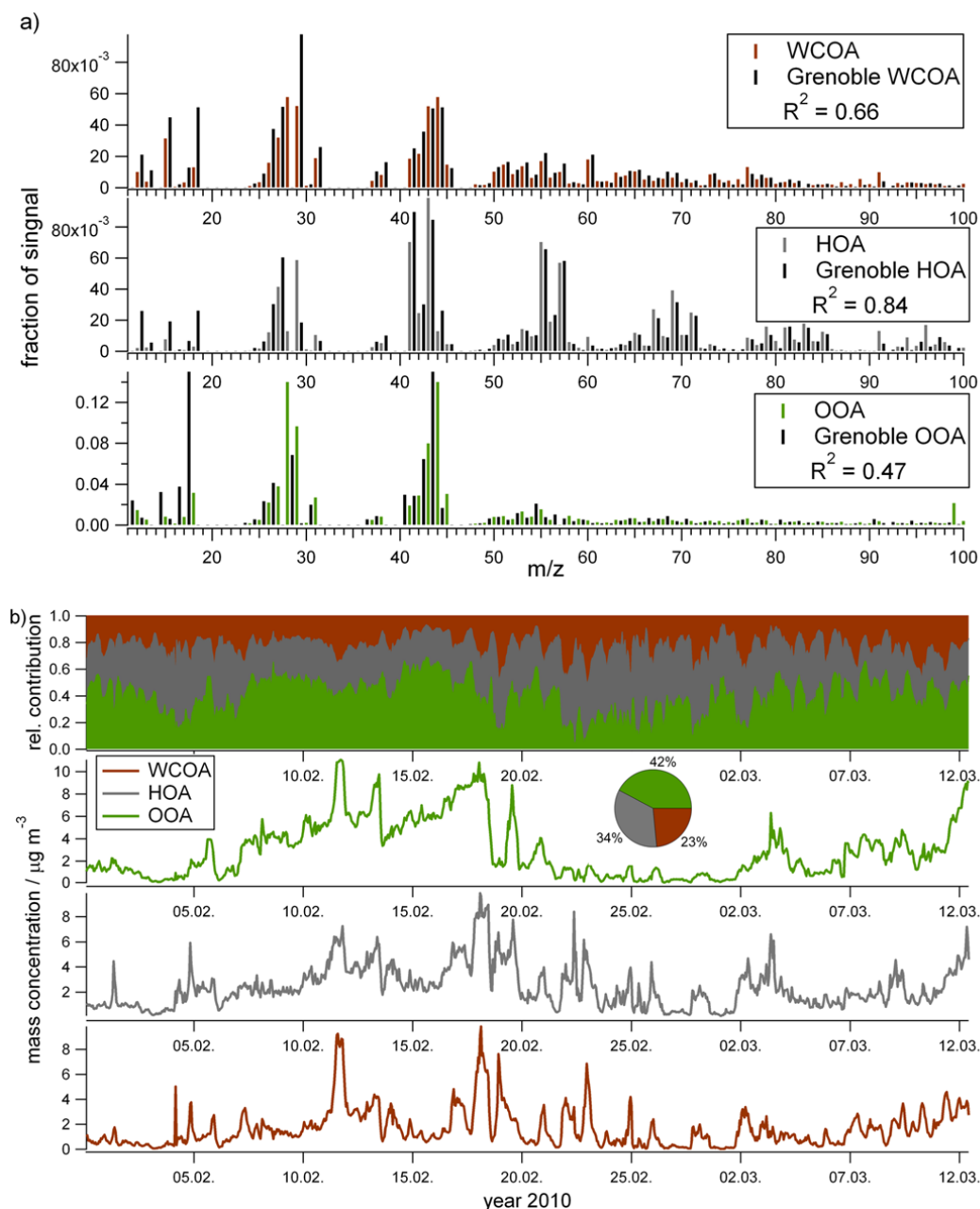


Fig. 2. AMS PMF results of the period from 31 January to 12 March, with FPEAK = 0.2. (a) Campaign calculated mass spectra of the PMF factors compared with reference mass spectra from Grenoble, January 2009 (Favez et al., 2010) and (b) time series of the hourly mean PMF factors and their averaged and relatively contribution to total organic matter.

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 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).

The average relative contribution of the OOA, HOA and WCOA factors are 42% (range 2–69%), 34% (range 19–78%) and 23% (range 6–62%), respectively. The contribution of OOA to total organic matter is approximately 55% in the periods of high PM concentrations and approximately 25% in the warm and humid periods. As it is indicated by the four-factor PMF solution, some parts of the OOA could originate from WC. For example Heringa et al. (2011) showed

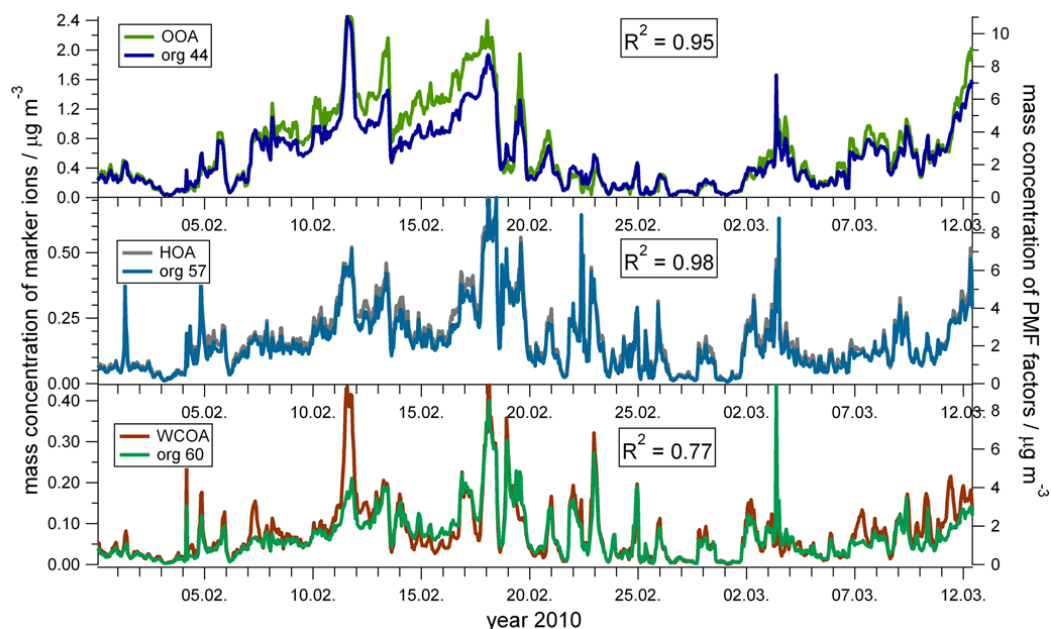


Fig. 3. Hourly averaged time series of WCOA (brown), HOA (grey) and OOA (green) PMF factors mass concentrations on the right axis correlated with hourly averaged mass concentrations of the marker ions m/z 60 (turquoise), m/z 57 (blue) and m/z 44 (light blue) from the AMS on the left axis.

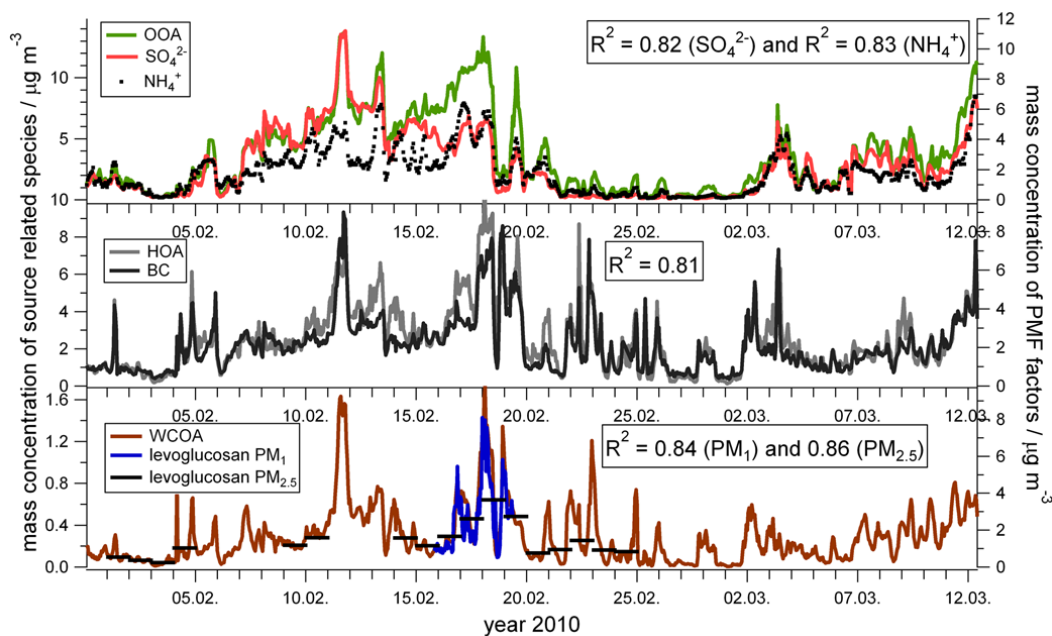


Fig. 4. Hourly averaged time series of OOA (green), HOA (grey) and WCOA (brown) PMF factors correlate with AMS sulphate (red), ammonium (black dots), $PM_{2.5}$ Aethalometer BC (black line) and hourly PM_1 (blue) and daily $PM_{2.5}$ (black line) levoglucosan GC-MS data.

that WC gas phase compounds (Hawthorne et al., 1989) could increase the SOA and the OOA production, respectively. During the warm and humid periods, HOA has a maximum contribution of around 60 % to the total organic matter.

Hence, freshly emitted aerosol has the largest influence in warm and rainy periods. The high content of HOA, compared to other studies, is probably due to the surroundings of the measurement site with the city circle motorway and some

main routes of the city being close by. The daily averaged contribution of WCOA, with about 20 % (range 10–30 %) to total OM mass, is quite constant during the whole campaign and shows no inverse correlation with the daily averaged temperatures. Nevertheless, diurnal variation of peak values can be observed, especially in the evening and at night, when regional domestic heating starts.

To support the interpretation of the PMF factors the time series of the marker ions m/z 44, 57 and 60 (Zhang et al., 2005; Aiken et al., 2009; Alfara et al., 2007) and the source associated species (SO_4^{2-} , NH_4^+ , BC and levoglucosan) were correlated with the factors time series and showed a correlation coefficient of $R^2 > 0.77$ (Figs. 3 and 4). The WCOA factor correlates well with the WC marker ion of m/z 60 ($R^2 = 0.77$, Fig. 3). The correlation of OOA with OOA marker ion m/z 44 is even higher ($R^2 = 0.95$). The main differences between the temporal variations of OOA and m/z 44 data are observed during the times when the HOA concentration is notably high. The HOA is highly correlated with the primary marker ion m/z 57 ($R^2 = 0.97$). Chirico et al. (2010) showed that aged diesel emissions contain high fractions of the oxygenated fragment of the m/z 57 signal which is produced by oxidative processes. However, the high correlation of m/z 57 and HOA found in our study is not surprising, because both main fragments which contribute to m/z 57, the oxygenated fragment ($\text{C}_3\text{H}_5\text{O}^+$) and the non-oxygenated fragment (C_4H_9^+), show a high correlation with HOA ($R^2 = 0.85$ and 0.88 , respectively). Additionally, the latter fragment contributes the most to the m/z 57 signal, which is approximately 47 %. It can also be seen that only the oxygenated fragment ($\text{C}_3\text{H}_5\text{O}^+$) provides good correlations ($R^2 = 0.80$ and 0.72) with WCOA and OOA, respectively.

A high correlation is found as well between the concentrations of the source-related species 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, the AMS sulphate data show a good correlation ($R^2 = 0.85$) with data from the sulphate monitor (Fig. SI-3.2). Primary aerosol mass HOA correlates well ($R^2 = 0.81$) with Aethalometer BC data. BC is mainly attributed to traffic and other combustion emissions like wood combustion (Sizdat et al., 2007). The WCOA factor is in good correlation ($R^2 = 0.84$) with the levoglucosan measurements from the hourly PM_{10} GC-MS filters and as well ($R^2 = 0.86$) with the levoglucosan measurements from the daily $\text{PM}_{2.5}$ GC-MS filters.

3.3 Wood combustion results

In Fig. 5, the diurnal variation of AMS levoglucosan equivalent concentration data is displayed as hourly averages of the whole campaign. The AMS levoglucosan equivalent concentration was calculated from the organic fraction of m/z 60

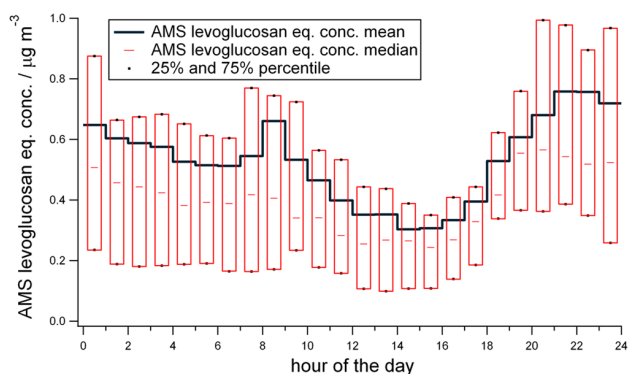


Fig. 5. Diurnal variation of AMS levoglucosan equivalent concentration displayed as a box plot during the whole campaign calculated from 14 285 data points.

by subtracting the organic background and multiplied by an instrument-specific levoglucosan standard factor (11.24 for our instrument) consisting of the ratio of m/z 60 to total organic signal from a levoglucosan standard mass spectrum (Aiken et al., 2009). The organic background has been found to be approximately 0.3 % of the total organic aerosol signal in several field campaigns, in periods and areas with absence of WC impacts (DeCarlo et al., 2008; Docherty et al., 2008). The calculation of the AMS levoglucosan equivalent concentration from the signal of m/z 60 is discussed in detail in Sect. 3.4. The WC contribution strongly increases during the evening period from 06:00 p.m. to 09:00 p.m. after the end of regular working time and rush hour, i.e. when people arrive at home and start domestic heating by wood combustion. During the night, the concentration remains approximately constant with a small decrease 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 a.m. to 10:00 a.m. with a maximum from 08:00 a.m. 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_{10} filters shows a similar profile, except for the high morning peak and some spikes due to the low number of GC-MS data points (Fig. SI-3.3). The AMS levoglucosan equivalent concentration to OM mass ratio indicates a longer emission period on the weekend from the morning hours until noon compared to working days, which is expected, considering the normal weekend activities where people are more likely to spend the morning at home.

The PMF factor diurnal variations are shown in Fig. 6. Similar to the AMS levoglucosan equivalent concentration

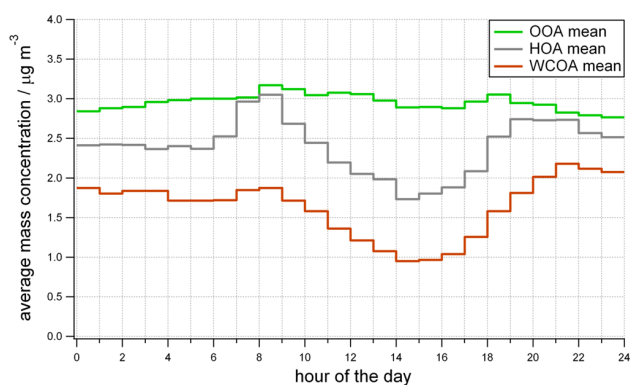


Fig. 6. Diurnal variation of the AMS PMF factor OOA (green), HOA (grey) and WCOA (brown) during the whole measurement period of the campaign.

variation, the WCOA variation shows a strong increase in the evening hours from 04:00 p.m. 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 OM 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 (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 largest fraction of the organic matter at any time and shows no distinctive maximum like the variations of HOA and WC.

For a discussion of the aerosol chemistry and the wood combustion impact on the aerosol the view of ratios are often considered, e.g. OM mass 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 OM to 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 wintertime. The OM to OC ratios for hydrocarbon-like and oxygenated organic aerosols have previously been 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 PM₁ levoglucosan analyzed by the GC-MS represents 3.4 % of the total OM 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 % at an urban background site in Zurich during January 2006. In our study the levoglucosan to OC

ratio amounts to 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 (range 0.03–0.9) provides a similar variation as the GC-MS levoglucosan variation (Fig. SI-3.3), only with stronger increases and decreases. Several studies (Puxbaum et al., 2007; Sullivan et al., 2008) pointed out that the fuel type used 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 of Grenoble (around 157 000 inhabitants), and higher than results obtained in Beijing (Zhang et al., 2008), where a major OC contribution may be related to traffic.

3.4 Correlation of AMS and one-hour PM₁ filter WC results

The wood combustion measurement data of the AMS are compared with hourly PM₁ filter GC-MS measurements of levoglucosan and additional anhydrosugars in this section. The signal of m/z 60 or rather the ion $C_2H_4O_2^+$ is the main marker of WCOA and is mainly formed from levoglucosan ($C_6H_{10}O_5$) (Alfarra et al., 2007; Aiken et al., 2009). During this Augsburg campaign the main contributor to the signal of m/z 60 in the ambient aerosol is the ion fragment $C_2H_4O_2^+$ (93 % of m/z 60). This is in agreement with results from 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 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 2.8 times higher than the levoglucosan concentration from the GC-MS measurements. Aiken et al. (2009) also found a higher factor of 3.2, thus an overestimation (offset) of the AMS levoglucosan equivalent concentration. The offset found in our study can be explained by other compounds that contribute to m/z 60 and raise the AMS levoglucosan equivalent concentration results. The other anhydrosugars like the WC compounds mannosan and galactosan contribute to m/z 60 as well; the GC-MS data additionally include these compounds to the levoglucosan concentration (Fig. 7a). This addition increases the levoglucosan concentration by approximately 10 %. The ratio of levoglucosan and mannosan is 11.4, which is close to the typical ratios for beech wood (14.8) and oak wood (14.2) combustion

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 WC in the emission studies and total OC in the ambient studies. The OC content in this study is calculated from the OM 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)
	softwood	0.04	
fire place	hardwood	0.076 to 0.334	Fine et al. (2004a)
	softwood	0.010 to 0.271	
wood stove	beech	0.08	Puxbaum et al. (2007)
	spruce	0.21	
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

(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, Lee et al. (2010) named the AMS levoglucosan equivalent concentration as AMS anhydrosugar equivalent concentration, which may be a more convenient expression and will be used in the following discussions. There must be other compounds co-emitted with the anhydrosugars sustaining the high correlation $R^2 = 0.84$. Various carboxylic acids are emitted from wood combustion (e.g. Fine et al., 2004b). 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., 2010). 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 long-chain carboxylic acids, e.g. fatty acids like dodecanoic acid and octadecanoic acid, as shown above. 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

on these acids. Dodecanoic acid, for example, shows high concentrations with an average of 60 ng m^{-3} . It is possible that not all of these compounds are completely covered by the subtracted background (0.3% of the total OM). 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 matches with the amount of subtracted organic background (0.3% of the total OM) from the m/z 60 signal of the calculation of the AMS levoglucosan equivalent concentration. Both show a correlation of their time series of $R^2 = 0.83$. The OOA contribution to the m/z 60 signal represents 70% of the organic background during the whole campaign, except in low PM concentration periods. Then the OOA roughly provides a value that is a factor of two lower 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 organic background is in a reasonable range for the SOA. Additionally, this discussion shows that beside levoglucosan as a main contributor other compounds are contributing to the signal of m/z 60, too. These compounds could come from WC (e.g. mannosan, galactosan or cellulose) or could be long-chain carboxylic acids (e.g. from food cooking, WC or SOA), which are not completely covered by the subtracted background.

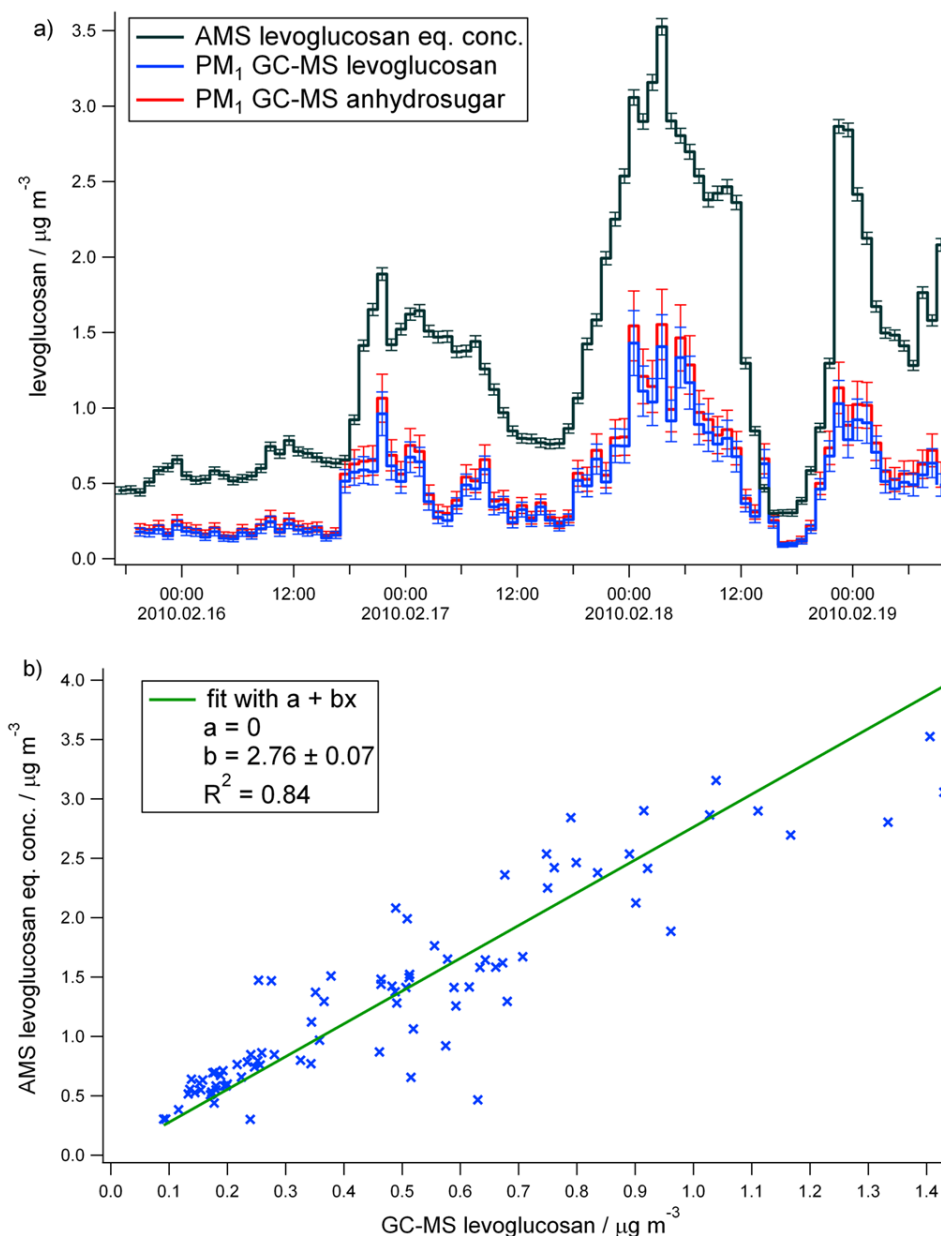


Fig. 7. (a) Time series of hourly mean AMS levoglucosan equivalent concentration (dark blue), PM₁ GC-MS levoglucosan (light blue) and sum of anhydrosugar (red) results in the week of 15 to 19 February. The error bars of the GC-MS data reflect the 15 % uncertainty associated with the method; the AMS levoglucosan equivalent concentration error bars were calculated with the SQUIRREL software for each species. (b) Scatter plot of hourly mean AMS levoglucosan equivalent concentration versus PM₁ GC-MS levoglucosan. Regression values are calculated with the orthogonal distance regression.

Similar to the diurnal variations, the time series of the PMF WCOA factor and the PM₁ GC-MS levoglucosan data show a high correlation of $R^2 = 0.84$ during the PM₁ filter sampling period (Fig. 8). The main disagreement occurs at the same time as for the AMS anhydrosugar equivalent concentration in the period from 03:00 a.m. to 06:00 a.m. on 17 February. Both 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 PM₁ filter period.

The slope between the WCOA and GC-MS levoglucosan is around 7 and is relatively low in comparison to other studies. A study of Lanz et al. (2008) estimated in Zurich in January 2006 a WCOA to GC-MS levoglucosan ratio of 12.5. Aiken et al. (2009) found a ratio of 16.3 in Mexico City; the WCOA derives here mainly from wild fires and

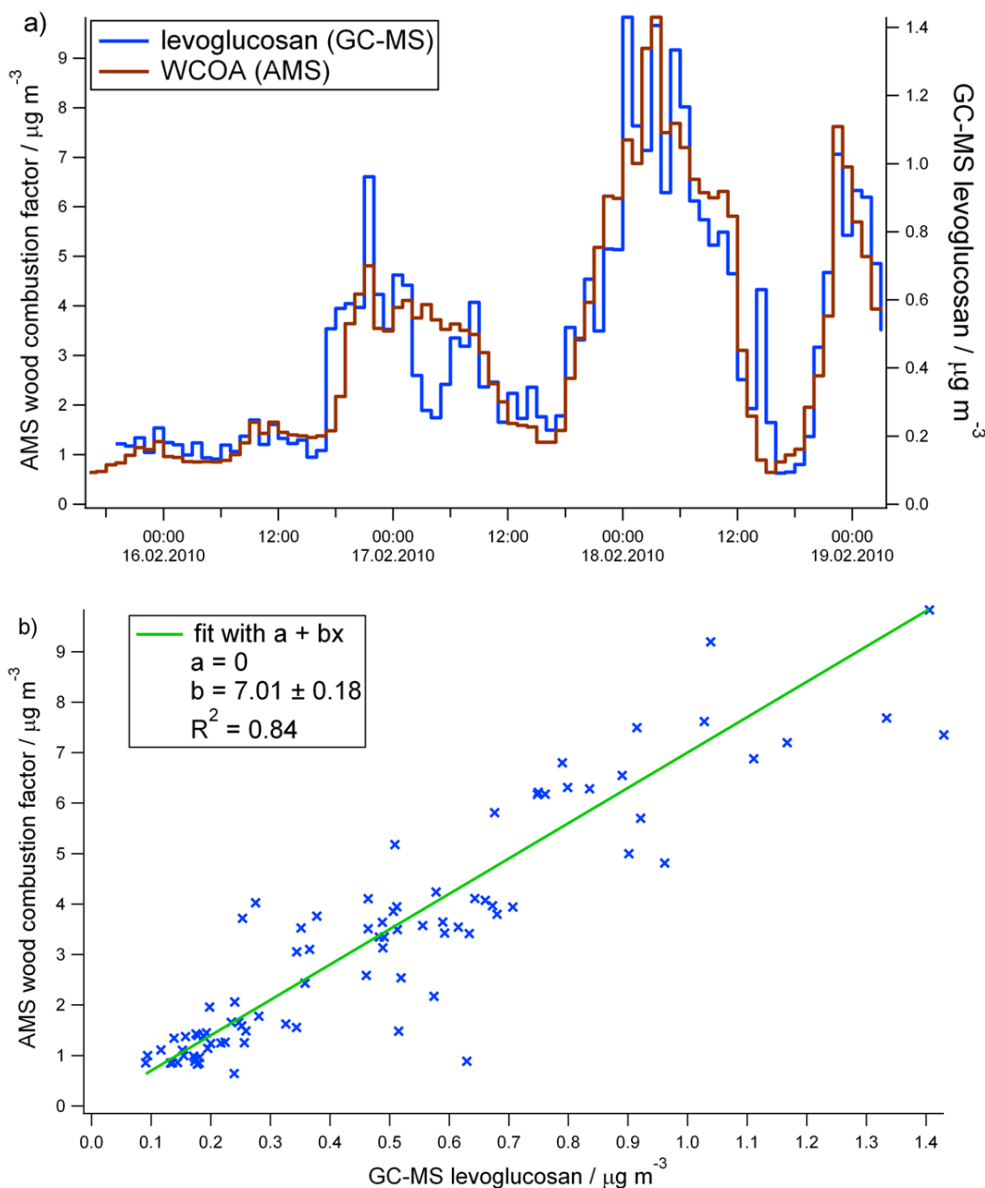


Fig. 8. (a) Time series of the hourly mean PMF WCOA factor (brown) and the hourly PM₁ GC-MS levoglucosan data (blue) during the week of 15 to 19 February. (b) Scatter plot of hourly mean PMF WCOA factor versus PM₁ GC-MS levoglucosan. Regression values are calculated with the orthogonal distance regression.

biomass burning. Similar to the levoglucosan to OC ratios as shown above in Sect. 3.3, the WCOA to levoglucosan ratio depends on the fuel type and the combustion conditions (e.g. Puxbaum et al., 2007; Hedberg et al., 2006).

Both estimations, the WCOA and the AMS anhydrosugar equivalent concentration, allow to observe variation with time of WC emission, with a good gradient correlation of $R^2 = 0.84$. However, the WCOA is more suitable for the quantitative observation (estimated magnitude) of WC emission than the AMS anhydrosugar equivalent concentration, due to the measured offset by the comparison with the GC-MS levoglucosan.

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 spectrometry methods. The first comparison of hourly PM₁ 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 organic matter with 35 % and nitrate with 28 % of the total mass measured by the AMS and Aethalometer in Augsburg during winter. This is typical for winter in Central Europe (Lanz et al., 2010). The organic aerosol fraction is based on three main sources found by PMF analysis, with the secondary process associated OOA as the largest contributor with 42 % and WCOA with 23 % as one of the main contributors. The influence of WC is particularly important for the aerosol composition with 28 % in the evening and the night hours, while the primary HOA emission factor is of higher concern during the morning rush hours. Here HOA contribution increases to 38 %. The levoglucosan to OC ratio on average amounts to 0.06 in this study and is comparable to other ambient WC observations.

The comparison of GC-MS levoglucosan measurements from the highly time resolved PM₁ filters with AMS data shows that either AMS WCOA or alternatively AMS levoglucosan equivalent concentration analysis have a high gradient correlation ($R^2 = 0.84$) and are therefore suitable for the observation of WC emission variation. Similar to Aiken et al. (2009), we found that the AMS levoglucosan equivalent concentration (AMS anhydrosugar equivalent concentration; Lee et al., 2010) is higher than the GC-MS levoglucosan concentration. Therefore, we argue that not only levoglucosan contributes to the WC marker ion at m/z 60 (HR fragment ion $C_2H_4O_2^+$). Additionally, other components from WC emissions, like mannosan or galactosan or, as shown in other studies, cellulose (Lee et al., 2010), could contribute to the signal of m/z 60. Different analyses 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 the m/z 60 signal. Therefore a quantitative estimation of the AMS anhydrosugar equivalent concentration is difficult. The analysis of the diurnal variation of the PMF factors appears to be important for the interpretation of the organic sources and their estimated magnitude, especially for WC. The PMF WCOA diurnal variation presents a similar profile as the hourly PM₁ GC-MS levoglucosan results.

Supplementary material related to this article is available online at: <http://www.atmos-chem-phys.net/12/6113/2012/acp-12-6113-2012-supplement.pdf>.

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