Organic aerosol source apportionment by offline-AMS over a full year in Marseille

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Abstract

We investigated the seasonal trends of OA sources affecting the air quality of Marseille (France) which is the largest harbor of the Mediterranean Sea. This was achieved by measurements of nebulized filter extracts using an aerosol mass spectrometer (offline-AMS). In total 216 $PM_{2.5}$ (particulate matter with an aerodynamic diameter <2.5 μm) filter samples were collected over 1 year from August 2011 to July 2012. These filters were used to create 54 composite samples which were analyzed by offline-AMS. The same samples were also analyzed for major water-soluble ions, metals, elemental and organic carbon (EC/OC), and organic markers, including n-alkanes, hopanes, polyaromatic hydrocarbons (PAHs), lignin

and cellulose pyrolysis products and nitrocatechols. The application of positive matrix factorization (PMF) to the water-soluble AMS spectra enabled the extraction of five factors, related to hydrocarbon-like OA (HOA), cooking OA (COA), biomass burning OA (BBOA), oxygenated OA (OOA), and an industry-related OA (INDOA). Seasonal trends and relative contributions of OA sources were compared with the source apportionment of OA spectra collected from the AMS field deployment at the same station but in different years and for shorter monitoring periods (February 2011 and July 2008). Online- and offline-AMS source apportionment revealed comparable seasonal contribution of the different OA sources. Results revealed that BBOA was the dominant source during winter representing on average 48% of the OA, while during summer the main OA component was OOA (63% of OA mass on average). HOA related to traffic emissions contributed on a yearly average 17% to the OA mass, while COA was a minor source contributing 4%. The contribution of INDOA was enhanced during winter (17% during winter and 11% during summer), consistent with an increased contribution from light alkanes, light PAHs (fluoranthene, pyrene, phenantrene) and selenium, which is commonly considered as an unique coal combustion and coke production marker. Online- and offline-AMS source apportionments revealed evolving levoglucosan:BBOA ratios, being higher during late autumn and March. A similar seasonality was observed in the ratios of cellulose combustion markers to lignin combustion markers, highlighting the contribution from cellulose rich biomass combustion, possibly related to agricultural activities.

1 Introduction

Outdoor particulate air pollution is estimated to be responsible for approximately 3.3 million premature deaths each year worldwide, and this number is projected to double by 2050 (Lelieveld et al., 2015). Organic aerosols (OA) can contribute up to 90% of the PM_1 (Jimenez et al., 2009), therefore understanding their main emission sources and formation processes is a key prerequisite for the development of appropriate mitigation policies.

In the Mediterranean basin, sources and trends of OA remain scarcely investigated, despite their deleterious impact in such a densely populated region. The Mediterranean region is characterized by an intense photochemistry during summer. Not surprisingly, the majority of the OA source apportionment studies conducted in the region using aerosol mass spectrometry (AMS) focused on the summer period (e.g., El Haddad et al., 2013; Minguillón

et al., 2011, 2016; Hildebrandt et al., 2011). Through positive matrix factorization (PMF) techniques, these studies revealed that during summer the oxygenated organic aerosol (OOA) fraction formed by oxidation of gaseous precursors, represented the largest part of OA. Amongst these studies, the field deployment of the AMS in Marseille, the largest port in the Mediterranean, has demonstrated that this instrument is well suited for quantifying the contribution of industrial emissions (El Haddad et al., 2013). In that work, the industrial OA factor was identified by the high correlation with heavy metals and AMS-polycyclic aromatic hydrocarbons (AMS-PAHs), moreover strong increments of the industrial factor concentrations were systematically observed when winds shifted to the west/south west, consistent with back-trajectory analysis highlighting the transport of industrial emissions from an industrial pole. Overall the industry-related OA contributed on average 7% of the bulk OA mass (El Haddad et al., 2011; 2013). However, these results were limited to 2 weeks of measurements during summer while the contribution of industrial emissions during the rest of the year remains unknown.

There is a general paucity of AMS and ACSM datasets in the Mediterranean region during winter. Exceptions include AMS campaigns (Mohr et al. 2012; Hildebrandt et al., 2011) covering a few weeks during late winter-early spring, and studies with an aerosol chemical speciation monitor (ACSM) (e.g., Minguillón et al., 2015, covering three weeks of monitoring). The measurement of organic markers and elements (e.g., Salameh et al., 2015; Reche et al., 2012) at different stations indicate a substantial contribution from biomass burning (BB). However, the sources and chemical composition of this fraction and its evolution during the year remain uncertain. Modelling results within the European Monitoring and Evaluation Programme (EMEP) have shown that the South of France, together with Portugal, can be a major hot spot in Europe for OA during February-March, possibly due to agricultural fires (Dernier van der Gon et al., 2015; Fountoukis et al., 2014). In this region, BBOA can derive from various processes such as agricultural land clearing activities, wildfires, and domestic heating, and therefore may have a variable chemical composition.

The current study capitalizes on the AMS measurements of offline samples collected over one year (2011-2012), in Marseille, an ideal environment for the characterization of urban emissions from biomass burning, traffic and industrial activities and their transformation under high photochemical activity. The source apportionment results obtained from PMF applied to the OA mass spectra are corroborated using a comprehensive set of offline

measurements including elemental and organic carbon (EC/OC) measurements, as well as measurements of elements by inductively coupled plasma mass spectrometry (ICP-MS), of molecular markers by gas chromatography mass spectrometry (GC-MS) and ultra-performance liquid chromatography mass spectrometry (UPLC-MS), and of major ions by ion chromatography (IC). We mainly focus on the sources and trends of winter OA and therefore we additionally analyzed an online AMS dataset acquired at the same location during the winter of the previous year. The comparison of online- and offline-AMS data, and organic marker concentrations enables an in-depth characterization of OA sources in Marseille, and in particular the identification of the main processes by which biomass smoke is emitted and transformed in this region.

2   Methods

2.1 Site description

Marseille is the second largest city in France with more than 1 million inhabitants (2010). It hosts the largest harbor in France and in the Mediterranean Sea. Many port-related industries, especially petrochemical companies, are located in a big cluster. These facilities are situated about 40 km NW from the city and include steel facilities, coke production plants, oil storing, refining plants, and several shipyards. The Marseille commercial harbor is located in the vicinity of this industrial cluster and represents the third-largest harbor of the world for crude oil storage and treatment. During summer, typical wind patterns in the city of Marseille favor the transport of polluted air masses from the industrial cluster to the city, including the sea breeze and the light Mistral wind from the Rhone valley. At night, the land breeze may transport air masses from an agricultural valley located east of the sampling site. A more detailed description of wind patterns in Marseille can be found in Drobinski et al. (2007) and Flaounas et al. (2009). The sampling location is classified as an urban background station and is situated in the urban park "Cinq Avenue" in a traffic-free zone near the city center (43°18'20'' N, 5°23'40''E; 64 m a.s.l.).

2.2 Yearly cycle dataset

Sample collection.

In total, 216 24-h (from midnight-to-midnight) integrated $PM_{2.5}$ pre-baked (500°C for 3 h) quartz fiber filters (150 mm diameter, Tissuquartz) were collected between 30 July 2011 and 20 July 2012 using a High-Volume sampler (Digitel DA80) operated at 500 L min^{-1} (Batch 1). Filter samples were subsequently wrapped in aluminum foil, sealed in polyethylene bags and stored at -18°C.

Offline-AMS analysis. This work discusses the offline-AMS analysis of 55 composite samples (created from the batch of 216 $PM_{2.5}$ filters collected) which were analyzed by Salameh et al. (*submitted*) for major ions, molecular markers and elements (Table S1). A thorough description of the offline-AMS analysis can be found in Daellenbach et al. (2016). One punch per filter sample (from 5 to 25 mm diameter depending on the filter loading and on the number of punches per composite sample) was prepared for analysis. Punches from the same composite sample were extracted together in 15 mL of ultrapure water (18.2 MΩ cm, total organic carbon < 5ppb, 25°C) in an ultrasonic bath for 20 min at 30°C. After extraction, filters were vortexed for 1 min, and the resulting liquids were filtered with 0.45 μm nylon membrane syringe filters.

The generated liquid extracts were atomized in air using a custom-made two-nozzle nebulizer. The generated aerosol was dried using a silica gel diffusion drier and then measured by a high resolution time-of-flight AMS (HR-ToF-AMS, running in V-mode). In the AMS, particles are flash vaporized (600°C) and the resulting gas is then ionized by electron impact (EI, 70eV), yielding quantitative mass spectra of the non-refractory submicron aerosol components, including OA, NO_3^-, SO_4^{2-}, NH_4^+, and Cl^-. A detailed description of the AMS operating principles, calibration protocols, and analysis procedures are provided by DeCarlo et al. (2006). In total about 10 mass spectra (mass range 12-300 Da, 60 sec averaging time) were collected per composite sample. Between each sample, a measurement blank was recorded via nebulization of ultra-pure water to minimize and monitor the possible memory effects of the system. In total five mass spectra were collected per each measurement blank. Offline-AMS data were processed and analyzed using the HR-ToF-AMS analysis software SQUIRREL (SeQUential Igor data RetRiEvaL) v.1.52L and PIKA (Peak Integration by Key Analysis) v.1.11L for IGOR Pro software package (Wavemetrics, Inc., Portland, OR, USA). HR

1 analysis of the mass spectra was performed in the mass range 12-115 Da and in total 217 ion

2 fragments were fitted.

3 The interference of NH_4NO_3 on the CO_2^+ signal was corrected according to Pieber et al.

4 (2016) as follows:

5 $$CO_{2,real} = CO_{2,meas} - \left(\frac{CO_{2,meas}}{NO_{3,meas}}\right)_{NH_4NO_3,pure} * NO_{3,meas}$$

6 (1)

7 where the $\left(\frac{CO_{2,meas}}{NO_{3,meas}}\right)_{NH_4NO_3,pure}$ correction factor was 2.5% as determined from aqueous

8 NH_4NO_3 measurements conducted regularly during the measurement period.

9 *Other offline measurements.* A complete list of the measurements performed can be found in

10 Table S1. To summarize, major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, oxalate,

11 malate, succinate, and malonate) were measured by ion chromatography (IC) according to the

12 methodology described by Jaffrezo et al. (1998). A subset of the filters was selected for CO_3^{2-}

13 quantification following the method described by Karanasiou et al. (2011). The method

14 encompasses the fumigation of the filter samples with HCl. The CO_2 evolved by this

15 acidification of the carbonates deposited on the filters is detected by thermal optical

16 transmittance determination. The CO_3^{2-} measurements agreed fairly well with the CO_3^{2-}

17 estimate from ion balance calculations based on IC data (Fig. S1). In the following discussion,

18 ion concentrations from filter samples always refer to the IC measurements unless otherwise

19 specified.

20 Elemental and organic carbon (EC and OC) were determined for each filter by thermal optical

21 transmittance using a Sunset Lab analyzer (Birch and Cary, 1996) following the EUSAAR2

22 protocol (Cavalli et al., 2010). The CO_3^{2-} concentration determined from the IC ion balance

23 was then subtracted from OC concentration. The water soluble OC (WSOC) was measured

24 with a total organic carbon analyzer (TOC) following the methodology described in Bozzetti

25 et al. (2016a) and references therein. Before the analyses, the liquid extracts were treated with

26 a 2 M HCl solution for 1-30 min to remove the inorganic C fraction. Total nitrogen (TN) was

27 determined using a TOC analyzer combustion tube. The NO_2 generated from the water

28 soluble (WS) N decomposition was detected by a chemiluminescence TNM-1 unit detector.

29 Organic markers were measured via GC-MS analysis, following the methodology described

30 in El Haddad et al. (2009; 2011), Favez et al. (2010) and Piot et al. (2012). In total 15

31 different polycyclic aromatic hydrocarbons (PAH), 19 alkanes (C19-C36), 8 hopanes, 5

phtalate esters, levoglucosan, 6 lignin pyrolysis compounds, 6 fatty acids, and 3 sterols were determined (Table S1). 33 chemical elements (Table S1) were quantified using ICP-MS according to the procedure described in Chauvel et al. (2010) and the modifications suggested in El Haddad et al. (2011). A subset of 20 composite samples was selected for the quantification of methyl-nitrocatechol isomers (Table S1) via Ultra Performance Liquid Chromatography coupled with an Electro Spray Ionization – ToF - MS (UPLC-ESI-ToF-MS), following the procedure described in Iinuma et al. (2010).

2.3 Intensive winter campaign

A HR-ToF-AMS was deployed at the same station (urban park "Cinq Avenue") between 25 January 2011 and 2 March 2011 to monitor the real-time NR-PM$_1$ aerosol chemical composition. Although February 2011 is not included in the sampling period covered by offline-AMS, these online measurements nonetheless provide a good opportunity to compare the separation, relative contributions and winter seasonal trends of the OA sources retrieved by the offline- and online-AMS source apportionment procedures. Summer offline-AMS results were instead compared with online-AMS source apportionment results reported by El Haddad et al. (2013). The AMS was operated with an averaging time of 8 minutes, and in total 5633 mass spectra were collected during the monitoring period. We performed an ionization efficiency (IE) calibration by NH$_4$NO$_3$ nebulization, and the resulting IE value of $1.76 \cdot 10^{-7}$ was applied to the dataset. The standard relative ionization (RIE) efficiency was assumed for organics (1.4), SO$_4^{2-}$ (1.2), NH$_4^+$ (4) and Cl$^-$ (1.3), while the collection efficiency (CE) was estimated using the composition dependent collection efficiency model (Middlebrook et al., 2012). Total AMS-PAHs were estimated from AMS data according to Dzepina et al. (2007).

Similarly to offline-AMS, online-AMS data were also processed and analyzed using HR-ToF-AMS Analysis software SQUIRREL (SeQUential Igor data RetRiEvaL) v.1.52L and PIKA (Peak Integration by Key Analysis) v.1.11L for IGOR Pro software package (Wavemetrics, Inc., Portland, OR, USA). HR analysis of the mass spectra was performed in the mass range 12-115 Da and in total 215 ion fragments were fitted.

A NO$_x$ analyzer was run in parallel to the AMS to monitor the real-time NO$_x$ concentration. A set of pre-baked (500°C for 3h) 24-h integrated PM$_{2.5}$ filter samples was also collected during this campaign (Batch 2) following the same sampling and storage procedure described in

1 Section 2.2. Filters were analyzed for major ions, metals, elemental and organic carbon

2 (EC/OC), and organic markers, including n-alkanes, hopanes, polyaromatic hydrocarbons

3 (PAHs), lignin and cellulose pyrolysis products using the techniques previously described in

4 Section 2.2 (Table S1).

6 Table 1. Monitoring periods.

Online-AMS	Offline-AMS
28 January 2011 – 02 March 2011	30 July 2011 – 20 July 2012

8 **2.4 Source apportionment**

9 *Implementation.* The online- and offline-AMS source apportionment results discussed in this

10 work were obtained from PMF analysis (Paatero and Tapper, 1994) of AMS spectra using the

11 Multilinear Engine (ME-2, Paatero 1999). The Source Finder toolkit (SoFi, Canonaco et al.,

12 2013, v.5.1) for Igor Pro (Wavemetrics, Inc., Portland, OR, USA) served as interface for data

13 input and results evaluation. PMF is a multilinear statistical tool used to describe the

14 variability of a multivariate dataset as the linear combination of static factor profiles times

15 their corresponding time series, as described in Eq. 2:

16 $\qquad x_{i,j} = \sum_{z=1}^{p} g_{i,z} \cdot f_{z,j} + e_{i,j}$ (2)

17 Here $x_{i,j}$, $g_{i,z}$, $f_{z,j}$, and $e_{i,j}$ represent respectively elements of the data matrix, factor time series

18 matrix, factor profile matrix and residual matrix, while subscripts i,j and z denote time

19 elements, variables (in our case AMS fragments), and discrete factor numbers, respectively. p

20 represents the total number of factors selected by the user for current given PMF solution. The

21 PMF algorithm returns only $g_{i,z}$ and $f_{z,j}$ values ≥ 0, and solves Eq. 2 by minimizing the object

22 function Q, defined as:

23 $\qquad Q = \sum_{i} \sum_{j} \left(\frac{e_{i,j}}{s_{i,j}} \right)^2$ (3)

1   Here $s_{i,j}$ is an element of the error input matrix. PMF is subject to rotational ambiguity, i.e.

2   different $\mathbf{G} \cdot \mathbf{F}$ combinations characterized by the same Q can exist. The ME-2 implementation

3   of the PMF algorithm offers an efficient exploration of the solution space by directing the

4   solution toward environmentally-meaningful rotations by constraining the factor profile

5   elements $f_{z,j}$ for one or more z factors. In the a-value implementation of ME-2, the elements of

6   the factor profile matrix $\mathbf{F}$ (in our case AMS fragments) are forced to predefined values $f_{z,j}$

7   allowing a certain variability defined by the a-value, such that the modelled element $f_{z,j}'$

8   satisfies Eq. 4:

9    $$\frac{(1-a)f_{z,n}}{(1+a)f_{z,m}} \leq \frac{f_{z,n'}}{f_{z,m'}} \leq \frac{(1+a)f_{z,n}}{(1-a)f_{z,m}} \tag{4}$$

10   where n and m represent any two arbitrary variables in the normalized $\mathbf{F}$ matrix. A complete

11   description of the a-value approach can be found elsewhere (Canonaco et al., 2013).

12   For the offline–AMS source apportionment, the PMF input data matrix was constructed as

13   follows: each composite sample is represented by approximately 10 time points i,

14   corresponding to the ~10 mass spectra collected per filter sample (section 2.4). Each point of

15   the data matrix is subtracted by the average corresponding measurement blank.

16   The error matrices were instead constructed as follows. For online-AMS source

17   apportionment, the error matrix elements $s_{i,j}$ were calculated according to Allan et al. (2003)

18   and Ulbrich et al. (2009), and included the uncertainty deriving from electronic noise, ion-to-

19   ion variability at the detector, and ion counting statistics. $s_{i,j}$ included also a minimum error

20   which was applied according to Ulbrich et al. (2009). For the offline-AMS source

21   apportionment, the error term $\delta_{i,j}$ was calculated in the same way, but a further term ($\sigma_{i,j}$)

22   including the blank subtraction uncertainty was propagated according to Eq. 5:

23   $$s_{i,j} = \sqrt{\delta_{i,j}^2 + \sigma_{i,j}^2} \tag{5}$$

24   Finally for both online- and offline-AMS we applied a down-weighting factor of 3 to all

25   variables with an average signal to an average error ratio lower than 2 (Ulbrich et al., 2009).

26   No variable with an average signal to error value lower than 0.2 was detected.

27   Dust and ash can contain significant amount of inorganic CO_3^{2-}. Both the IC balance and the

28   CO_3^{2-} measurements revealed non-negligible contributions from CO_3^{2-} in the $PM_{2.5}$ fraction

29   (Fig. S1). Preliminary PMF results also resolved a factor correlating with Ca^{2+} (SI) which was

30   characterized by high fCO_2^+, suggesting a possible solubilisation of CO_3^{2-} from dust which

could affect the OA mass spectral fingerprint. Overall, as discussed in the SI, we could not achieve a clear inorganic dust separation using PMF, therefore we opted for a correction of the PMF input matrices. The measured pH of our filter extracts was never >8, therefore we can exclude the presence of CO_3^{2-} in the extracts, but rather assume all solubilized CO_3^{2-} to exist as HCO_3^-. Direct measurements of nebulized standard $NaHCO_3$ aqueous solutions, revealed that thermal decomposition of HCO_3^- on the AMS vaporizer (600°C) releases CO_2 (Fig. S2). Currently no HCO_3^- correction for the OA spectra is implemented in the standard AMS fragmentation table (Aiken et al., 2008), therefore the measured CO_2^+ signal needs to be subtracted from the OA AMS spectra. Offline-AMS PMF input matrices were corrected for HCO_3^- and rescaled for $WSOM_i$ (= $WSOC_{TOC}\cdot(OM:OC)_{\text{offline-AMS}})_i$ according to the procedure described in the Supplementary information, SI.

Online-AMS source apportionment optimization. In the following we describe the optimization of the online-AMS source apportionment results. In order to optimize the source separation we performed sensitivity analyses on PMF solutions. We adopted different optimization strategies for online- and offline-AMS source apportionments (SI) as we encountered dissimilar mixings between sources. This is not surprising as the two methods are characterized by different time resolution and different monitoring time extension (1 year for offline-AMS, 1 month for online-AMS), which in turn result in different variabilities apportioned by the PMF algorithm (daily for online-AMS *vs.* seasonal for offline-AMS).

In order to optimize the source separation, we performed sensitivity analyses on PMF solutions according to the following scheme:

I) Selection of the number of factors based on residual analysis.

II) Qualitative evaluation of the unconstrained PMF solution in comparison with the constrained PMF solutions (*a*-value approach: COA and/or HOA constraints)

III) Constrain of both the HOA and COA factors profiles adopting an *a*-value approach. *a*-value sensitivity analysis (121 PMF runs performed scanning all the COA and HOA *a*-value combinations, a-value scanning steps: 0.1).

IV) Classification of the 121 PMF runs based on the cluster analysis of the COA diurnal cycles. Selection of the best clusters, and corresponding PMF solutions.

V) PMF rotational ambiguity exploration. 100 bootstrap (Davison and Hinkley, 1997; Brown et al., 2015) PMF runs were performed by simultaneously

1   varying the COA and HOA *a*-value combinations (using only the optimal *a*-

2   value combinations identified from step IV). The average of the 100 bootstrap

3   runs represented the online-AMS source apportionment average solution. The

4   corresponding standard deviation represents the source apportionment

5   uncertainty.

6   For online-AMS we selected a 4-factor solution based on residual analysis. We investigated

7   the time dependent $Q(t)/Q_{exp}(t)$ evolution when increasing the number of factors. Q/Q_{exp} is

8   defined as the ratio between Q (as defined in Eq. 3) and the remaining degrees of freedom of

9   the model solution (Q_{exp}) calculated as $i \cdot j - (j+i)p$ (Canonaco et al., 2013). A decrease of the

10   Q/Q_{exp}, from lower to higher order solutions indicates an improvement in the variation

11   explained by the model. In particular we calculated the $\Delta(Q/Q_{exp}(t))$ obtained as the difference

12   between the $Q/Q_{exp}(t)$ for a (*z*)–factor solution minus the $Q/Q_{exp}(t)$ value obtained from the (*z*-

13   1)–factor solutions, where *z* indicates the number of factors. We observed a large reduction of

14   $\Delta(Q/Q_{exp}(t))$ until 4 factors (Fig. S4). Higher order solutions provided only minor

15   contributions to the explained variability and in terms of solution interpretability resulted in a

16   splitting of primary sources which could not be unambiguously associated to specific aerosol

17   sources or processes.

18   Using an *a*-value approach, we constrained HOA and COA profiles from Mohr et al. (2012)

19   and Crippa et al. (2013b) respectively. Leaving COA and/or HOA unconstrained enabled

20   resolving COA only by increasing the number of factors (>5 factor solutions) while in the 4

21   factor solutions we observed a splitting of an OOA factor which could not be attributed to

22   specific processes. Unconstrained PMF yielded HOA and COA time series well correlating

23   with the constrained solutions; however in the unconstrained case, HOA and COA factor

24   profiles showed higher fCO_2^+ in comparison with literature studies (Crippa et al., 2013b;

25   Mohr et al., 2012; Bruns et al., 2015; Docherty et al., 2011; Setyan et al., 2012; He et al.,

26   2010,) and in comparison with the constrained PMF runs. This in turn resulted in higher HOA

27   and COA concentrations, with background night concentrations 2-3 times higher than in the

28   constrained solutions, possibly indicative of mixings with oxidized aerosols (Fig. S5). Similar

29   differences between constrained and unconstrained PMF runs were also observed in Elser et

30   al. (2016). Also the HOA:NO_x ratio ($\mu g\ m^{-3}/\mu g\ m^{-3}$) matched typical literature values reported

31   for France (0.02 Favez et al., 2010) in the constrained PMF case (0.023), while for the

32   unconstrained approach it showed higher values (0.033).

1   For both offline- and online-AMS the constrained HOA profiles were from Mohr et al.

2   (2012), while the COA profiles were from Crippa et al. (2013b). The HOA profile from Mohr

3   et al. (2012) was selected for offline-AMS consistently with Daellenbach et al. (2016), since

4   the same factor recovery distributions were applied in this work. The same profile was

5   applied to online-AMS for consistency. Overall, as discussed in the SI, the HOA profiles from

6   literature showed high cosine similarities with each other, indicating that the AMS mass

7   spectral fingerprints from traffic exhaust are relatively stable from station to station and

8   consistent also with direct emission studies, making the selection of the constrained factor

9   profiles not crucial. More variability instead is observed among COA literature profiles. For

10   COA we selected the profile from Crippa et al. (2013b) which showed the lowest $fC_2H_4O_2^+$

11   value among the considered ambient literature spectra (Crippa et al., 2013b; Mohr et al.,

12   2012). This guaranteed a better separation of COA from BBOA, as $C_2H_4O_2^+$ is strongly

13   related to levoglucosan fragmentation (Alfarra et al., 2007).

14   An a-value sensitivity analysis was performed by scanning all possible a-value combinations

15   for HOA and COA given by an a-value range 0-1 with a step size of 0.1. In order to optimize

16   the source apportionment results, we retained only the PMF solutions satisfying an acceptance

17   criterion described hereafter.

18   PMF factors were associated to specific aerosol emissions/processes based on mass spectral

19   features, diurnal cycles, and time series correlations with tracers. The identified factors were

20   associated to traffic (HOA), cooking (COA), biomass burning (BBOA), and oxygenated

21   organic aerosol (OOA). A thorough interpretation of the PMF factors will be discussed in the

22   Results section. Given the absence of widely accepted tracers for COA emissions, the

23   optimization of the COA contributions was based on the analysis of the COA diurnal cycles.

24   From the HOA and COA a-value sensitivity analysis we obtained a set of 121 PMF solutions

25   each one including both factor profiles and factor time series. PMF solutions obtained in this

26   way were categorized according to a cluster analysis of the normalized COA diurnal cycles

27   (Elser et al. 2016 and references therein). The k-means clustering approach enables

28   classifying the PMF solutions into k clusters, by minimizing a cost function (C):

29   $C=\Sigma_{i,z}((x_i-\mu_{z,i})^2)$ (6)

30   where C represents the sum of the Euclidian distances between each observation (x_i) and its

31   respective cluster centre (μ_{zi}), according to Eq. 6.

32   The number of clusters (k) that best represents the data is a critical choice in order to

33   perform a proper cluster analysis. The addition of a cluster ($k+1$) on one hand adds

complexity to the solution, while on the other hand decreases the cost function. A typical strategy to select the right number of clusters is to explicitly penalize the addition of new clusters by using Bayesian information criteria. This approach consists in adding a penalty term to Eq. 6 proportional to the number of clusters (k):

$$C\text{'} = \Sigma_{i,z}((x_i - \mu_{z,i})^2) + k \cdot ln(D) \tag{7}$$

where D denotes the dimensionality of the clusters (24 in our case, as we consider diurnal cycles with hourly time resolution). In this study the $C\text{'}$ function showed the minimum at 5 clusters (Fig. S6). The absence of convexity properties (i.e. several local minima can exist and the solution strongly depends on the initialization) represents a possible drawback of the k-means algorithm, therefore 100 random initializations of the k-means algorithm were conducted.

The best clusters are selected based on a novel statistical analysis of the HOA, COA and BBOA average cluster spectra (SI). Briefly, a cluster was retained if the HOA, COA, and BBOA average cluster spectra were not statistically different from the average reference HOA, COA, and BBOA spectra from literature (Crippa et al., 2013b; Mohr et al., 2012; Bruns et al., 2015; Docherty et al., 2011; Setyan et al., 2012; He et al., 2010, Table S3). A complete description of the best clusters selection is reported in the SI (Figs. S6-S10). Overall, three clusters were retained and 2 were rejected. Finally, we retained only the PMF solutions that were attributed to the 3 best clusters in more than 95% of the k-means random initializations (Fig. S9).

In order to explore the rotational ambiguity of our PMF model we performed 200 PMF runs by initiating the PMF algorithm using different input matrices. The 200 different input matrices were generated using a bootstrap approach (Davison and Hinkley, 1997; Brown et al., 2015). In short, the bootstrap approach creates new input matrices by randomly resampling mass spectra (i elements) from the original input matrices. Note that some mass spectra are resampled multiple times, while others are not represented at all. On average we randomly resampled 63±1% of the original spectra per bootstrap PMF run. Finally, each bootstrap PMF run was initiated by randomly varying the HOA and COA a-values using the {a-value HOA; a-value COA} combinations previously selected as optimal from the cluster analysis (Fig. S10). Only solutions showing a higher COA diurnal correlation with the three selected clusters than with the two rejected clusters were retained. In this way we rejected 3.7% of the solutions. In the following we present the average bootstrap solution. The source apportionment uncertainty is calculated as the variability of the retained bootstrap PMF runs.

Offline-AMS source apportionment optimization.

3   In this section we discuss the optimization of the offline-AMS source apportionment. The
4   PMF input matrices included 217 ions and 538 time elements deriving from about 10 AMS
5   mass spectral repetitions collected for each of the 54 composite samples.

6   In order to optimize the source separation, we performed sensitivity analyses on PMF
7   solutions according to the following scheme:

8   I)   Selection of the number of factors based on residual analysis.

9   II)   Qualitative evaluation of the unconstrained PMF solution in comparison with
10   the constrained PMF solutions (*a*-value approach: COA and/or HOA
11   constraints)

12   III) PMF rotational ambiguity exploration. 1080 bootstrap (Davison and Hinkley,
13   1997; Brown et al., 2015) PMF runs were performed by simultaneously
14   varying the COA and HOA *a*-value combinations. PMF solutions were
15   retained based on the correlation of the PMF factors with external tracers. The
16   PMF solutions retrieved from this step are relative to the water-soluble
17   fraction. The corresponding water-soluble OC factor concentrations were
18   determined by dividing the water-soluble OM factor concentrations (PMF
19   output) by the OM:OC ratio determined from the corresponding factor mass
20   spectrum.

21   IV)   Retained water-soluble OC PMF solutions from step (III) were rescaled to the
22   total OC concentrations by applying factor recoveries. Factor recoveries were
23   fitted (using *a*-priori information) to match total OC. Only PMF solutions and
24   factor recoveries fitting OC with yearly and seasonally homogenous residuals
25   were retained. The average of the retained PMF solutions represented the
26   average source apportionment results. The corresponding standard deviation
27   represented the source apportionment uncertainty.

28   Based on analysis of the PMF residuals, we selected a 5-factor solution to explain the
29   variability of our dataset (Fig. S11). Similar to online-AMS, we monitored the decrease in
30   Q/Q_{exp} when increasing the number of factors (z). In this study, a large Q/Q_{exp} decrease was
31   observed until 5 factors. We also observed a clear $\Delta Q/Q_{exp}$ structure removal until 5 factors,
32   with higher order solutions leading to additional factors that were not attributable to specific

1   aerosol sources/processes. The 5 separated factors included HOA, COA, BBOA, OOA, and

2   industry-related OA (INDOA). The complete validation of the PMF factors will be discussed

3   in the Results section.

4   As already mentioned, the HOA and COA profiles were constrained using an *a*-value

5   approach. Consistently with online-AMS we constrained the profiles according to Mohr et al.

6   (2012) and Crippa et al. (2013b) respectively. Unconstrained PMF runs for offline-AMS did

7   not resolve HOA and COA factors. To explore the rotational ambiguity of our PMF model we

8   performed 1080 bootstrapped PMF runs. In this case we performed a higher number of

9   bootstrap runs than online-AMS because the COA and HOA *a*-value combinations could not

10   be separately optimized because the offline-AMS method cannot resolve diurnal patterns.

11   Each PMF run was also initiated using different input matrices. As previously mentioned the

12   input matrices contained about 10 mass spectral repetitions per filter sample, therefore the

13   bootstrap algorithm was implemented to randomly resample 54 filters samples, each one with

14   all the corresponding mass spectral repetitions. The final generated matrices included 54

15   samples; note that some filter samples could be resampled more times, while others were not

16   resampled at all. On average $63\pm5\%$ of the original samples were resampled. Finally, each of

17   the PMF runs was initiated by randomly varying the HOA and COA *a*-values. The optimal

18   PMF solutions were selected based on 6 acceptance criteria including:

19   1) Significantly ($p=0.05$) positive Pearson correlation coefficient R between BBOA and
20   levoglucosan.

21   2) Significantly positive R between HOA and NO_x.

22   3) Significantly positive R between INDOA and Se.

23   4) BBOA correlation with levoglucosan (R) significantly higher than the correlation
24   between COA and levoglucosan.

25   5) HOA correlation with NO_x significantly higher than the correlation between COA and
26   NO_x.

27   6) COA correlation with Se significantly smaller than the correlation between INDOA
28   and Se.

29   Criteria 1-3 analyse the correlation between factor and marker time series. The significance of

30   a correlation was determined by calculating the Fisher transformed correlation coefficient z

31   (Garcia, 2011):

1 $$z = 0.5 * \ln\left(\frac{1+R}{1-R}\right) = \arctan(R) \tag{8}$$

2 where R is the Pearson correlation coefficient between factor and marker time series.

3 Subsequently we conducted a *t*-test to verify the significance (α=0.95) of the correlation:

4 $$t = \frac{R}{\sqrt{\frac{1-R^2}{N-2}}} \tag{9}$$

5 Here, N represents the number of samples (54). For a confidence interval of 95% the

6 minimum significant correlation was $R = 0.23$. For criteria 4-6, in order to evaluate whether

7 HOA, BBOA and INDOA correlated significantly better than COA with their corresponding

8 markers, we compared the z values obtained between each factor and its corresponding tracer

9 (e.g. BBOA and levoglucosan) and between COA and the same tracer (e.g. levoglucosan),

10 using a standard error on the z distribution of $1/\sqrt{N-3}$ (Zar, 1999).

11 In total, we retained 1.5% of the PMF runs. The criteria that discarded the largest number of

12 solutions were the ones based on COA (4-6) correlation with tracers of other sources. This

13 suggests that for this dataset the COA separation from other sources was particularly difficult

14 due to the absence of high temporal resolved data which aids the separation of a distinct COA

15 diurnal cycle. Moreover, this separation is also complicated by the small COA contribution

16 estimated by both online- and offline-AMS source apportionments (on average 0.4 µg m^{-3} as

17 discussed in the following sections). Furthermore, the relatively small COA factor recovery

18 (R_{COA} median 0.54) hampers the COA apportionment by offline-AMS.

19 The PMF performed on offline-AMS mass spectra returned water-soluble OA factor

20 concentrations, W$SKOA_i$. To rescale the water-soluble OA concentration to the total OA,

21 KOA_i, we used the factor recoveries (R_k) reported by Daellenbach et al. (2016) for the HOA,

22 COA, BBOA, and OOA factors (R_{HOA}, R_{COA}, R_{BBOA}, R_{OOA}).

23 $$KOA_i = WSKOA_i/R_{KOA} \tag{10}$$

24 This is the first offline-AMS study where an INDOA factor was identified. Therefore, we

25 determined the INDOA recovery (R_{INDOA}) in this study, by performing a single parameter fit

26 according to Eq. 11:

27 $$OC_i = \frac{WSHOA_i}{\frac{OM}{OC}_{HOA} \cdot R_{HOA}} + \frac{WSCOA_i}{\frac{OM}{OC}_{COA} \cdot R_{COA}} + \frac{WSBBOA_i}{\frac{OM}{OC}_{BBOA} \cdot R_{BBOA}} + \frac{WSOOA_i}{\frac{OM}{OC}_{OOA} \cdot R_{OOA}} + \frac{WSINDOA_i}{\frac{OM}{OC}_{INDOA} \cdot R_{INDOA}} \tag{11}$$

1 500 different fits were performed for each of the retained PMF solutions. Moreover each fit

2 was initiated using different R_{KOA} combinations randomly selected from the R_{KOA}

3 combinations determined by Daellenbach et al. (2016) and reported in Bozzetti et al. (2016a).

4 In order to account for possible WSOC and OC systematic measurement biases, each fit was

5 initiated by also perturbing the OC_i, $WSKOA_i/(OM:OC)_{WSKOC}$, and R_{KOA} inputs assuming for

6 each parameter a possible bias of 5%, corresponding to the WSOC and OC measurement

7 accuracy (we note that the sum of the $WSKOC_i/(OM:OC)_{WSKOC}$ terms equals $WSOC_i$ neglecting the

8 PMF residuals). Finally the input OC_i was randomly perturbed within its measurement

9 uncertainty assuming a normal distribution of the errors. Among the performed fits we

10 retained the recovery combinations and factor time series associated with OC_i unbiased

11 residuals (residual distribution centered on 0 within the 1st and 3rd quartiles) for all seasons

12 together and for summer and winter separately (Fig. S12). Accordingly, we retained 13% of

13 the solutions. All the retained factor recovery combinations can be found at

14 http://doi.org/10.5905/ethz-1007-75. The median INDOA recoveries were estimated as 0.69

15 (1st quartile 0.65, 3rd quartile 0.73, Fig. S13), while the retained R_{KOA} for the other sources

16 were consistent within the quartiles with the R_{KOA} values reported by Daellenbach et al.

17 (2016) despite their input value was perturbed as described above. The variability of the

18 retained solutions is considered as our best estimate of the source apportionment uncertainty,

19 which accounts for offline-AMS repeatability, model rotational uncertainty explored

20 bootstrapping the input matrices and scanning the HOA and COA a-value sensitivity, and

21 R_{KOA} uncertainties. Overall, for a generic factor KOA, we estimated the corresponding

22 average relative uncertainty as follows: we calculated the campaign averages of the KOA

23 concentrations for each of the v retained PMF solutions ($\overline{KOA_v}$). The relative uncertainty of

24 the KOA concentration was calculated as the standard deviation of $\overline{KOA_v}$ divided by its

25 average.

26 We also explored a 4-factor solution without constraining the COA profile. In this case we

27 performed 100 bootstrap PMF runs by randomly varying the HOA a-value. Results revealed

28 the COA separation (in the 5-factor solution with COA constrained) affected the HOA

29 separation more than the other factors (BBOA, OOA, INDOA). Overall, when comparing the

30 4- and 5-factor solutions (without and with COA constrained, respectively) HOA showed not

31 statistically different concentrations within our estimated source apportionment uncertainty

32 for 85% of the samples, BBOA and OOA for 96%, and INDOA for 94%. This is probably due

1 to the high similarity between COA and HOA spectra (SI, "Best cluster selection" Section),

2 which are both characterized by high contributions from hydrocarbons.

4 **3   Source apportionment validation**

5 Figure 1 displays the stacked seasonal average concentrations of the measured $PM_{2.5}$

6 components (ions measured by IC, elements measured by ICP-MS, EC by the EUSAAR

7 method, and OM estimated as the sum of the offline-AMS PMF factors). Higher

8 concentrations were observed during winter than in summer due to the enhanced contributions

9 of NO_3^- and OM. NO_3^- increased during winter and autumn due to NH_4NO_3 partitioning into

10 the particle phase at lower temperatures. OM concentrations were higher during winter due to

11 the strong BBOA contributions.

12 Overall OM was the dominant $PM_{2.5}$ component over the whole year highlighting the

13 importance of studying its sources. OM represented 46% of the total mass with higher relative

14 contributions during winter (51%) than in summer (37%). SO_4^{2-} represented the second most

15 abundant $PM_{2.5}$ component, contributing on average 12% of the mass. Among the other

16 components, EC contributed 9% of the mass, NO_3^- 9% ($13\%_{avg}$ during winter and $3\%_{avg}$

17 during summer), NH_4^+ 8%, the sum of the elements 7% (3% during winter and 13% during

18 summer, possibly because of dust resuspension), CO_3^{2-} 6%, Ca^{2+} 2%. K^+, Cl^-, Na^+, and Mg^{2+}

19 individually did not exceed 1% of the mass. In the following, subscripts *avg*, and *med* denote

20 average and median values, respectively.

21 **3.1 Online-AMS source apportionment validation**

22 PMF factors were associated to aerosol sources/processes based on mass spectral features

23 (Fig. 2), correlation with tracers (Fig. 3), and diurnal cycles (Fig. 4). The HOA was well-

24 correlated with NO_x (*R*=0.86), with peaks during rush hours (centered on 8h and 19h) and

25 higher concentrations during the first half of the campaign. The average HOA:NO_x ratio (μg

26 m^{-3}/μg m^{-3}) was 0.023, consistent with Favez et al. (2010). The COA diurnal variation showed

27 two peaks at lunch and dinner time (12.00 and 21.00), as observed in other cities (Elser et al.,

28 2016; Mohr et al., 2012). The BBOA factor profile showed the highest fC$_2$H$_4$O$_2^+$ and

29 fC$_3$H$_5$O$_2^+$ contributions among the apportioned factors. Previous studies (Alfarra et al., 2007)

30 associated the high fC$_2$H$_4$O$_2^+$ and fC$_3$H$_5$O$_2^+$ contributions in BBOA AMS spectra to the

31 fragmentation of anhydrous sugars from cellulose pyrolysis. The BBOA time series was well-

1 correlated with levoglucosan (R=0.74) and AMS-PAHs (R=0.88). Note that AMS-PAHs are

2 not unique BBOA tracers, but in general they derive from combustion sources (see SI for the

3 comparison between AMS-PAHs and GC-MS PAHs). In this specific dataset they could

4 partially derive from traffic, although from the AMS-PAHs multilinear regression, we

5 estimated that 79% of the AMS-PAHs are related to BBOA and 21% to HOA, indicating that

6 BBOA dominates the PAH emissions. The AMS-PAHs:HOA ratio was 0.0020, while the

7 AMS-PAHs:BBOA was 0.0028.

8 In general, industrial emissions can be an important source of PAHs at this location as

9 discussed in El Haddad et al. (2013). In presence of an industrial contribution, the BBOA *vs.*

10 AMS-PAHs correlation would decrease. In this work the correlation between AMS-PAHs and

11 the $C_2H_4O_2^+$ fragment, typically related to levoglucosan fragmentation (Alfarra et al., 2007),

12 was high (R=0.87) and no AMS-PAHs spike was observed without a simultaneous increase of

13 $C_2H_4O_2^+$ (Fig. S15). Moreover the industrial-related OA factor resolved by El Haddad et al.

14 (2013) was clearly associated to wind directions from W/SW (225°-270°), while in this work

15 wind directions were oriented from W/SW only for 7% of the monitoring time, furthermore

16 without being associated to any significant increase in the AMS-PAHs concentration (Fig.

17 S16), indicating the absence of clear industrial episodes.

18 The BBOA diurnal cycle, similarly to AMS-PAHs, showed higher values at night than during

19 the day (Fig. 4). In addition, the BBOA highest concentrations were detected at night and

20 associated to slow wind speeds from the E/NE which is consistent with the night land breeze

21 direction. Moreover, strong enhancements of the BBOA factor concentrations were perceived

22 when the wind direction shifted to the E/NE (typically around 18 o'clock during the

23 monitoring period) suggesting that BBOA could be transported from the valleys nearby

24 Marseille (Fig. S18).

25 We calculated the BBOC time series by dividing the BBOA concentrations by the

26 OM:OC$_{BBOA}$ ratio calculated from the average BBOA HR spectrum (1.60). The average

27 BBOC:levoglucosan ratio [μg m^{-3}/μg m^{-3}] was 0.15, comparable to other European studies

28 (Zotter et al., 2014; Herich et al., 2014; Minguillón et al., 2011).

29 The OOA profile showed the most oxidized mass spectral fingerprint with an O:C ratio of

30 0.67 in comparison to the values of 0.35 retrieved for BBOA, 0.12 for COA and 0.03 for

31 HOA. The OOA time series was well correlated with the NH_4^+ time series (R=0.86),

32 suggesting a probable secondary origin of the OOA factor (Lanz et al., 2008). The OOA

1   diurnal cycle was flat, suggesting OOA to be representative of regionally-transported

2   oxygenated aerosols, consistent with the conclusions of El Haddad et al. (2013).

3   **3.2 Offline-AMS source apportionment validation**

4   PMF factors from the offline-AMS dataset were related to aerosol sources/processes based on

5   mass spectral features (Fig. 5), seasonal trends and correlation with tracers (Fig. 6). A

6   comparison of the online-AMS and offline-AMS factor profiles is reported in the SI. In the

7   following, for a generic k factor, we calculated the corresponding KOC_i time series dividing

8   KOA_i by the OM:OC ratio determined from the average HR-AMS factor profile.

9   During summer, when biomass burning contributions to EC are low, HOA correlated well

10   with EC ($R = 0.76$) and yielded an HOC:EC (Hydrocarbon-like OC = HOA/(OM:OC)$_{HOA}$)

11   ratio of 0.64, similar to other European studies (El Haddad et al., 2009 and references

12   therein). Over the whole year, the retained PMF solutions showed an HOA correlation with

13   NO_x (R) spanning between 0.23 and 0.49. These low correlations are comparable to the ones

14   found by El Haddad et al. (2013) at the same station by online-AMS. In this case, the

15   relatively low HOA correlation with NO_x is probably due to the low R_{HOA} (median 0.11)

16   which together with the low HOA concentration (1.5 µg m$^{-3}_{avg}$, Results section), results in

17   small water-soluble HOA concentrations, leading to an uncertain HOA apportionment. This

18   was already reported in previous offline-AMS studies (Daellenbach et al., 2016; Bozzetti et

19   al., 2016a). Although the HOA variability could not be well captured, the estimated HOA

20   concentration was corroborated by the average HOA/NO_x (0.02 µg m^{-3}/µg m^{-3}) which was

21   found to be consistent with El Haddad et al. (2013) for the same station and with Favez et al.

22   (2010) for an alpine location in France.

23   BBOA was identified from its mass spectral features, with the highest $fC_2H_4O_2^+$ and $fC_3H_5O_2^+$

24   contributions among the apportioned factors, consistent with the findings of Alfarra et al.

25   (2007). BBOA correlated well with biomass combustion tracers measured by GC-MS, such as

26   levoglucosan (R=0.76), acetosyringone (R=0.71) and vanillic acid (R=0.84). The winter

27   average levoglucosan:BBOC [µg m^{-3}/µg m^{-3}] ratio was equal to 0.12, consistent with other

28   studies in Europe (Zotter et al., 2014; Herich et al., 2014; Minguillón et al., 2011).

29   The fourth factor (INDOA) was related to industrial emissions due to the high correlation

30   with light alkanes (C19-C22, $0.77 \leq R \leq 0.86$), Se (R=0.54), Pb (R=0.44) and with some PAHs

such as pyrene ($R=0.74$), fluoranthene ($R=0.77$), and phenantrene ($R=0.74$). Among the measured PAHs, pyrene, fluoranthene and phenantrene showed the lowest correlations with levoglucosan (Table S1, $R = 0.31$, 0.29, and 0.27 respectively), suggesting that these particular PAHs were overwhelmingly emitted by INDOA rather than BBOA. We note that phenanthrene, pyrene, and fluoranthene together represent $9.6\%_{avg}$ of the PAHs mass quantified by GC-MS, indicating that PAHs are overwhelmingly emitted by BBOA. While Se is considered to be a unique coal marker in the literature (Weitkamp et al., 2005; Park et al., 2014), in Marseille this source is likely related to coke and steel production facilities (El Haddad et al., 2011). The average INDOA OM:OC (1.60) was intermediate between the OM:OC ratios of HOA (1.23) and COA (1.28), and those of BBOA (1.85) and OOA (1.82). El Haddad et al. (2013) resolved an industrial OA factor at the same station by online-AMS PMF. In that work the authors suggested a probable contribution of oxygenated OA to the resolved industrial factor, probably deriving from (photo)chemical aging during the transport from the industrial facilities to the receptor site occasionally accompanied by new particle formation processes within the industrial plume (as observed by the increased ultrafine particle number concentration associated to W/SW wind directions) . Considering the average wind speed from W/SW (0.8 km/h), and the distance between the receptor site and the Marseille commercial harbor ($\sim$ 40 km) we estimate an aging time of several hours, which could lead to a more oxidized fingerprint in comparison to the fresh primary emissions (Huang et al., 2014). Overall this factor explained the largest fraction of the variability of S- and Cl-containing organic fragments such as C_2HSO^+, CH_2SO^+, $CH_3Cl_2^+$, $CH_4SO_3^+$, $C_3H_3SO_2^+$, and $C_7H_{16}^+$.

The last factor was defined as OOA as it showed a highly oxygenated fingerprint with the largest CO_2^+ fractional contributions (fCO_2^+) among the apportioned factors (14%, in comparison with 11% for BBOA, 2% for HOA, and 1% for COA and INDOA). This factor showed on average the largest contributions over the year. Overall, the $OOA:NH_4^+$ ratio was 2.3_{avg}, in line with the values reported by Crippa et al. (2014) for 25 different European sites (2.0_{avg}; minimum value 0.3; maximum 7.3).

Previous offline-AMS (Bozzetti et al., 2016a; Bozzetti et al., 2016b; Daellenbach et al., 2016) and online-ACSM studies (e.g., Canonaco et al., 2015) conducted in Switzerland and Lithuania reported the separation of two OOA factors characterized by different seasonal trends and different $C_2H_3O^+:CO_2^+$ ratios. In particular, the OOA factor characterized by the

highest $C_2H_3O^+$:CO_2^+ ratio contributed mostly during summer and was linked to secondary OA from biogenic emissions. Here we calculated a $(C_2H_3O^+$:$CO_2^+)_{OOA}$ ratio by subtracting the $C_2H_3O^+$ and CO_2^+ contributions deriving from primary sources, from the measured $C_2H_3O^+$ and CO_2^+ (Canonaco et al., 2015):

$$\frac{C_2H_3O^+}{CO_2^+}_{OOA,i} = \frac{C_2H_3O^+_{meas,i} - HOA_i \cdot fC_2H_3O^+_{HOA} - BBOA_i \cdot fC_2H_3O^+_{BBOA} - INDOA_i \cdot fC_2H_3O^+_{INDOA} - COA_i \cdot fC_2H_3O^+_{COA}}{CO_2^+_{meas,i} - HOA_i \cdot fCO_2^+_{HOA} - BBOA_i \cdot fCO_2^+_{BBOA} - INDOA_i \cdot fCO_2^+_{INDOA} - COA_i \cdot fCO_2^+_{COA}} \quad (12)$$

Overall, $C_2H_3O^+_{OOA}$, and $CO_2^+_{OOA}$ did not show a clear seasonality (Fig. S19), which hampered the separation of two OOA sources. Even though another OOA factor was not separated, El Haddad et al. (2013) estimated for the same location during summer a substantial contribution of secondary biogenic aerosol using ^{14}C measurements (no measurements conducted in other seasons). As a consequence the OOA factor resolved in this work explains both secondary biogenic and aged/secondary anthropogenic sources. The absence of a clear increase in the $(C_2H_3O^+$:$CO_2^+)_{OOA}$ ratio in Marseille during summer could be explained by the large emissions of anthropogenic secondary OA (SOA) precursors during winter, leading to a different $(C_2H_3O^+$:$CO_2^+)_{OOA}$ seasonality in comparison with previous offline-AMS studies (Daellenbach et al., 2016, Bozzetti et al. 2016a), which were conducted either at rural sites characterized by different types of vegetation, or in smaller urban areas. In general, several parameters affect the biogenic SOA concentrations and their separation, e.g. intensity of the biogenic precursor sources, air masses photochemical age, and NO_x concentrations. All those parameters were different in Marseille from previous offline-AMS studies which were conducted in central/northern Europe.

4. Results and discussion

4.1 OA source apportionment results and uncertainties.

In this study, we present one of the first OA source apportionments conducted over an entire year in the Mediterranean region. This work represents also the first comparison between HR online-AMS and HR offline-AMS source apportionments conducted at the same location, despite in two different periods. Previous studies (Daellenbach et al., 2016) reported a comparison between offline-AMS and online-ACSM results.

Although related to different years and size-fractions (PM_1 online-AMS, $PM_{2.5}$ offline-AMS), the offline-AMS source apportionment returned average seasonal factor concentrations not

1 statistically different to online-AMS for both winter (Fig. 7) and summer (comparison with El

2 Haddad et al., 2013, Fig. 8). We note that the total OC concentration quantified by online-

3 AMS for PM_1 and by the thermal-optical procedure used for the offline-AMS source

4 apportionment of $PM_{2.5}$ was not different on a seasonal scale considering our uncertainty

5 which includes time variability and measurements uncertainties.

6 Both online and offline-AMS source apportionment revealed that BBOA was the largest OA

7 source during winter. Offline-AMS source apportionment estimated an average BBOA

8 concentration during winter 2011-2012 of 5.2 μg m$^{-3}_{avg}$, representing 43%$_{avg}$ of the OA.

9 Similarly, online-AMS source apportionment revealed a BBOA concentration of 4.4$_{avg}$ μg m^{-3}

10 (corresponding to 42% of OA) during February 2011. During summer, the offline-AMS

11 BBOA concentration dropped to an average of 0.3 μg m$^{-3}_{avg}$ representing 5% of the OA. Not

12 surprisingly such low BBOA contributions were not resolved by online-AMS source

13 apportionment during summer (El Haddad et al., 2013). On average the offline-AMS BBOA

14 relative uncertainty was 9%. As a comparison, the online-AMS BBOA average relative

15 uncertainty was 6%. Overall for both online- and offline-AMS, the BBOA contributions were

16 the least uncertain among the primary sources, possibly because of the high loadings and the

17 distinct seasonal and diurnal BBOA variability in comparison with the other separated factors.

18 A comparison between the offline- and online-AMS source apportionment uncertainties can

19 be carried out with the caveat that the online-AMS source apportionment uncertainties

20 estimated in this work should be considered as a low estimate as they do not account for the

21 AMS mass error deriving mostly from CE, and particle transmission. This source of

22 uncertainty affects the total OA mass but not the relative contribution of the factors. By

23 contrast, the OA mass uncertainty was accounted for in the offline-AMS source

24 apportionment as the OA mass was rescaled to external measurements (WSOC and OC), the

25 uncertainty of which was propagated in the final source apportionment error (Section 2.4).

26 On a yearly scale, the offline-AMS source apportionment revealed that OOA was the largest

27 OA source, with the highest relative contributions during summer due to the reduced BBOA

28 emissions. The OOA concentration during summer was estimated from offline-AMS at 3.0 μg

29 m$^{-3}_{avg}$, corresponding to 55% of the OA mass. El Haddad et al. (2013) also reported OOA to

30 be the dominant OA fraction during summer with a similar average concentration of 2.9 μg m^{-}

31 ^{3}. During winter, the OOA concentration was estimated by online-AMS to be 3.9$_{avg}$ μg m^{-3}

32 corresponding to 38% of the OA, while the OOA relative uncertainty was 4%. As a

comparison, the OOA relative uncertainty from offline-AMS was $6\%_{avg}$. The offline-AMS source apportionment revealed similar OOA concentrations during winter (3.4 µg m^{-3}_{avg} corresponding to $27\%_{avg}$ of the OA). Even though during winter the OOA concentration was higher than in summer, possibly due to partitioning and due to the shallower boundary layer, the relative contribution decreased because of the strong BBOA contributions.

HOA is one of the most uncertain factors, with an average relative uncertainty of 39% estimated from offline-AMS and 10% from online-AMS analysis, where the larger uncertainty observed for offline-AMS derives mostly from the low R_{HOA} and from the lower time resolution which does not capture the traffic diurnal variability. On average, the HOA concentration predicted by offline-AMS was 1.5 µg m^{-3}, corresponding to 17% of the OA. The estimated HOA concentration by online-AMS during February 2011 was 1.6 µg m^{-3}_{avg} (16% of OA). These values are higher than the ones of El Haddad et al. (2013) who estimated a traffic contribution of 0.8 µg m^{-3}_{avg} during July 2008.

The COA contributions were only minor (average of 0.3 µg m^{-3}), representing on average 4% of the OA mass according to the offline-AMS source apportionment. The online-AMS winter source apportionment returned similar concentrations with 0.4 µg m^{-3}_{avg}, equivalent to $4\%_{avg}$ of the OA. Overall, due to the low concentrations, the COA contributions were uncertain in both source apportionments (6% for online-AMS, 73% for offline-AMS).Similarly to HOA, the larger uncertainty observed for offline-AMS was most possibly due to the low $R_{COA,}$ and the low time resolution which did not enable the COA separation based on the diurnal variability. The summer COA contribution was not resolved from HOA by El Haddad et al. (2013), possibly because the COA reference mass spectrum was not constrained and because of the lack of HR data which typically aid the separation of the two sources.

Finally, the INDOA factor concentration estimated from offline-AMS was on average 2.1 µg m^{-3} during winter and 0.6 µg m^{-3}_{avg} during summer, where this seasonal trend was driven by a strong episode that occurred during early February. The offline-AMS relative uncertainty was estimated as 17%. As previously discussed (Section 3.1), this factor was not separated by online-AMS analysis (February 2011) because of the absence of clear events, which in the offline-AMS dataset were observed only over a short period during January-February 2012. An industrial factor was instead resolved by El Haddad et al. (2013) during summer 2008, with an average concentration of 0.3 µg m^{-3}_{avg}. In that study, the industrial OA factor was also characterized by a low background intercepted by ten-fold spiking episodes.

From the sum of the offline-AMS factor concentrations we estimated the total OM mass. Using this OM and the measured OC we calculated the OM:OC ratio to be 1.40 on average. Specifically, during winter this ratio was 1.55, which is consistent with the online-AMS values determined from the HR-AMS spectra (median = 1.52, 1st quartile = 1.46; 3rd quartile 1.59). The bulk OM:OC variability was driven by the source variabilities. Indeed the relative contribution of the most oxidized source (OOA) was higher during summer (mostly due to the absence of BBOA), however also the relative contributions of the less oxidized sources (such as HOA and COA) were higher during summer mostly due to low BBOA contributions. The BBOA mass spectrum instead was associated with intermediate OM:OC ratios comprised between the values of COA and OOA, and therefore influenced less strongly the bulk OM:OC ratio. Overall the combination of these effects led to a higher bulk OM:OC during winter.

4.2 Insights into the BBOA origin during winter

Methyl-nitrocatechols measurements showed high correlations with BBOA (Fig. 9, R=0.95) and no correlation with OOA (R=0.06, offline-AMS source apportionment). Similarly high correlations were already observed in other studies (e.g. Poulain et al., 2011). This large correlation difference suggests that the variability of the methyl-nitrocatechols is likely explained by the BBOA source. However, methyl-nitrocatechols are secondary compounds deriving from the nitration of catechols which can be either directly emitted by wood combustion (Schauer et al., 2001), or generated by OH· oxidation of cresols directly released by wood combustion (Iinuma et al., 2010). m-cresol/NO_x photooxidation experiments (Iinuma et al., 2010) revealed a total contribution of all methyl-nitrocatechol isomers to the catechol SOA of approximately 10%. Assuming methyl-nitrocatechols to be entirely apportioned to the BBOA factor, we estimate a methyl-nitrocatechol-SOA contribution to BBOA on the order of 8%, indicating that part of the BBOA factor is of secondary origin. Previous studies (Atkinson and Arey, 2003) revealed an o-cresol life-time in the atmosphere of 2.4 minutes towards NO_3, and 3.4 h towards OH (at 298 K, dark conditions). This would suggest that such fast SOA formation can be better traced by the high time resolution online-AMS source apportionment (8 minutes) than by the offline-AMS with 24 h time resolution, and in any case only in the BB plume or in the vicinity of the emission source. Nevertheless we did not observe statistically different ratios (within 1σ, error calculated as the time variability) of $OOA:NH_4^+$ (1.5_{avg} and

1 1.25$_{avg}$ for the offline-AMS and online-AMS source apportionments, respectively),

2 OOA:BBOA (0.65$_{avg}$ and 0.89$_{avg}$ respectively), and levoglucosan:BBOC (1.13$_{avg}$ and 1.15$_{avg}$

3 respectively, Fig. 10) during winter, suggesting that despite the different time resolutions, the

4 online and offline methods provide a comparable BBOA-SOA separation. Overall these

5 findings suggest that rapid SOA formation is not well captured by PMF and rapidly formed

6 SOA compounds (such as nitrocatechols) can be systematically attributed by PMF to factors

7 commonly considered as "primary" (BBOA in this case).Both online- and offline-AMS

8 source apportionment revealed for the two different winter seasons a comparable temporal

9 evolution of the levoglucosan:BBOC ratio (Fig. 10, and Fig. 11). This ratio showed typical

10 literature values for domestic wood combustion in Europe during January and early February

11 (0.05-0.2, Zotter et al., 2014; Herich et al., 2014; Minguillón et al., 2011), while during late

12 autumn and March (Fig. 11) it increased up to 0.3, highlighting an evolution of the BBOA

13 chemical composition. A similar seasonal trend was observed for the levoglucosan:vanillic

14 acid, levoglucosan:syringic acid, and levoglucosan:non sea salt-K$^+$ (nss-K$^+$, calculated

15 according to Seinfeld and Pandis, 2006) ratios (Fig. 11). Although the online dataset was

16 limited to one month of measurements, the levoglucosan:vanillic acid ratio also showed a

17 statistically significant increasing trend from early February to the beginning of March

18 (confidence interval of 95%, Mann-Kendall test). These results suggest the occurrence of

19 different types of biomass combustions during low temperature winter days compared to late

20 autumn and early spring: as levoglucosan derives from cellulose pyrolysis (>300°C), while

21 vanillic and syringic acid result from lignin combustion (Simoneit et al., 1998, Sullivan et al.,

22 2008). Different reactivities / volatilities of BBOA markers may complicate this analysis. For

23 this reason we discuss in the following the levoglucosan stability, and propose that the major

24 driver of the observed seasonal trends is the occurrence of different BBOA combustions.

25 Previous studies revealed the levoglucosan reactivity toward OH· radical oxidation (Hennigan

26 et al., 2010) both in gas and aqueous phase (Hoffmann et al., 2010). In the following we

27 analyze the levoglugocan and nss-K$^+$ time series in order to investigate the possible effects of

28 levoglucosan chemical stability and different types of biomass combustions on the seasonal

29 evolution of the levoglucosan:nss-K$^+$ ratio. During summer nss-K$^+$ derives mostly from dust,

30 while levoglucosan is depleted by both photochemistry (Hennigan et al., 2010) and low

31 BBOA emissions. Not surprisingly the levoglucosan:nss-K$^+$ ratio showed lower average

32 values in summer (0.23) than in winter (3.14). During winter nss-K$^+$ is considered to be

33 mostly emitted by BBOA, and consistently in our dataset it shows a good correlation with

BBOA tracers (R=0.66 with syringic acid). Overall, the levoglucosan:nss-K$^+$ ratio during the cold season manifests a behavior that is opposite to the photochemical activity (with temperature considered as a proxy) as it shows higher values during March and late autumn (up to 7.11) and lower in January, February (minimum = 2.79; Fig. 11) when temperature is lower and photochemistry is less intense. For these reasons we relate the winter levoglucosan:nss-K$^+$ variability to different types of combustion rather than to a levoglucosan depletion due to photochemistry. Furthermore we observed the highest levoglucosan concentrations (late autumn) simultaneously with the highest relative humidity (89%) values, suggesting the depletion of levoglucosan by OH· radical oxidation in aqueous phase to be not significant (Hoffmann et al., 2010).

A similar winter seasonal behavior was observed also for plant waxes. Plant waxes concentrations were estimated from high molecular weight n-alkanes (C24-C35) according to the methodology described by Li et al. (2010). This methodology is based on the observation that alkanes from epicuticular waxes preferentially contain an odd number of carbon atoms (Aceves and Grimalt, 1993; Simoneit et al., 1991). This was observed for a large variety of plants including broad leaf trees, conifers, palms, shrubs, grasses, and groundcover (Hildemann et al., 1996 and references therein). Waxes showed the highest concentrations during late autumn (up to 0.16 μg m^{-3}) and in May (up to 0.17 μg m^{-3}), while the minima were observed during winter (minimum 0.007 μg m^{-3}). In general, high molecular weight n-alkanes are typically detected in atmospheric aerosol in significant amounts during the growing season. In a similar way, Hildemann et al. (1996) estimated the highest plant waxes concentrations in April-May in Los Angeles and Pasadena where the climate is similar to Marseille. Similarly we observed the highest concentrations during May. However, comparable plant waxes concentrations were observed also in late autumn during the period characterized by the highest levoglucosan:lignin combustion tracers (Fig 11), suggesting a possible emission from open combustion of green wastes.

Taken together the above observations suggest the occurrence of combustion of cellulose-rich material during March and late autumn, compared to lignin rich biomass burning for residential heating during January. The combustion of cellulose-rich material is possibly related to agricultural waste burning at the beginning and at the end of the agricultural cycle. The occurrence of emission of biomass plumes due to land clearing episodes during March has already been reported in other parts of Europe (Ulevicius et al., 2016), and has been

1 previously modelled for southern France (Dernier van der Gon et al., 2015, Fountoukis et al.,
2 2014).

3 In this study we related the evolution of the BB composition over the cold season to the
4 combustion of cellulose-rich and lignin-rich fuels, considering that lignin end cellulose are
5 contained in different ratios in different biomass fuels. This designation should not be
6 considered as an oversimplification of the combustion processes or of the fuel complexity, but
7 rather as a classification of the BB aerosol based on our observations of increasing lignin
8 pyrolysis products over cellulose pyrolysis products during the coldest days.

9 We note that BB is described in our PMF models by only one factor which therefore
10 potentially represents a combination of several types of biomass burning sources. Increasing
11 the number of factors did not lead to an unambiguous separation of different BBOA sources,
12 however, the comparison with source-specific markers revealed a real BBOA composition
13 evolution over the winter season with higher cellulose to lignin combustion tracer ratios
14 observed during late autumn and early spring in comparison to January/February. This
15 hypothesis of at least two types of BB sources (one linked to domestic heating, another to
16 agricultural activities) is also supported by the direct PMF analysis of the organic and
17 inorganic markers measured for batch 1 (Salameh et al., *submitted*).

5 Conclusions

20 $PM_{2.5}$ filter samples were collected during an entire year (August 2011 to July 2012) at an
21 urban site in Marseille, France. Filter samples were analyzed by water extraction followed by
22 nebulization of the liquid extracts and subsequent measurement of the generated aerosol with
23 an HR-ToF-AMS (Daellenbach et al., 2016).

24 PMF analysis was conducted on the offline-AMS mass spectra and on online-AMS data
25 collected at the same station during February 2011. Offline-AMS source apportionment
26 results were also compared with a previous online-AMS source apportionment study of two
27 weeks during July 2008 at the same location (El Haddad et al., 2013). The methods returned
28 statistically similar seasonal factor concentrations, although different years and size fractions
29 were considered (PM_1 for online-AMS, $PM_{2.5}$ for offline-AMS). OOA was the major source
30 of OA during summer representing on average 55% of the OA mass, while BBOA was the
31 dominant OA source during winter contributing on average 43% of the OA. Smaller

contributions were estimated for HOA, INDOA and COA, representing 17%, 12%, and 4% of the OA mass, respectively. The contribution of primary anthropogenic sources (HOA + BBOA + COA + INDOA) was substantial over the year ($62\%_{avg}$ of OA), with larger absolute and relative contributions during winter (73% of OA_{avg}) associated with an intense biomass burning activity.

Coupling offline- and online-AMS data with molecular markers showed increasing levoglucosan:BBOC ratios during the late winter-early spring period in both 2011 and 2012. This trend was also observed for the ratios between cellulose and lignin combustion markers (e.g. levoglucosan:vanillic acid), with ratios approaching more typical domestic wood combustion European values during January/early February, and values characterized by higher values of cellulose-combustion markers during late autumn and March indicative of the influence of different types of fuels, possibly related to agricultural-related activities.

From the offline-AMS source apportionment, we observed a high BBOA correlation with nitrocatechols deriving from the nitration of catechols directly emitted by biomass combustion. These secondary components are rapidly formed in the atmosphere in presence of $NO_3\cdot$ (life time of a few minutes). Overall, despite the different time resolution, online- and offline-AMS provided a comparable SOA-BBOA separation during winter. Nevertheless, in case of fast SOA formation (relative to the time scale of the online-AMS time resolution, or relative to the transport time to the receptor site) this separation can be hindered, and further efforts are needed to improve the SOA separation from BBOA.

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Experimental design: A. S. H. Prévôt, I. El Haddad, N. Marchand, and C. Bozzetti

Filter collections and online-AMS measurements: N. Marchand and D. Salameh.

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WSOC and TN analysis: P. Fermo and R. Gonzalez

Sunset, and IC analysis: J.-L. Jaffrezo

GC-MS analysis: D. Salameh, and N. Marchand

Nitrocatechols analysis: Y. Iinuma

1   Carbonates analysis: M. C. Minguillón

2   Data analysis and validation: C Bozzetti, and I. El Haddad

3   PMF analysis: C. Bozzetti

4   All authors read and commented on the manuscript.

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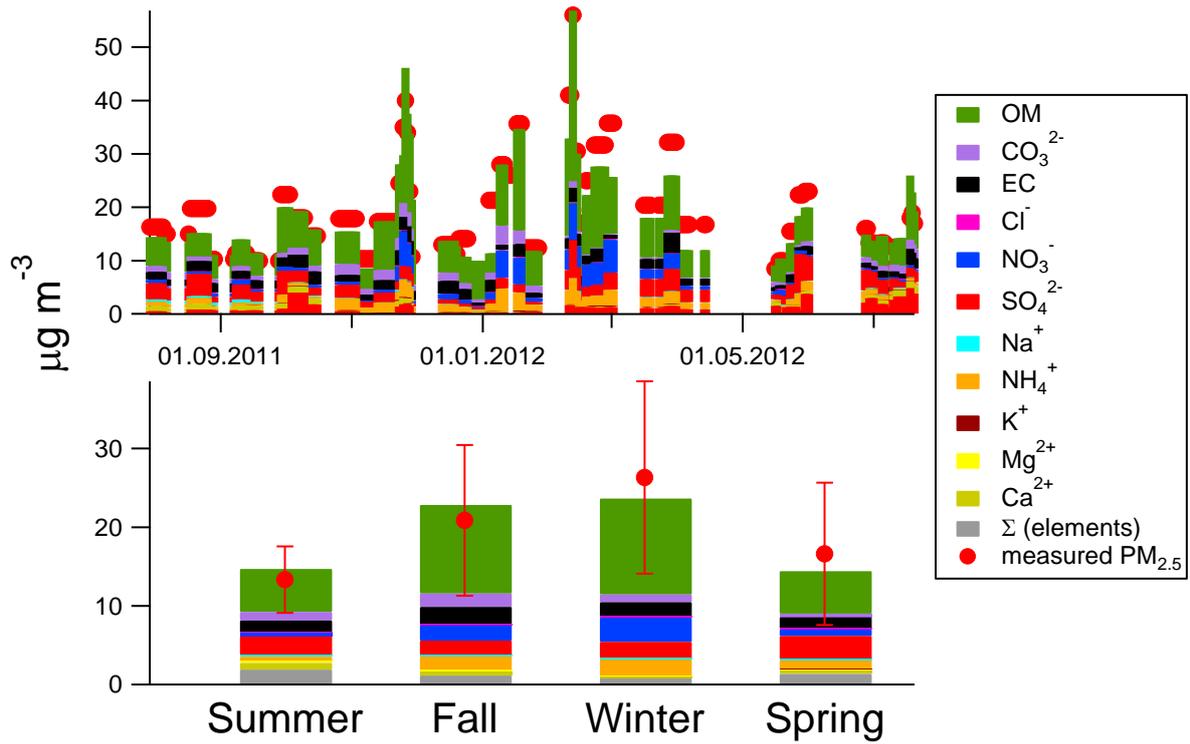
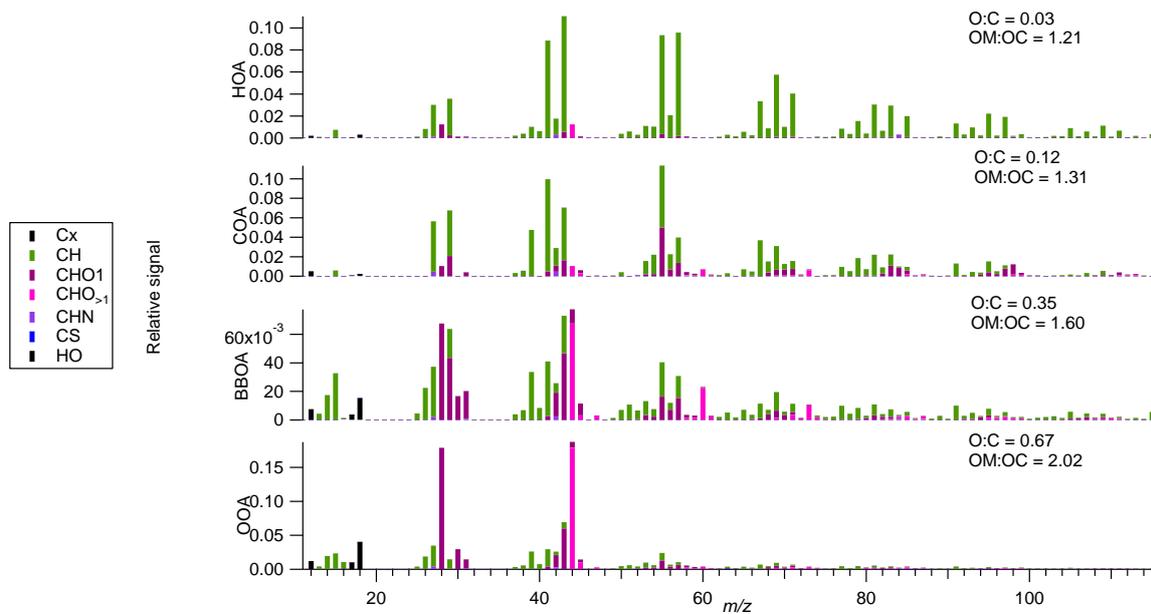
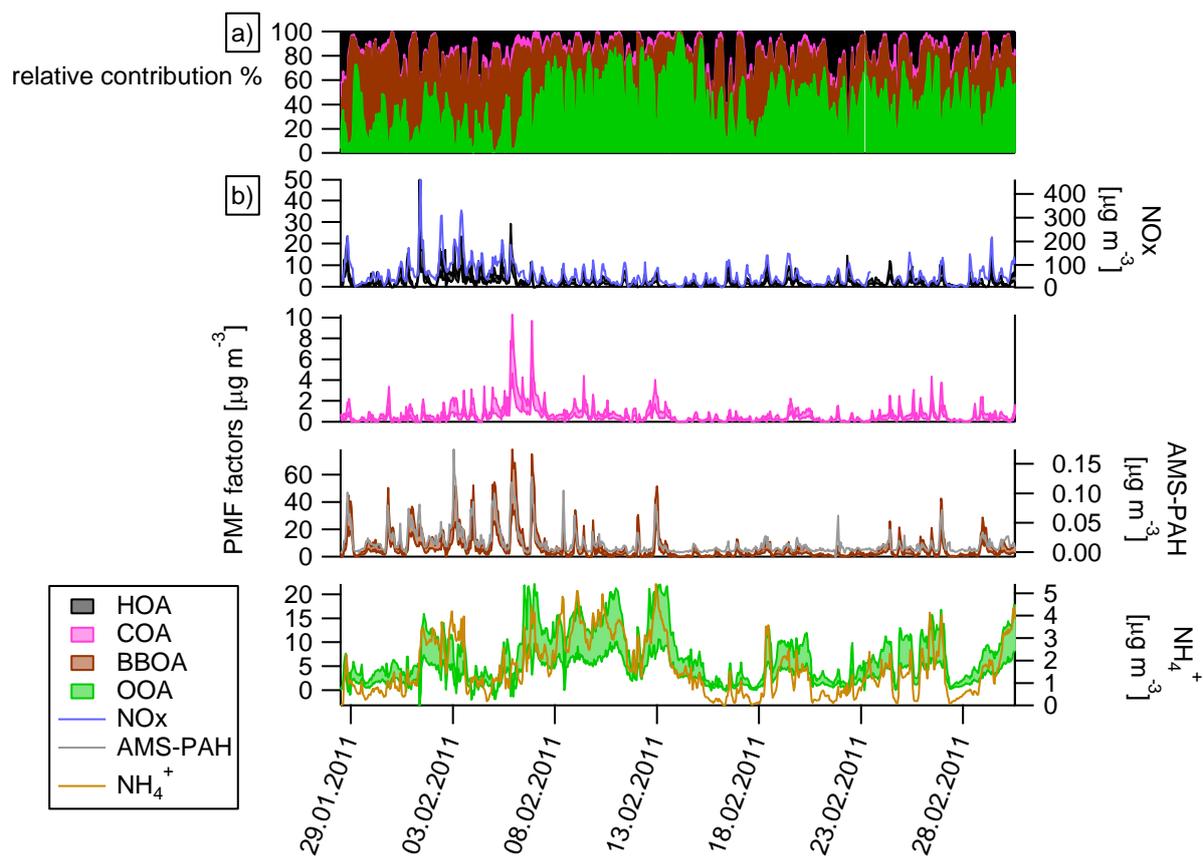
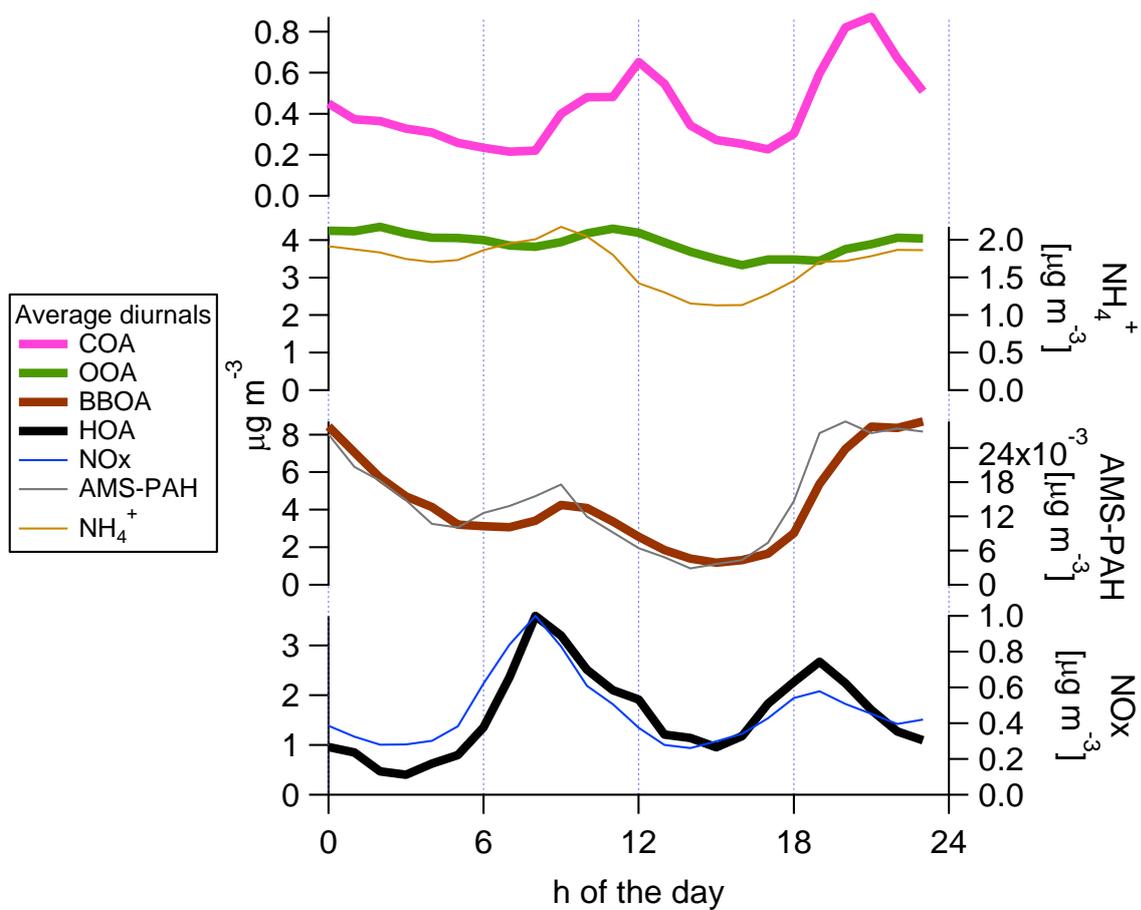
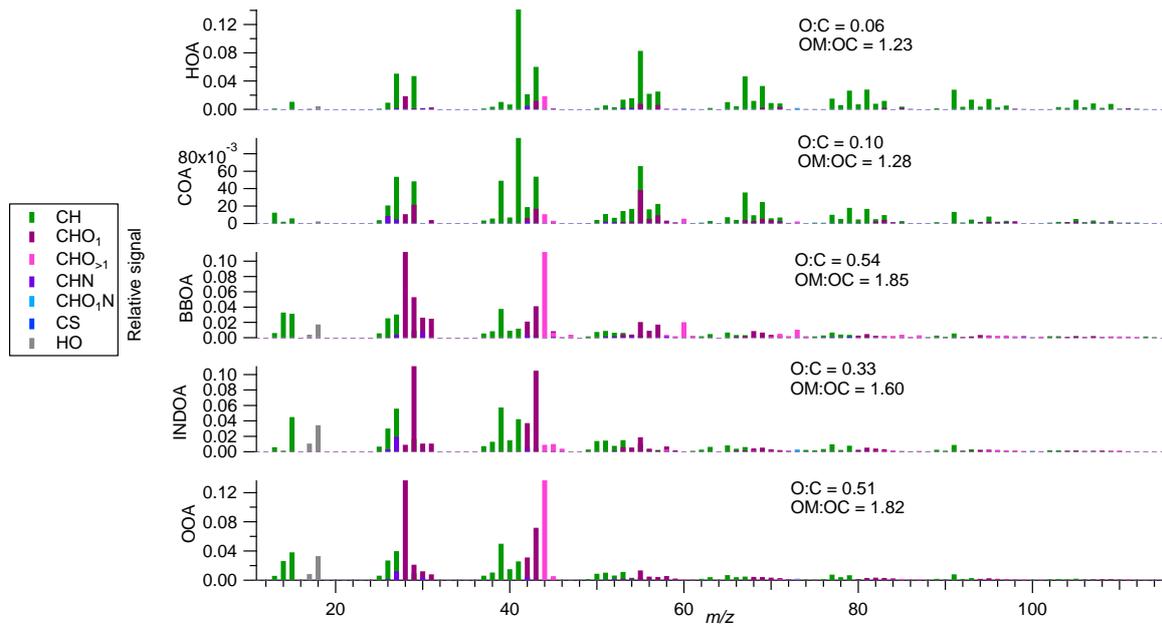
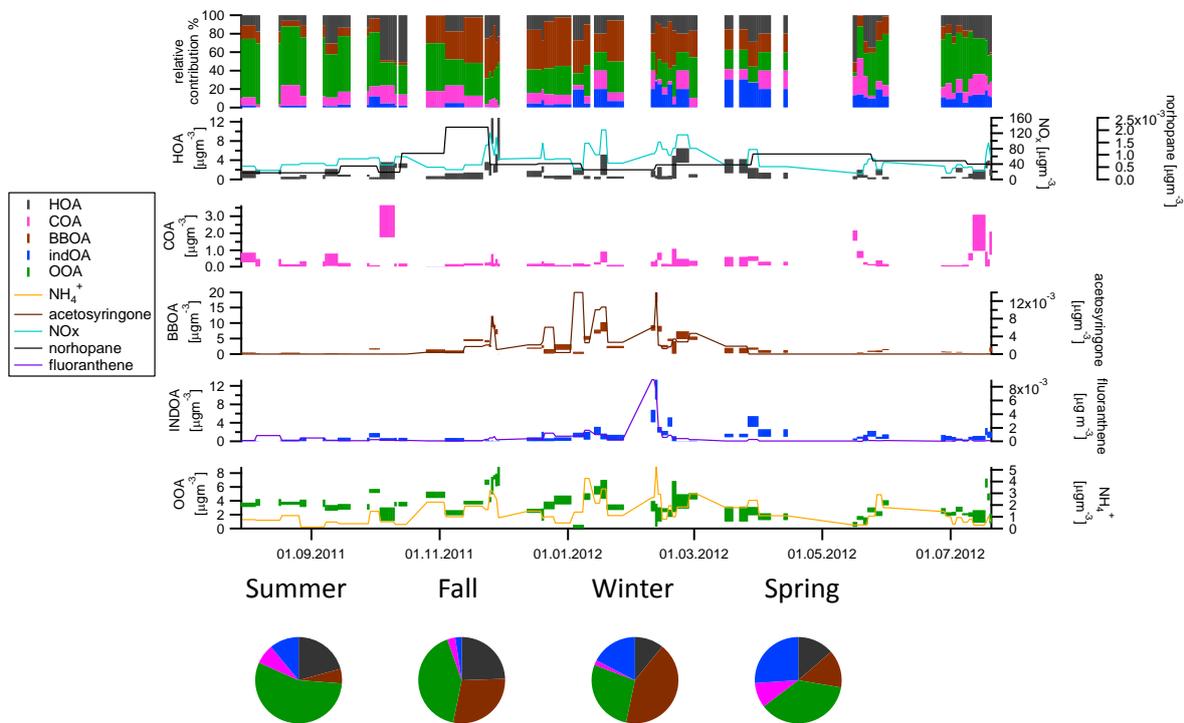


Figure 1. PM$_{2.5}$ composition: stacked average seasonal concentrations. Measured PM$_{2.5}$ error bars represent the seasonal standard deviation. OM was estimated as the sum of the offline-AMS source apportionment factors.

2   Figure 2. Online-AMS: average PMF factor mass spectra.

4   Figure 3. Online-AMS: a) PMF factors relative contributions. b) Time series of PMF factors

5   and corresponding tracers. Shaded areas denote the model uncertainties.

3   Figure 4. Online-AMS: average diurnal cycles of PMF factors and corresponding tracers.

2 Figure 5. Offline-AMS: water soluble average mass spectra.

7 Figure 6. Offline-AMS: a) PMF factors relative contributions. b) Time series of PMF factors

8 and corresponding tracers. Bars denote the model uncertainties.

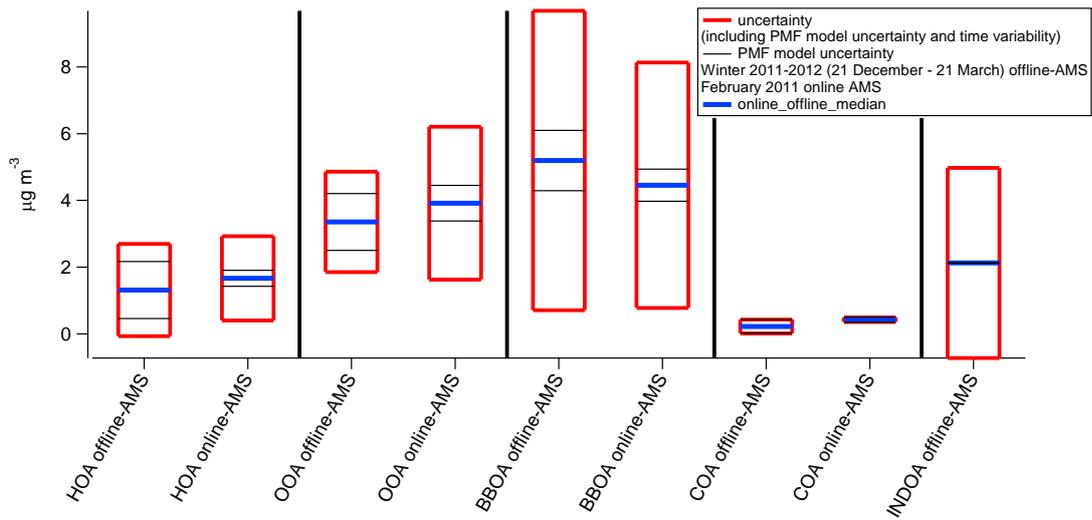



Figure 7. Online (PM$_1$) and offline-AMS (PM$_{2.5}$) comparison. Bars represent the error including temporal variability and model uncertainty.

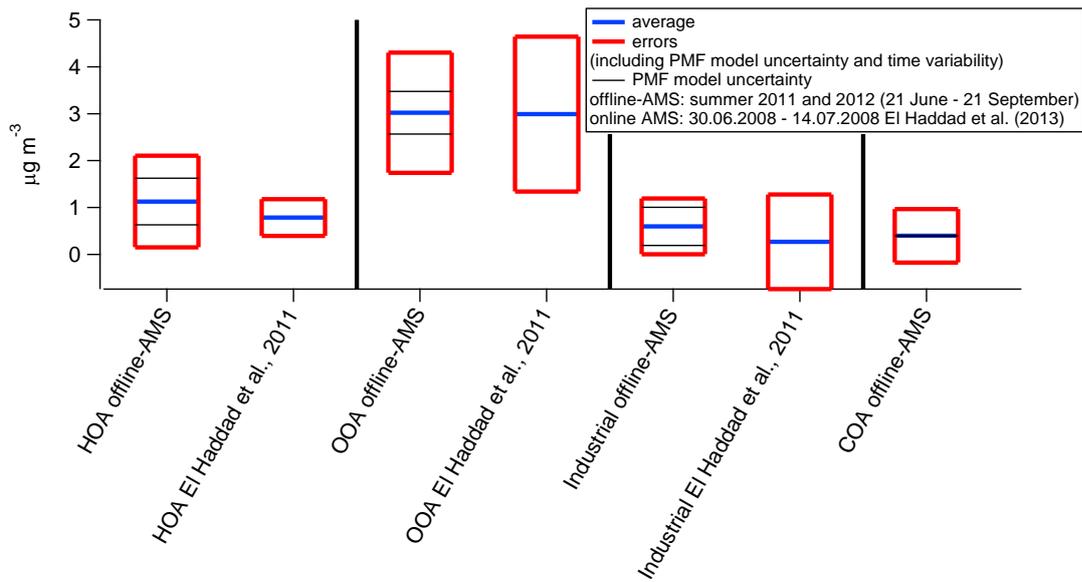
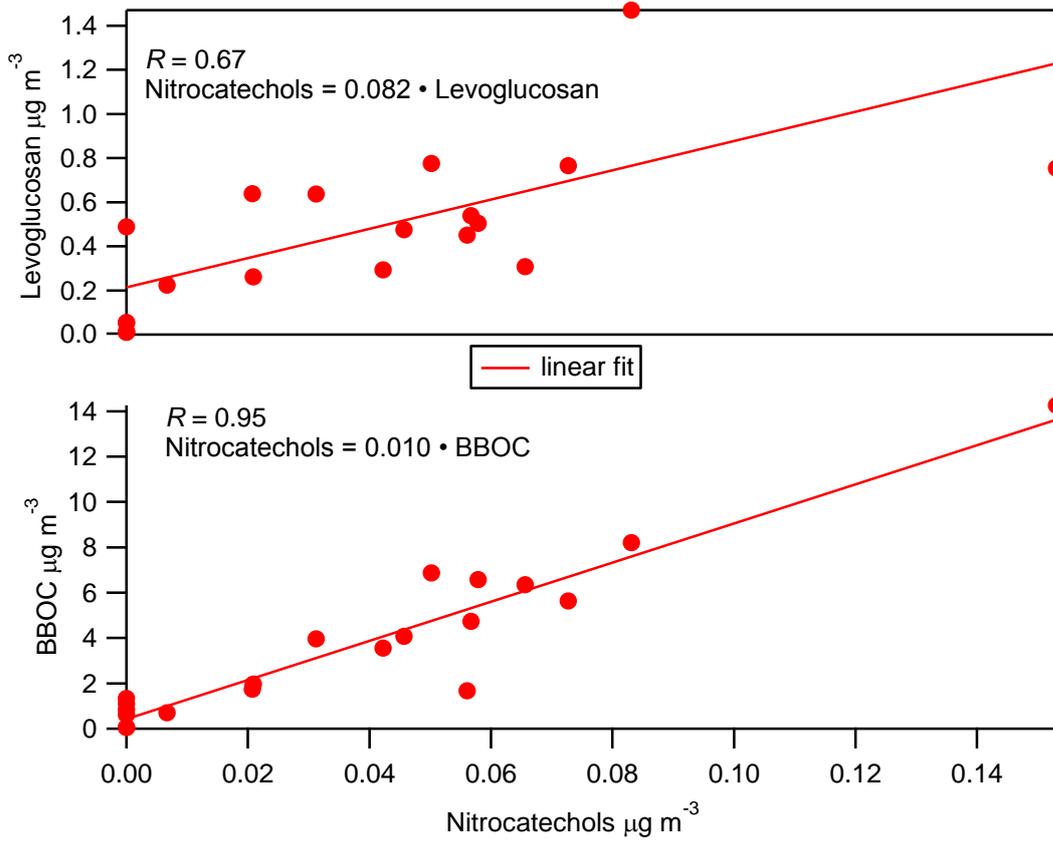
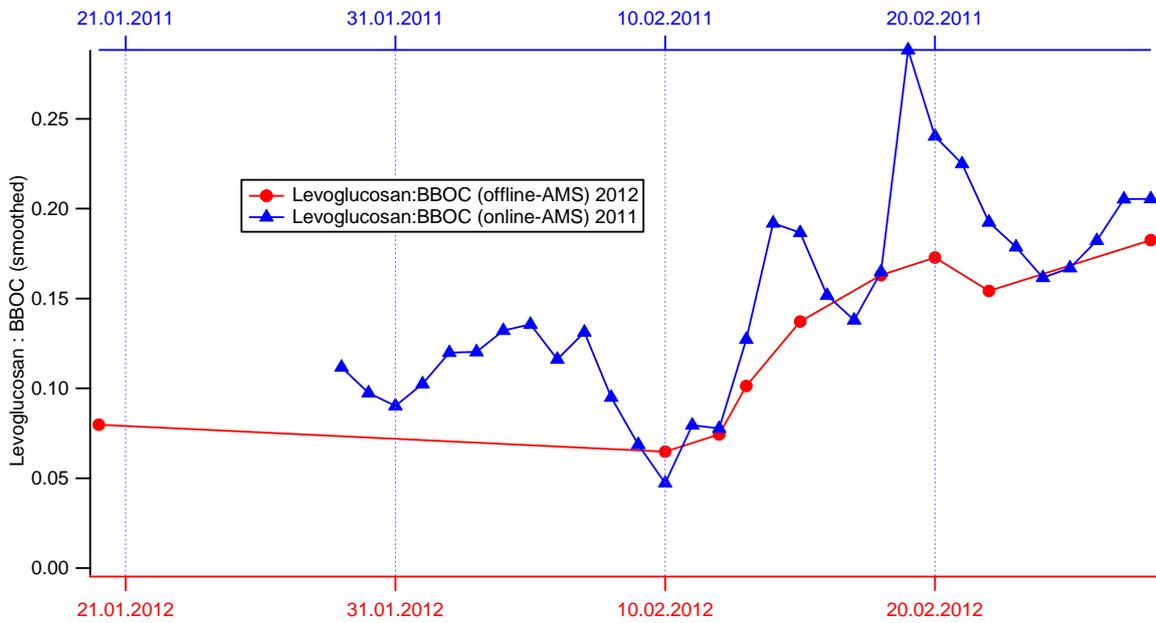
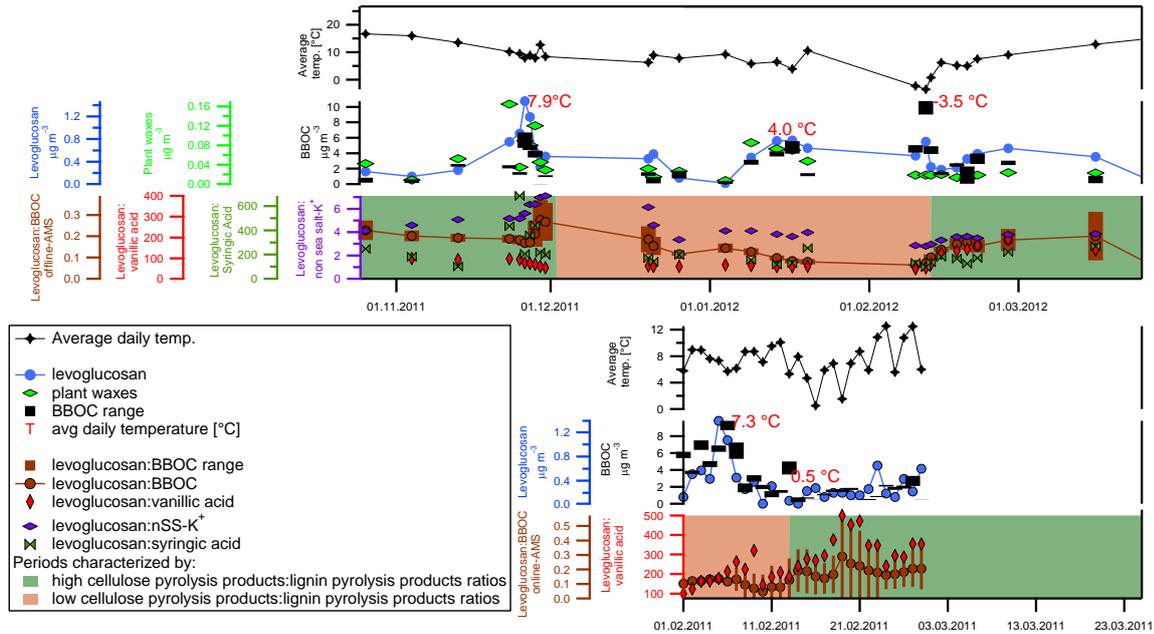



Figure 8. Online (PM$_1$, El Haddad et al., 2013) and offline-AMS (PM$_{2.5}$) comparison. For offline-AMS bars represent the error including temporal variability and model uncertainty. For online-AMS bars represents only the temporal variability.

2 Figure 9. Correlation between the sum of nitrocatechols (Table S1) with levoglucosan and

3 BBOC.

1 Figure 10: Offline-AMS (February 2012) and online-AMS (February 2011) smoothed time-
2 dependent levoglucosan:BBOC ratios. We note that the levoglucosan:BBOC comparison
3 should not be considered on a day-to-day basis where the levoglucosan:BBOC ratio in the two
4 different years can be coincidentially equal or different, but rather on a monthly time scale
5 where, as discussed in the manuscript, we observed a statistically significant (p=0.05)
6 evolution of the levoglucosan:BBOC ratio which is similarily captured by the two models.

10 Figure 11: Online- and offline-AMS time-dependent levoglucosan:BBOC,
11 levoglucosan:vanillic acid, levoglucosan:syringic acid, and levoglucosan:K^+ ratios. The plant
12 waxes concentrations were determined from GC-MS measurements of alkanes with an odd
13 number of carbons (Li et al., 2010). As discussed in the main text the spike observed in late
14 autumn could be related to incomplete green waste combustion.