

1 **Aerosol source apportionment from 1-year-measurements**  
2 **at the CESAR tower at Cabauw, NL**

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1 **Abstract**

2 Intensive measurements of submicron aerosol particles and their chemical composition were  
3 performed with an Aerosol Chemical Speciation Monitor (ACSM) at the Cabauw  
4 Experimental Site for Atmospheric Research (CESAR) in Cabauw, NL, sampling at 5 m  
5 height above ground. The campaign lasted nearly one year from July 2012 to June 2013 as  
6 part of the EU-FP7-ACTRIS project (Q-ACSM Network). Including equivalent black carbon  
7 an average particulate mass concentration of  $9.50 \mu\text{g m}^{-3}$  was obtained during the whole  
8 campaign with dominant contributions from ammonium nitrate (45%), organic aerosol (OA,  
9 29%), and ammonium sulfate (19%). 12 exceedances of the World Health Organization  
10 (WHO)  $\text{PM}_{2.5}$  daily mean limit ( $25 \mu\text{g m}^{-3}$ ) were observed at this rural site using  $\text{PM}_{10}$   
11 instrumentation only. Ammonium nitrate and OA represented the largest contributors to total  
12 particulate matter during periods of exceedance.

13 Source apportionment of OA was performed season-wise by Positive Matrix Factorization  
14 (PMF) using the Multilinear Engine 2 (ME-2) controlled via the source finder (SoFi). Primary  
15 organic aerosols were attributed mainly to traffic (8% - 16% contribution to total OA,  
16 averaged season-wise) and biomass burning (0% - 23%). Secondary organic aerosols (SOA,  
17 61% - 84%) dominated the organic fraction during the whole campaign, particularly on days  
18 with high mass loadings. A SOA factor which is attributed to humic-like substances (HULIS)  
19 was identified as a highly oxidized background aerosol in Cabauw. This shows the  
20 importance of atmospheric ageing processes for aerosol concentration at this rural site. Due to  
21 the large secondary fraction, the reduction of particulate mass at this rural site is challenging  
22 on a local scale.

# 1 1 Introduction

2 Atmospheric aerosols have large impacts on the climate directly by scattering and absorbing  
3 short wave radiation. Besides the resulting influence on the visibility (Ramanathan et al.,  
4 2007; Romanou et al., 2007), this can have a cooling or heating effect on the atmosphere  
5 (IPCC, 2013). The indirect effect refers to the impact of particles on cloud formation and their  
6 properties.

7 In addition, particles can impact adversely on human health by e.g. increasing the probability  
8 of cardiopulmonary and lung cancer mortality (Pope et al., 2002). The World Health  
9 Organization (WHO) recently estimated that globally, 3.7 million deaths were attributable to  
10 ambient air pollution in both cities and rural areas in 2012 (EU, 2008). This mortality is  
11 reported to be due to exposure to small particulate matter (PM<sub>10</sub>), which can cause  
12 cardiovascular and respiratory disease, and cancers. Particles with lower diameters such as  
13 PM<sub>2.5</sub> or PM<sub>1</sub> are reported to have enhanced toxicological effects since they can deposit more  
14 deeply in the respiratory system and remain suspended for longer periods of time (Pope and  
15 Dockery, 2006). Therefore, a number of institutions established several air quality standards  
16 for different particle sizes to limit aerosol mass. The WHO air quality guideline (global  
17 update 2005, WHO (2006)) defines a PM<sub>2.5</sub> daily mean limit of 25 µg m<sup>-3</sup> and a PM<sub>2.5</sub> annual  
18 mean limit of 10 µg m<sup>-3</sup>. The European Union Air Quality Directive 2008/50/EC provides  
19 only a target value of the annual mean limit of PM<sub>2.5</sub> of 25 µg m<sup>-3</sup> (EU, 2008).

20 Air quality and climate effects are not only depending on the particle number concentration  
21 and size, but also on their chemical composition. This information is not only relevant to  
22 investigate the nature and magnitude of each effect, but also for the identification and  
23 quantification of aerosol sources and mitigation strategies for a potential reduction of aerosol  
24 mass concentrations. Major inorganic components of PM<sub>1</sub> consist mainly of ammonium  
25 nitrate (NH<sub>4</sub>NO<sub>3</sub>) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), formed in the presence of ammonia  
26 (NH<sub>3</sub>), nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>), respectively (Seinfeld  
27 and Pandis, 2006). Therefore NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> are strongly attributed to  
28 anthropogenic sources (Finlayson-Pitts and Pitts, 2000). Since the reactions leading to  
29 inorganic aerosol happen from gaseous precursors in the atmosphere, the condensed products  
30 are considered as secondary aerosols, while primary aerosols like black carbon (BC) are  
31 emitted directly.

32 In contrast, organic aerosols (OA), which can also be of primary (POA) or secondary (SOA)  
33 origin, consist of up to hundreds of thousands of different molecules (Goldstein and Galbally,

1 2007), where SOA contributes on average 70% to organic aerosol mass (Hallquist et al.,  
2 2009). SOA is formed by gas to particle conversion of atmospherically oxidized semi- and  
3 low-volatile organic compounds (VOC's). Guenther et al. (1995) estimated a global VOC  
4 budget in the order of 1150 Tg carbon per year. Biogenic VOC's (BVOC's) contribute  
5 approximately 90% of total VOC, including isoprene (50% of total BVOC's), monoterpenes  
6 (15%), and sesquiterpenes (3%) (Guenther et al., 2012). In turn, 10% of emitted VOC's are of  
7 anthropogenic origin, including e.g. alkanes, alkenes, benzene and toluene.

8 The investigation of the aerosol composition is critical for the development of climate models,  
9 since the composition influences important particle properties. However, its determination is  
10 still challenging, especially in case of OA, which contribute significantly to atmospheric  
11 particulate matter (Jimenez et al., 2009). In fact, the lack of knowledge on particle  
12 composition is a key contribution to the large uncertainty for the determination of the total  
13 anthropogenic radiative forcing (IPCC, 2013).

14 The development of online aerosol mass spectrometric techniques during the last decades  
15 enhanced the possibilities to investigate aerosol chemical composition in real-time (DeCarlo  
16 et al., 2006; Jayne et al., 2000; Jimenez et al., 2003). The Aerosol Mass Spectrometer (AMS,  
17 Aerodyne Research Inc., Billerica, MA, USA) is a powerful instrument to quantitatively  
18 measure the chemical composition of the non-refractory fraction of  $PM_{10}$  (NR- $PM_{10}$ ) with high  
19 time and mass resolution. Due to the high amount of maintenance from skilled and trained  
20 personnel needed for continuous operating measurement campaigns using an AMS are usually  
21 not exceeding one or two months (Sun et al., 2012). Since the variation of aerosol  
22 composition is very high depending on measurement site and season (Jimenez et al., 2009),  
23 long term measurements ( $\geq 1$  year) are clearly needed. At a European level, this effort is  
24 supported by the Aerosols, Clouds and Traces gases Research InfraStructure network  
25 (ACTRIS) program that aims at pooling high-quality data from state-of-the-art  
26 instrumentation such as the Aerodyne Aerosol Chemical Speciation Monitor (ACSM). The  
27 Quadrupole-ACSM (Q-ACSM) is specially designed for long-term continuous and real-time  
28 measurements of mass concentrations and composition of NR- $PM_{10}$  species (Ng et al., 2011b).

29 In this study, an ACSM was used to measure the submicron aerosol chemical composition  
30 from 11.07.2012 to 03.06.2013 at the CESAR tower in Cabauw, NL, as part of the EU-FP7-  
31 ACTRIS project. A collocated Multi-Angle Absorption Photometer (MAAP, Thermo  
32 Scientific Model 5012), provided equivalent black carbon (eBC) data. Organic aerosol data  
33 was further analyzed by Positive Matrix Factorization using the Multilinear Engine 2

1 (Paatero, 1999) via the source finder (SoFi, Canonaco et al. (2013)). This data set shows the  
2 long-term variability of particle composition and is used for source apportionment of  
3 atmospheric aerosols at this North Western European rural site, with the focus on periods  
4 where air quality standards were violated. This information can be further used to establish  
5 strategies for the reduction of particulate matter.

## 1 **2 Methodology**

### 2 **2.1 Site description: CESAR**

3 The CESAR tower is 220 m high and managed and operated by the Royal Netherlands  
4 Meteorological Institute (KNMI, The Netherlands). It is located in a rural site (51.970°N,  
5 4.926°E) near Cabauw, the Netherlands, about 20 km south-west of the city of Utrecht and  
6 about 45 km south east of the Dutch North Sea coast. The site conditions are typical for North  
7 Western Europe. They can either be maritime or continental, depending on the wind direction.  
8 The surface elevation changes in the surrounding are at most a few meters over 20 km. The  
9 tower ground is approximately 0.7 m below sea level, the diurnal variation of the temperature  
10 is relatively stable (Vermeulen et al., 2011). The direct surroundings of the tower have a  
11 relatively low population density. The nearby region is used mainly by agriculture, with a  
12 mixture of intensively and extensively managed grassland. These are used also for animal  
13 keepings like cattle and sheep, besides nearby located chicken farms.

14 The tower is equipped with external platforms and booms at 2 m, 10 m, 20 m, 40 m, 80 m,  
15 140 m, and 200 m. At all these levels, meteorological observations of standard parameters like  
16 wind speed, wind direction, dew point temperature, and ambient temperature are routinely  
17 performed (Ulden and Wieringa, 1996). These data sets are available at the CESAR data base  
18 (KNMI, 2013). In addition, other meteorological data like precipitation, radiation and remote  
19 sensing, including lidar, radar and radiometer techniques, are acquired at the tower and  
20 submitted to the CESAR data base. Also concentrations of gaseous compounds, including  
21 greenhouse gases, are monitored at CESAR (Russchenberg et al., 2005; Vermeulen et al.,  
22 2011). The National Institute for Public Health and the Environment (RIVM, the Netherlands)  
23 provides hourly data from gaseous CO, NO, NO<sub>2</sub>, SO, SO<sub>2</sub>, and O<sub>3</sub>, but also daily PM<sub>10</sub>  
24 measurements. Data of ambient CO<sub>2</sub>, CH<sub>4</sub> (both measured at 20 m, 60 m, 120 m, and 200 m  
25 height), and Radon 222 (<sup>222</sup>Rn, measured at 20 m and 200 m height) is determined by ECN on  
26 a time scale of 30 minutes. A map indicating the land use of the Netherlands is given in the  
27 supplement (Fig. S1).

28

## 1 **2.2 ACSM sampling and data analysis**

2 The ACSM measures the NR-PM<sub>1</sub> fraction, including the organic fraction (Org), ammonium  
3 (NH<sub>4</sub>), nitrate (NO<sub>3</sub>), sulfate (SO<sub>4</sub>), and chloride (Chl), using mass spectrometric information  
4 on a time base of approximately 30 minutes. The ACSM used in this work is equipped with a  
5 commercial grade Quadrupole Residual Gas Analyzer (RGA), thus it is also called a Q-  
6 ACSM. This instrument is described in detail by Ng et al. (2011b). The RGA provides unit  
7 mass resolution (UMR) mass spectra. Fractions of measured UMR signals were assigned to  
8 individual aerosol species using the fragmentation table introduced by Allan et al. (2004). Due  
9 to the automated zeroing system used for the ACSM, adjustments of the fragmentation table  
10 entries concerning interferences from air beam molecules are not needed. All ACSM data  
11 processing and analysis within this work was performed using software provided by  
12 Aerodyne Research (ACSM Local, version 1.531, ARI (2012) ) within IGOR Pro version  
13 6.2.3.

14 Recent studies showed good agreements of ACSM data with data from other aerosol  
15 instruments like the High Resolution Time-of-Flight AMS (HR-ToF-AMS) in ambient  
16 measurement campaigns, even in highly polluted areas such as Beijing (Sun et al., 2012; Sun  
17 et al., 2011). An intercomparison of two collocated ACSM's resulted in strong correlations  
18 ( $R^2 = 0.8$ ) and agreements within 27% (Budisulistiorini et al., 2014). Crenn et al. (2015)  
19 reported similar results from the intercomparison of 13 ACSM's, a ToF-ACSM's, a ToF-  
20 AMS, and other collocated instruments in the region of Paris, France. There, the same ACSM  
21 instrument (S/N A140-145) as the one used for this study was tested. Those results indicate  
22 that the ACSM can be used as a suitable and cost-effective alternative to the AMS for aerosol  
23 composition measurements due to its capability of stable and reproducible operation.

24 Mass calibrations were performed approximately every month and were based on determining  
25 the instrument response factor (RF) (Ng et al., 2011b) using monodisperse NH<sub>4</sub>NO<sub>3</sub> (320 nm)  
26 as calibration substance and a Condensation Particle Counter (CPC, TSI 3022a) as reference  
27 instrument (Jayne et al., 2000; Jimenez et al., 2003). An average RF<sub>NO<sub>3</sub></sub> of  $2.74 \pm 0.45 \cdot 10^{-11}$   
28 was obtained and used for the calculation of aerosol mass concentrations. Instead of  
29 performing a mass calibration for every aerosol species, relative ionization efficiencies  
30 (RIE's), compared to that of nitrate, were used. The RIE's of NH<sub>4</sub> and SO<sub>4</sub> were determined  
31 directly during the mass calibrations by measuring dry NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles after  
32 another. Averaged over all calibrations, a RIE<sub>NH<sub>4</sub></sub> of  $7.53 \pm 0.21$  and a RIE<sub>SO<sub>4</sub></sub> of  $0.81 \pm 0.10$   
33 were found and used for the whole data set. Calibration results gained from this particular

1 instrument during an intercomparison in Paris as described by Crenn et al. (2015) were within  
2 the uncertainty or only slightly different ( $RF_{NO_3}=2.34 \cdot 10^{-11}$ ,  $RIE_{NH_4}=6.54$ ,  $RIE_{SO_4}=0.62$ )  
3 considering the large differences between individual instruments at the intercomparison. RIE  
4 values of 1.4 and 1.3 for organics and chloride, respectively, were taken from the literature  
5 (Alfarra et al., 2004; Canagaratna et al., 2007).

6 A site specific, time resolved particle collection efficiency (CE) correction algorithm  
7 (equations are given in the supplement) was applied, which was developed by Mensah et al.  
8 (2012), using SMPS data as reference. In contrast to the commonly used constant value of 0.5  
9 this CE correction accounts for the high ammonium nitrate mass fraction (ANMF) found at  
10 this site and is thus more suitable for the data presented here. Another algorithm for  
11 composition dependent CE determination (Middlebrook et al., 2012) was also tested for its  
12 validity. It uses a threshold ratio of measured to predicted  $NH_4$  to switch between two  
13 different equations to determine the CE. The threshold value of 0.75 is close to the observed  
14 ratio of measured over predicted  $NH_4$  of this data set, resulting in large discontinuities of CE  
15 values and in consequence, discontinuous changes in aerosol mass concentrations. Therefore  
16 the Middlebrook algorithm was not used for this data set, which showed at the same time low  
17 ratios of measured to predicted  $NH_4$  and high AMNF's. According to Ng et al. (2011b) and  
18 Sun et al. (2012), the variability of the instrument performance was corrected based on the  
19 inlet pressure and  $N_2$  signal, as well as the signals derived from the internal naphthalene  
20 source were taken to correct for the mass dependent ion transmission efficiency of the RGA.

21 The detection limits for each species were not determined within this work, but are reported to  
22 be 0.148, 0.284, 0.012, 0.024, and  $0.011 \mu g m^{-3}$  ( $3\sigma$ ) for organics, ammonium, nitrate, sulfate,  
23 and chloride, respectively, at an averaging time of 30 minutes (Ng et al., 2011b).

24 During the whole campaign, the ACSM was located inside the CESAR tower building. Its  
25 inlet was placed on the roof of the building at approximately 5 m height above ground. The  
26 inlet head was equipped with a  $PM_{2.5}$  cyclone (URG-2000-30EN, URG Corporation, Chapel  
27 Hill, USA). The sample air was pulled through a 10 m copper line (ID = 6.5 mm) at a flow  
28 rate of  $9 L min^{-1}$ . From this flow, a subsample of  $1 L min^{-1}$  was diverted to a Nafion dryer  
29 (RH < 40%) of which approximately  $80 mL min^{-1}$  entered the ACSM. This resulted in a total  
30 residence time of 18 seconds.

31



## 1 **2.3 Collocated aerosol measurements**

2 The following collocated aerosol instruments were used for cross-validation of the ACSM  
3 data: (i) a Scanning Mobility Particle Sizer (SMPS, TSI 3034), operated by the Netherlands  
4 Organization for Applied Scientific Research (TNO, The Netherlands), (ii) a Monitor for  
5 Aerosol and Gases (MARGA, Applikon Analytical BV), operated by ECN, and (iii) a HR-  
6 ToF-AMS, which was operated by Forschungszentrum Juelich during the first 6 days of the  
7 ACSM campaign. In addition, BC data obtained by a MAAP instrument (TNO, The  
8 Netherlands) was included into the analysis.

9 The MAAP instrument has been introduced by Petzold and Schönlinner (2004) and Petzold et  
10 al. (2005). It is designed for the determination of the black carbon (BC), which is a product of  
11 incomplete combustion. There is in the scientific community a general consensus over what  
12 black carbon is in terms of properties (Bond et al., 2013) The MAAP measures the strong  
13 visible light absorption property of BC by simultaneous measurements of the radiation  
14 penetrating through and scattered back from a particle-loaded fiber filter. According to  
15 Petzold et al. (2013), optical BC determined by MAAP is to be referred to as equivalent black  
16 carbon (eBC). One property of BC is that it is highly refractory with a vaporization  
17 temperature near 4000K (Schwarz et al., 2006), thus BC is not vaporized at 600°C and cannot  
18 be measured by the ACSM. The MAAP achieves a time resolution of 5 minutes with an  
19 uncertainty of 12% (Petzold and Schönlinner, 2004). A mass absorption cross section (MAC)  
20 of  $6.6 \text{ m}^2 \text{ g}^{-1}$  for a wavelength of 637 nm (Müller et al., 2011) was chosen to convert the  
21 measured particle absorption coefficient to eBC mass concentrations. Although the MAAP  
22 has no size selective inlet beside the  $\text{PM}_{10}$  heads described below, it can be assumed that eBC-  
23 containing aerosol generally fall into the submicron size range (Bond et al., 2013). Thus eBC  
24 mass concentrations are considered as part of the  $\text{PM}_1$  fraction from hereon. As seen later the  
25 eBC fraction is rather low throughout the campaign, meaning that the overall error of this  
26 assumption is not significant.

27 The SMPS (TSI, Model 3034) is a sequential combination of several integrated components:  
28 an impactor, a neutralizer, a differential mobility analyser and a condensation particle counter.  
29 It determines the size distribution of particles in a range of 10 nm to 487 nm (electromobility  
30 diameter). The SMPS aerosol mass concentration was calculated from the measured volume  
31 distributions using the particle density determined by the aerosol composition information  
32 derived from the ACSM and the MAAP. Assuming spherical particles, the total density is  
33 computed by using the densities of the aerosol species, weighted by their mass fractions. Bulk

1 densities of  $\text{NH}_4\text{NO}_3$  ( $1.72 \text{ g cm}^{-3}$ ) and  $(\text{NH}_4)_2\text{SO}_4$  ( $1.77 \text{ g cm}^{-3}$ ), and densities of  $1.8 \text{ g cm}^{-3}$   
2 for BC (Bond and Bergstrom, 2006; Park et al., 2004) of organics ( $1.4 \text{ g cm}^{-3}$ , Hallquist et al.  
3 (2009)) were taken into account. Considering its low influence on the total particle density at  
4 this site, it is acceptable to set the density for chloride to  $1 \text{ g cm}^{-3}$  (Mensah et al., 2012).

5 During the presented campaign, the MAAP and the SMPS were connected to the common  
6 aerosol inlet which sampled at 60 m height. This inlet consisted of four  $\text{PM}_{10}$  size selective  
7 heads at the top, followed by a Nafion dryer to keep the relative humidity (RH) of the sample  
8 air below 40%. The stainless steel pipe, ranging from the aperture at 60 m to the basement,  
9 has an inner diameter of 0.5" (= 1.27 cm) and ends in a manifold, where the sampled air is  
10 distributed to a variety of different instruments, including the MAAP and the SMPS, each  
11 with its own sample flow. An overall sample flow of  $60 \text{ L min}^{-1}$  was adjusted inside the 60 m  
12 pipe, assuring laminar conditions.

13 SMPS data was corrected size dependently for (diffusional) losses in the inlet system and  
14 SMPS system itself according to Henzing (2011) who compared theoretical findings with  
15 measured losses that are obtained by measuring simultaneously before and after the various  
16 parts of the inlet system at the CESAR tower. In addition, particles of different compositions  
17 were measured in 2013 simultaneously at the pipe entrance at 60 m height and in the  
18 basement (J. S. Henzing, personal communication). For more than 8000 simultaneous  
19 observations, the results showed that aerosol measurements through this 60 m sampling line  
20 underestimate  $\text{PM}_{10}\text{-eBC}$  by approximately 33% with an uncertainty of 7%. Therefore, eBC  
21 obtained from the MAAP are divided by a factor of 0.66 to account for these losses. For the  
22 inorganic species penetrations through this inlet line were reported to be 62-73% for nitrate,  
23 55-64% for sulfate, and 54-56% for ammonium. However these results were not used for  
24 corrections in this work.

25 The MARGA measures water soluble components of both the gas and aerosol phase  
26 simultaneously, including the aerosol species nitrate, ammonium, sulfate, and chloride. It uses  
27 a Wet Annular Denuder (WAD) followed by a Steam Jet Aerosol Collector (SJAC). The  
28 operational and calibration procedures, as well as details of the data analysis are given by  
29 Trebs et al. (2004). During the campaign the MARGA collected alternately the  $\text{PM}_1$  and  
30  $\text{PM}_{2.5}$  fraction of ambient particles at ambient RH and temperature, each fraction sampled  
31 hourly with a measurement error smaller than 10% (Schaap et al., 2011). The detection limits  
32 for the most abundant aerosol species were 0.05, 0.10, 0.08,  $0.01 \mu\text{g m}^{-3}$  ( $4\sigma$ , Rumsey et al.  
33 (2014)) for ammonium, nitrate, sulfate, and chloride, respectively.

1 The MARGA inlet was equipped with a PM<sub>10</sub> size selective head (Rupprecht and Pataschnick,  
2 R&P), placed on the roof of the tower building next to the ACSM inlet aperture at 5 m height.  
3 The sample air was transferred into the instrument within a polyethylene tube with an inner  
4 diameter of 0.5" (= 1.27 cm) and a sample flow of 16.7 L min<sup>-1</sup>, which is either directed  
5 through a PM<sub>1</sub> or a PM<sub>2.5</sub> size selective cyclone. A detailed description of the MARGA inlet  
6 system at the Cabauw tower was previously described by Schaap et al. (2011). There, wall  
7 losses were investigated and found to be less than 2% for several gaseous and particulate  
8 compounds. To compare with the ACSM, only MARGA data containing PM<sub>1</sub> composition is  
9 considered within this work.

10 An Aerodyne HR-ToF-AMS was connected to the MARGA inlet during the first 6 days of the  
11 campaign. As the ACSM is built upon AMS, the latter measures likewise the chemical  
12 composition of the PM<sub>1</sub> non-refractory (NR) fraction. Instrumental details are available in  
13 Jayne et al. (2000), Jimenez et al. (2003), and DeCarlo et al. (2006).

14

## 15 **2.4 Statistical methods of organic aerosol data analysis**

16 Source apportionment of organic aerosol components was performed using Positive Matrix  
17 Factorization (PMF, Paatero (1997); Paatero and Tapper (1994)) via the ME-2 solver  
18 (Paatero, 1999). PMF is a bilinear model and assumes that the original data set, containing  
19 variable mass spectra over time, is a linear combination of a given number of factors, each  
20 with a constant mass spectrum and its contributions over time. It has been successfully used in  
21 AMS ambient studies apportioning the measured organic mass spectra in terms of  
22 source/process-related components (Zhang et al., 2011). With the ME-2 solver it is possible to  
23 introduce a priori mass spectral information and hence to reduce the rotational ambiguity, i.e.  
24 similar PMF results with the same goodness of fit, of PMF solutions (Paatero and Hopke,  
25 2003).

26 The extraction of OA data and error matrices as mass concentrations in  $\mu\text{g m}^{-3}$  over time, as  
27 well as their preparation for PMF/ME-2 according to Ulbrich et al. (2009), was done within  
28 the ACSM software. Only  $m/z$ 's  $\leq 100$  were considered here since they represented nearly the  
29 whole OA mass (around 98%) and did not interfere with ion fragments originating from  
30 naphthalene (e.g.,  $m/z$  127, 128, and 129, see also Sec. 2.2). From these matrices, the  $m/z$  12  
31 was discarded because it showed negative signals, probably due to too short delay time of the  
32 quadrupole scan (125 ms) after a valve switch (Fröhlich et al., 2015). In addition, the  $m/z$ 's 37

1 and 38 were also removed from the organic matrices of the whole campaign except for winter  
2 2013. This was done because the signal at these masses showed high interferences with the  
3 chloride related ions  $^{37}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$ . Including these ions lead to unreasonable PMF factors  
4 which mainly contained only these two masses and represented the chloride time series,  
5 whereas during Winter 2013 no such interferences were observed.

6 The interface source finder (SoFi, Canonaco et al. (2013)), version 4.8, was used to control  
7 ME-2 for the PMF runs of the ACSM OA data adopting the source apportionment strategy  
8 developed by Crippa et al. (2014). Briefly, unconstrained PMF runs were first investigated  
9 with 1 to 10 factors and a moderate number of seeds (10 to 15) for each factor number. If  
10 Primary Organic Aerosol (POA) factor profiles like hydrocarbon-like OA (HOA) or OA from  
11 biomass burning (BBOA) were found, site specific POA mass spectra or spectra derived from  
12 the data base were constrained and a sensitivity analysis performed on the tightness of  
13 constraint (a-value, Lanz et al. (2008)). Since aged OA (or oxidized OA, OOA) factors show  
14 more variability between measurement sites in terms of their mass spectra (MS) than POA, it  
15 is not appropriate to constrain SOA factor profiles using reference spectra derived from  
16 different locations (Canonaco et al., 2015). According to Crippa et al. (2014), HOA MS  
17 should be more constrained (a-value between 0 and 0.2) than BBOA MS ( $a \approx 0.3$ ), since the  
18 BBOA fingerprint shows higher variations depending on the burning type and conditions  
19 (Alfarra et al., 2007). In each step, either in unconstrained or constrained approaches, the  
20 following criteria for finding a proper solution were used based on the recommendations from  
21 Ulbrich et al. (2009) and Canonaco et al. (2013):

- 22 • The quality parameter  $Q/Q_{\text{exp}}$  was minimized.
- 23 • Factor profiles have reasonable mass spectra, as expected for the measurement site.
- 24 • Factor time series have high correlations with respective external data sets such as  
25 gaseous  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NO}_x$ , and particulate nitrate, sulfate and black carbon.
- 26 • When a proper solution is found, 50 seed runs were used to find the global minimum  
27 for  $Q/Q_{\text{exp}}$ .
- 28 • Investigation of the rotational ambiguity of the solution space is carried out using the  
29 a-value approach for the constrained factor profiles

30

## 1 **3 Results and discussion**

### 2 **3.1 Cross-validation of particulate total mass and chemical species** 3 **concentrations**

4 The particle density during the ACSM campaign was determined using the chemical  
5 composition data from the ACSM and the MAAP and resulted in an average of  $1.63 \pm$   
6  $0.12 \text{ g cm}^{-3}$ . The time series of the particle density is given in the supplement. It was used to  
7 calculate the SMPS total mass concentration from its measured volume concentration  
8 throughout the campaign. Due to the relatively low signal-to-noise ratio of the ACSM, the  
9 density shows scattering only during periods with low mass loadings. Therefore it does not  
10 influence the cross-validation with the SMPS mass significantly. Figures S3 and S4 show the  
11 time series of the SMPS mass and the combined mass concentrations measured by ACSM and  
12 MAAP and the correlation plot of both data sets, respectively. Using 12275 common data  
13 points for the linear fit, a good qualitative and quantitative agreement (Slope:  $1.16 \pm 0.01$ ,  
14 intercept:  $-1.05 \pm 0.06$ ,  $R^2 = 0.78$ ) was observed. Excluding eBC data resulted in a slope of  
15  $1.13 \pm 0.01$ , an intercept of  $-1.14 \pm 0.06$ , and a  $R^2$  of 0.78. The negative offset can be  
16 explained by minor influences of sea salt and dust particles, which can be detected well by the  
17 SMPS and MARGA but not by the ACSM with a sufficient sensitivity. But the low value of  
18 the intercept shows already that the uncertainty introduced by these aerosol components is  
19 rather low in general. This can also be explained by the low concentrations of Mg, Na, K and  
20 Ca as measured by the MARGA (see below) and the assumption that the majority of dust  
21 particles is most likely found in particles with diameters larger than 1 or even  $2.5 \mu\text{m}$   
22 (Finlayson-Pitts and Pitts (2000) and references therein).

23 Since the MARGA measures routinely the water soluble inorganic aerosol compounds, data  
24 from ACSM inorganic species were synchronized and compared to corresponding MARGA  
25  $\text{PM}_{10}$  data for the whole measurement period. The temporal overlap with the collocated high  
26 resolution AMS was between 11 and 17 July 2012. The correlation parameters of individual  
27 aerosol species and respective total masses between the ACSM data and the data sets from the  
28 MARGA and AMS are given in Table 1, using 1943 and 294 common data points,  
29 respectively. The corresponding correlation graphs are shown in the supplement (Fig. S5 and  
30 S6). Except for chloride, high correlation coefficients were achieved. Furthermore, the  
31 comparison to both total mass time evolutions shows very high qualitative and quantitative  
32 agreement. The quantitative difference between ACSM- and AMS-organics is also very low,  
33 and the discrepancies in case of ammonium and nitrate are within the stated  $\pm 30\%$  accuracy

1 of the AMS and ACSM (Ng et al., 2011b) and the  $\pm 10\%$  for the MARGA-NO<sub>3</sub>, respectively  
2 (Makkonen et al., 2012). Similar variations were also found by Crenn et al. (2015) as well as  
3 Budisulistiorini et al. (2014). The latter reported of a comparison between two collocated  
4 ACSM's ( $\pm 27\%$ ,  $R^2 = 0.21$  for Chl,  $R^2 > 0.8$  for the other species) and between these  
5 ACSM's and a continuous Tapered Element Oscillating Microbalance (TEOM, PM<sub>2.5</sub>)  
6 instrument. Note that the major ions used for nitrate detection in AMS and ACSM (NO<sup>+</sup> and  
7 NO<sub>2</sub><sup>+</sup>) are produced from both inorganic and organic nitrate (e.g. Farmer et al. (2010)). The  
8 higher ACSM nitrate compared to MARGA nitrate can therefore also be explained by the  
9 presence of organic nitrates. In case of nitrate the ACSM and MARGA comparison cannot be  
10 seen as independent. The underestimation of the ACSM in case of sulfate exceeding the  
11 uncertainties may arise from calibration issues. The mass calibration procedure used in this  
12 work was mainly adopted from AMS procedures which may not be directly suitable for the  
13 ACSM. The RIE of sulfate might be overestimated due to high observed background signals  
14 during the calibration using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles. An overestimated RIE<sub>SO<sub>4</sub></sub> results in  
15 underestimated mass concentrations. This would in turn explain the low SO<sub>4</sub> mass  
16 concentrations comparing to the MARGA and AMS. Additionally, the ACSM fragmentation  
17 table could not be adjusted for interferences of ions from different aerosol species on the same  
18 m/z properly because ACSM software used in this study did not allow plotting time series for  
19 specific fragments apportioned by the fragmentation table. Thus, the standard table had to be  
20 used. Furthermore, the MARGA measured only low concentrations of Mg, Na, K and Ca  
21 (average sum: 0.08  $\mu\text{g m}^{-3}$ ). Thus, contributions of their corresponding sulfate salts, for which  
22 the ACSM is less sensitive, are negligible in this context. It should also be noted, that chloride  
23 concentrations can originate from particulate organic and inorganic chloride components  
24 originating from e.g. sea salt. For the latter, the ACSM is much less sensitive than the  
25 MARGA. As described above, influences from sea salt can be considered rather low. In turn,  
26 the MARGA might be less sensitive to organic chlorides, as they are likely less water soluble  
27 than inorganic chlorides. These explanations would explain the low agreement between the  
28 two instruments in case of chloride.

29 Overall, the comparison of the data measured by the ACSM and MAAP with collocated  
30 aerosol instruments showed a good reliability, precision, and in most cases a good accuracy  
31 over the whole campaign, including periods with high and low mass loadings. Therefore, the  
32 here obtained chemical composition can be used qualitatively and quantitatively for the  
33 source apportionment of aerosol components at this rural site. Major discrepancies to the  
34 SMPS especially during some of the pollution events like 16 to 27 January 2013 and 5 to 8

1 May 2013 (see below) can be explained by the correction of losses through the 60 m inlet line  
2 which was done size dependently and did not account for losses of individual species as  
3 mentioned in chapter 2.3. Furthermore, discrepancies can also result from the different  
4 sampling heights of the SMPS and MAAP (both at 60 m) and ACSM and MARGA (both  
5 5 m), through which the instruments may sampled partly within different layers with different  
6 mass concentrations. As the quantitative agreements of individual inorganic species as well as  
7 of total inorganics between the ACSM and the MARGA during these periods are much  
8 higher, the mass loadings determined from these instruments are more reliable than the SMPS  
9 data.

10

### 11 **3.2 Aerosol chemical composition**

12 A meteorological overview of this campaign, including wind direction, precipitation, Radon-  
13 222 measurements and ambient temperature and relative humidity (RH) is provided in Fig.  
14 S7. Table S1 shows temperature and RH values averaged over selected periods (see below). If  
15 not stated else, all data shown in this chapter is in UTC (local time minus 1 or 2 hours,  
16 respectively) and averaged and synchronized to the ACSM data resolution of 30 minutes.  
17 Summing up the ACSM and MAAP data, a total mass concentration of  $9.5 \mu\text{g m}^{-3}$  was  
18 measured on average, with a maximum of  $78.4 \mu\text{g m}^{-3}$  and a minimum of  $0.2 \mu\text{g m}^{-3}$ .

19 Data coverage of 75% for one day and 90% for one calendar year, respectively, is defined  
20 mandatory for a proper risk assessment according to the WHO air quality guideline. The last  
21 requirement could not be achieved either with the ACSM or with the MARGA between July  
22 2012 and June 2013 (70% and 71% coverage, respectively). Nevertheless, the average total  
23 mass derived from the combination of the MARGA  $\text{PM}_{2.5}$  data (including all water soluble  
24 inorganic components  $\text{NO}_3$ ,  $\text{NH}_4$ ,  $\text{SO}_4$ , Cl, Na, K, Mg, and Ca), MAAP eBC and ACSM  $\text{PM}_1$   
25 organics resulted in  $12.5 \mu\text{g m}^{-3}$  during this time, clearly exceeding the WHO  $\text{PM}_{2.5}$  annual  
26 mean limit ( $10 \mu\text{g m}^{-3}$ ) by 25%. Even the  $\text{PM}_1$  concentration inferred from ACSM + MAAP  
27 data (campaign average  $9.5 \mu\text{g m}^{-3}$ ) approached the WHO  $\text{PM}_{2.5}$  limit.

28 The time series of the daily mean total mass derived from both combinations (MARGA- $\text{PM}_{2.5}$   
29 + ACSM-Org + eBC and ACSM-total + eBC), where the required data coverage of 75% was  
30 reached, are shown in Fig. 1. The WHO  $\text{PM}_{2.5}$  daily mean limit of  $25 \mu\text{g m}^{-3}$  was exceeded on  
31 17 and 12 days, respectively. 8 and 7 exceedances were observed during a period with high  
32 pollution from 16 to 27 January 2013, respectively.

1 In Fig. 2 the average contributions of individual species are shown as pie charts (a) and  
2 stacked time series (b). A technical problem of the MAAP instrument was responsible for the  
3 lack of BC data from 15 February 2013 to 25 April 2013. To determine properly average  
4 species contributions for each pie chart the campaign was therefore not divided strictly  
5 season-wise, but into five periods. The first two sections represent the summer (July-August-  
6 September) and autumn (October-November-December) 2012, while the first half of 2013  
7 was divided into periods with and without BC data. Larger gaps in ACSM data occurred  
8 mainly due to problems with the RGA detector, in addition to minor measurement gaps for  
9 maintenance and calibrations.

10 Overall, particulate nitrate and organics were the dominant species, representing 39% and  
11 29% of the total aerosol, respectively. Both compounds show similar contributions in summer  
12 (period 1) and autumn 2012 (period 2), whereas in winter (January-February-March, period 3  
13 and beginning of 4) and spring (April-May-June, periods 4 and 5) the  $\text{NO}_3$  fraction increased  
14 up to an average of 46% of the total particulate mass, and the organic and eBC fractions  
15 decreased. The contributions of the other components showed only small variations between  
16 the seasons (see Table S2).

17 The most significant pollution events (17 to 21 August 2012, 21 to 25 October 2012, 16 to 27  
18 January 2013, and 5 to 8 May 2013) are highlighted with shaded backgrounds in Fig. 2.  
19 During these events, MARGA  $\text{PM}_{2.5}$  data showed up to 33% higher (e.g. on 17 to 21 August  
20 2012) total inorganic masses than ACSM  $\text{PM}_1$  inorganics as implicated in Fig. 1. As  
21 mentioned above the number and proportions of exceedances of the WHO  $\text{PM}_{2.5}$  daily mean  
22 limit is therefore even higher than when only  $\text{PM}_1$  data is considered. During the last three  
23 events, northerly and north-easterly winds dominated. The period 16 to 27 January 2013  
24 showed also the lowest temperatures (average:  $-4^\circ\text{C}$ ) with respect to the whole campaign and  
25 a temperature inversion between 2 m and 40 m height in the in the morning 25 January 2013,  
26 where both instruments showed total mass concentrations of ca.  $20 \mu\text{g m}^{-3}$ . On the other hand,  
27 no temperature inversion was seen during times when very high ( $> 40 \mu\text{g m}^{-3}$ ) aerosol mass  
28 loadings were observed, even in winter times. Many sudden drops of the particulate mass can  
29 be either explained by changes in wind direction and/or precipitation events, like in case of  
30 the two latter pollution events (16 to 27 January 2013, and 5 to 8 May 2013).

31 Figure 3 shows the diurnal patterns of each individual species and the total particulate mass  
32 for the whole campaign. Corresponding plots with data averaged separately for the five  
33 chosen periods can be found in the supplement (Fig. S8). Overall,  $\text{NO}_3$  showed the largest



1 diurnal variation, with a maximum during the night/morning hours, reflecting its nighttime  
2 production and a minimum during the day due to the volatility of  $\text{NH}_4\text{NO}_3$ . This pattern is  
3 more pronounced in the warmer periods 1 and 5. Since the majority of ammonium is  
4 originated from  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4$  has a similar pattern to that of  $\text{NO}_3$ .  $\text{SO}_4$ , which is mainly  
5 formed photochemically during the day from gaseous  $\text{SO}_2$ , showed peaks during daytime,  
6 although its overall variation is rather low. The maxima of BC can be attributed to direct  
7 emissions from traffic (morning and evening rush hours) and biomass burning events  
8 (domestic heating in the evenings/nights). Finally, OA showed peaks at the evening hours  
9 during the colder periods and a daytime minimum during the summer. More detailed  
10 discussion of the diurnal patterns of individual OA factors is given below.

11 An ion balance of all inorganic compounds indicates that too less  $\text{NH}_4$  was measured to  
12 neutralize all  $\text{NO}_3$  and  $\text{SO}_4$  to their corresponding ammonium salts. The measured  $\text{NH}_4$  mass  
13 concentration against the predicted  $\text{NH}_4$  from the ion balance is plotted in the supplement  
14 (Fig. S9) and resulted in a slope of  $0.83 \pm 0.00$ . One uncertainty of the ion balance is  
15 introduced by the use of RIE's for the inorganic species. As shown below we consider  
16 uncertainties of RIE to be of minor importance in explaining the observed low particulate  
17  $\text{NH}_4$  concentration. It should be noted that for the calculation of the ion balance all measured  
18  $\text{NO}_3$  is considered. In addition to  $\text{NH}_4\text{NO}_3$  organic nitrates give rise to nitrate signal in the  
19 AMS, albeit with distinct difference in relative ion abundance (Alfarra et al., 2004; Fry et al.,  
20 2011; Fry et al., 2009). It was not possible to distinguish the organic and inorganic nitrate  
21 fraction based on their mass spectra with the ACSM. Since a relatively high amount of  
22 particulate organic nitrates was found in previous campaigns at CESAR using an AMS  
23 (Mensah, 2011), and the region is characterized by high  $\text{NH}_3$  emissions (Derksen et al., 2011),  
24 the potential contribution of organic nitrates to the gap in the ion balance was explored as  
25 follows.

26 In contrast to the ion balance from the ACSM data, MARGA  $\text{PM}_1$  measurements during the  
27 whole campaign showed a nearly 1:1 correlation of measured against predicted  $\text{NH}_4$  (slope of  
28 the linear regression line:  $1.03 \pm 0.00$ ,  $\text{Pearson-R}^2 = 0.97$ ), but with a negative offset of ca.  
29  $0.30 \pm 0.01 \mu\text{g m}^{-3}$ . This offset, which is at least 3 times higher than the detection limits of the  
30 MARGA, cannot be explained by including positive metal ions to the ion balance since the  
31 sum of Mg, Na, K and Ca mass concentrations had low contribution to particulate mass as  
32 mentioned in section 3.1. Thus, significant influence of their nitrate salts to total nitrate can be  
33 excluded. In addition, as the MARGA is measuring the water-soluble nitrate fraction, the

1 MARGA-NO<sub>3</sub> can be considered to be exclusively NH<sub>4</sub>NO<sub>3</sub>. This assumption is acceptable,  
2 as shown by using the MARGA-NO<sub>3</sub> instead of the ACSM-total-NO<sub>3</sub> for the ion balance of  
3 ACSM data (including ACSM-SO<sub>4</sub>, -Chl and -NH<sub>4</sub>), following a procedure given by Xu et al.  
4 (2015) who calculated the organic nitrate fraction by subtracting the inorganic nitrate  
5 concentrations measured by a particle-into-liquid sampler (PILS, see Orsini et al. (2003))  
6 from ToF-AMS total nitrate concentrations. In the Cabauw data set, the correlation of  
7 measured against predicted NH<sub>4</sub> resulted in a nearly 1:1 regression line without a significant  
8 offset (Fig. S10). This is in agreement with the MARGA internal ion balance which also  
9 indicates neutralized inorganic aerosols. Therefore, the mass concentration of nitrate groups  
10 associated with organic molecules (hereafter called organic nitrate or OrgNO<sub>3</sub>), can be  
11 estimated by subtracting the MARGA-nitrate from the ACSM-nitrate concentration. The  
12 OrgNO<sub>3</sub> time series using this approach is plotted in Fig. S11, the respective diurnal variation  
13 averaged over for each period and for the entire campaign in Fig. S12. An average mass  
14 fraction of 9% was calculated for OrgNO<sub>3</sub> (average concentration: 0.43 μg m<sup>-3</sup>) in respect to  
15 total ACSM-NO<sub>3</sub>. Note that the organic nitrate concentrations may be biased low considering  
16 that, although the nitrate concentrations from both instruments are considered PM<sub>1</sub>, the  
17 transmission efficiency of the ACSM decreases for particles with diameters between ca.  
18 800 nm to 1 μm. This may also explain the slightly negative OrgNO<sub>3</sub> values seen in Figure  
19 S11. The organic nitrate fraction shows for nearly all periods and for the whole campaign a  
20 maximum concentration in the night, followed by a decrease during the day. Particulate  
21 organic nitrates found in this study may therefore be considered as mainly semi-volatile as the  
22 evaporation from particles is dominating during warmer daytime. Due to the low temperatures  
23 within period 3, evaporation is less important during this time as seen by the daytime  
24 maximum. These findings are in agreement with previously reported relatively high AMS  
25 organic nitrate fractions by Mensah (2011) in May 2008 (0.5 μg m<sup>-3</sup>, 35% of total nitrate,  
26 5.2% of total aerosol mass) and March 2009 (0.2 μg m<sup>-3</sup>, 10% of total nitrate, 3.6% of total  
27 aerosol mass) in Cabauw.

28

### 29 **3.3 Factor analysis of organic aerosols**

30 Prior to PMF analysis, the ACSM data set was subdivided into four data sets, which were  
31 explored by PMF separately, mainly due to the operational time of the ACSM that are in the  
32 following referred as: (i) July-August-September 2012: Summer 2012; (ii) October-  
33 November-December 2012: Autumn 2012; (iii) January-February-March 2013: Winter 2013;

1 (iv) April-May-beginning of June 2013: Spring 2013. A more detailed overview of the  
2 selected seasons is given in Table S3.

3 Figure 4 summarizes the time series of PMF factor classes (two POA factors: HOA and  
4 BBOA; and two SOA factors: OOA and a humic-like substances (HULIS) related factor, see  
5 below for descriptions) found for all seasons, except for BBOA in Summer 2012. A  
6 corresponding graph dividing these PMF results into the five periods according to Fig. 2 is  
7 shown in Fig. S13. The POA profiles were constrained within ME-2 using the HOA and  
8 BBOA mass spectra found by ME-2 operated PMF analyses by Crippa et al. (2014) at the  
9 CESAR tower in Cabauw in March 2009. For the HOA profile, a constant  $a$ -value of 0.1 was  
10 found to be most suitable for every season. If observed, the BBOA  $a$ -value was set to either  
11 0.2 (Autumn 2012) or 0.3 (Winter and Spring 2013). The  $a$ -values based on different  
12 sensitivity tests for each season as described by Canonaco et al. (2013). Factor profiles  
13 including fractional contributions of marker ions ( $f_{44}$ ,  $f_{43}$ , and  $f_{60}$ ) and diurnal variations for  
14 Winter 2013 are displayed in Fig. 5 as a representative example. Corresponding graphs for  
15 every season are shown in Fig. S14 and S15, respectively. Table S4 gives an overview of the  
16 temporal correlations of each factor with external data sets, while scatter plots from Winter  
17 2013 profiles against profiles found in May 2008 at CESAR by Crippa et al. (2014) are given  
18 in Fig. S16.

19 As mentioned, no significant BBOA influence was seen in Summer 2012. Thus, a three-factor  
20 solution was chosen for this season and consequently, no BBOA time series exists at that  
21 time. For all other factors the time series are continuous on 1 October 2012, i.e. analysis of  
22 separate data files leads to a consistent result in terms of both factor profiles and  
23 concentrations. The SOA factors showed always higher contribution (54% - 84%, averaged  
24 season-wise) to total organics compared to POA (16% - 46%). For all PMF factors, no  
25 preferential wind direction was observed over the entire campaign. During the pollution  
26 events mentioned above, OOA originated mostly from the directions between  $20^\circ$  and  $180^\circ$  in  
27 respect to the tower. This is not the case for HULIS, which origins varied throughout all  
28 directions, also during pollution events.

29 The seasonal average HOA contribution to total organic mass was highest in Summer 2012  
30 and lowest in Spring 2013 (16% and 8%, respectively). All HOA diurnal patterns (Fig. 5b)  
31 showed a maximum at 7 and 11 am (LT) and a slight increase in the evening, emphasizing  
32 that its main source is related to traffic likewise to BC (see Sec. 3.1). In Winter 2013, these  
33 maxima were less distinctive comparing to the other seasons. HOA Highest temporal

1 agreements with HOA were seen by the POA tracers BC, NO<sub>x</sub> and CO ( $R^2 = 0.38, 0.47,$  and  
2  $0.47,$  respectively) over the entire campaign.

3 The BBOA profile showed a very high contribution of m/z 60, which is dominated by the  
4 C<sub>2</sub>H<sub>4</sub>O<sub>2</sub><sup>+</sup> ion. This fragment is characteristic for anhydrosugars such as levoglucosan (Alfarra  
5 et al., 2007) which are established markers of wood combustion processes (Simoneit and  
6 Elias, 2001; Simoneit et al., 1999). The fractions of m/z 60 to the BBOA profile in Autumn  
7 2012 (3.7%) and Winter 2013 (3.2%) are higher than in Spring 2013 (2.4%). As mentioned,  
8 BBOA was not found in Summer 2012. This was verified by the fact that the contribution of  
9 m/z 60 to the BBOA profile decreases for higher a-values in that season, which is an  
10 indication for the non-existence of BBOA. The highest contributions of BBOA to total  
11 organics were seen in the colder Autumn (23%) and Winter seasons (15%). This and the  
12 diurnal maximum during the evenings and nights match the expectations for a factor linked  
13 with domestic heating activities, together with the fact, that this factor was not seen during the  
14 warmer summer season. Averaged over the whole campaign, the contribution to total organics  
15 was 13%, including Summer 2012, where its fraction was set to zero. In Winter, the  
16 correlations with eBC and CO were higher ( $R^2 = 0.64$  and  $0.57,$  respectively) than over the  
17 whole campaign ( $R^2 = 0.39$  and  $0.49,$  respectively), meaning that these compounds are  
18 reasonably more attributed to domestic heating during the colder periods comparing to the  
19 contribution of heating to BC and CO during the other seasons in this region.

20 The OOA profile is similar to a MS pattern as expected for a low volatile OOA (LVOOA)  
21 factor. The correlation coefficients (Pearson- $R^2$ ) with the OOA and LVOOA spectra given by  
22 Ng et al. (2011a) are 0.94 and 0.97, respectively. Similar agreement was found compared to  
23 the LVOOA factor observed by Mensah (2011) and Crippa et al. (2014) ( $R^2 = 0.97$  and  $0.94,$   
24 respectively) at the CESAR tower in May 2008. The OOA factor showed a night-time  
25 maximum and a day-time minimum. This is rather characteristic for a semi volatile OOA  
26 (SVOOA) behavior, as well as the high agreement with NO<sub>3</sub> over the whole year ( $R^2 = 0.63$ ),  
27 as described by Lanz et al. (2007). The correlation to the LVOOA associated compound SO<sub>4</sub>  
28 is less significant ( $R^2 = 0.48$ ). OOA dominated the organic fraction in Winter and Spring 2013  
29 (47% and 48% contribution, respectively; 33% over the whole year). During the defined  
30 pollution events the increase of the OOA mass concentration (up to  $11.8 \mu\text{g m}^{-3}$ ), relative to  
31 the campaign average ( $1.05 \mu\text{g m}^{-3}$ ), is much stronger compared to the other PMF factors,  
32 demonstrating that this factor is mainly responsible the high total OA mass during these  
33 periods.

1 The so called HULIS factor showed the highest  $f_{44}$  values of all factors, increasing from  
2 Summer 2012 to Spring 2013 from 0.23 to 0.35. The HULIS factor class was first observed  
3 by Mensah (2011) in previous AMS campaigns at the CESAR tower in May 2008 and March  
4 2009. The identification and characterization of this factor class was done in the 2008  
5 campaign by the comparison with data from an ion-exchange chromatographic method for  
6 direct quantification of humic-like substances (HULIS) and from water-soluble organic  
7 carbon (WSOC) analyzed offline on a set of filters collected in parallel (Paglione et al., 2014).  
8 The HULIS factor provided the highest contribution to the total organic mass over the entire  
9 campaign (41%) and was the dominant factor in Summer and Autumn 2012. Since it had no  
10 distinct diurnal variation and preferential wind direction, it can be considered as regional  
11 background aerosol at this rural site. Additionally, the variation between the seasonal average  
12 concentrations of HULIS within the ACSM data set is less than  $\pm 10\%$ . Also the comparison  
13 to the most important tracers (Table S4 in the supplement) showed no preferential attribution,  
14 either to a low-volatile ( $R^2 = 0.41$  with  $\text{SO}_4$ ), semi-volatile ( $R^2 = 0.39$  with  $\text{NO}_3$ ) or to primary  
15 organic aerosol ( $R^2 = 0.47$  with eBC). These characteristics were also reported for the HULIS  
16 factor found at CESAR in May 2008 (Crippa et al., 2014; Mensah, 2011). The correlation of  
17 the sum of the secondary inorganic species  $\text{NO}_3$  and  $\text{SO}_4$  with the sum of the OOA and  
18 HULIS time series gives a coefficient of  $R^2 = 0.70$ , which is slightly higher than with OOA  
19 only ( $R^2 = 0.67$ ). This might confirm the SOA character of the HULIS factor. The reason why  
20 HULIS was the dominant factor in Summer and Autumn 2012, is due to the lower mass  
21 concentrations of the other factors compared to the remaining periods. In turn, OA mass  
22 increased during pollution events mainly due to the increase of the other SOA factor, namely  
23 OOA. A number of studies are published with different theories on the formation and sources  
24 of atmospheric HULIS. It shows similarities to terrestrial humic acids (HA) and fulvic acids  
25 (FA) due to their (poly-) acidic nature, but with lower molecular weight ( $< 1000$  amu) than  
26 HA or FA (Graber and Rudich, 2006; Kiss et al., 2003). On the other hand, solid-phase  
27 extraction protocols for HULIS associate them with the more hydrophobic fraction of water-  
28 soluble aerosols (e.g. Varga et al. (2001)). Graber and Rudich (2006) suggested that the  
29 formation of HULIS happens by oligomerization of lighter organic acids in liquid droplets in  
30 the atmosphere within time scales of hours to days. This emphasizes, that HULIS is an  
31 ubiquitous background factor at Cabauw, characterized as regionally well mixed aerosol of  
32 long atmospheric lifetime.

33 Note that the correlation (Pearson- $R^2$ ) of the POA factors with eBC data is relatively low  
34 ( $R^2 = 0.38$  and  $0.39$  with HOA and BBOA, respectively), while in turn HULIS shows a higher

1 correlation with eBC,  $R^2 = 0.47$ . Furthermore, correlation coefficients of the POA factors with  
2 CO and  $\text{NO}_x$  time series do not exceed values above 0.47. Low correlations of POA and those  
3 tracers, e.g. HOA with CO or BC varying from far below 0.5 to slightly above 0.5 were also  
4 seen in a number of previous studies at remote and rural sites (Canonaco et al., 2013;  
5 Minguillón et al., 2015; Schmale et al., 2013; Setyan et al., 2012), including Cabauw (Crippa  
6 et al., 2014; Mensah et al., 2011). There, low concentrations of POA factors and (e-)BC to  
7 total aerosol mass were determined and resulted in higher uncertainties for the identification  
8 of these factors, likewise in this study. Nevertheless, the correlations POA factors with CO  
9 and  $\text{NO}_x$  are still by far higher than the correlation of these tracers with the SOA factors,  
10 which, together with the very high agreement of m/z 60 with BBOA, underlines the correct  
11 identification of HOA and BBOA. The higher correlation of HULIS with eBC can be  
12 understood in the light of a study by Andreae and Gelencser (2006) who pointed out that the  
13 fiber filters, as used by the MAAP, loaded with macroscopic amounts of humic like  
14 substances samples look very dark brown or nearly black. A possible partly interference of  
15 HULIS with BC measurements can therefore not be excluded and would explain why the  
16 HULIS factor, in contrast to the POA factors, has a relatively high correlation coefficient with  
17 BC data. The use of instruments like an aethalometer or a particle soot absorption photometer  
18 as used in other studies would reduce these interferences (Andreae and Gelencser, 2006;  
19 Petzold et al., 2013), but were not available during the campaign. Though given the relatively  
20 low contribution of eBC to total aerosol mass, a possible partial interference with HULIS is of  
21 minor importance regarding total aerosol masses.

22 The source apportionment as described here used a data set which was subdivided into the  
23 four seasons prior to PMF analysis. A single PMF analysis of the whole data set with  
24 constrained HOA and BBOA profiles lead to solutions with a highly overestimated BBOA  
25 factor in the summer, compared to the results when the seasons were explored individually  
26 (see Fig. S17 and S18 in the supplement). Furthermore, the contributions of individual factors  
27 change significantly in some periods, especially for the OOA factor during pollution events.  
28 This is mainly driven by the different OOA-*f44* and -*f43* values. This behavior is independent  
29 from applied  $\alpha$ -values for BBOA may result from the uncertainty of this statistical tool. Since  
30 there was no evidence of BBOA seen in the separate analysis of the summer period (e.g. low  
31 fraction of m/z 60 in the organic mass spectrum and no correlation of the constrained BBOA  
32 factor with POA tracers, no matter which  $\alpha$ -value was used), the solutions derived from the  
33 single PMF analysis was reasonably rejected.

1

### 2 **3.4 Composition and sources of aerosols during pollution events**

3 The investigation of the aerosol composition during the pollution events showed that the  
4 majority was contributed from secondary aerosols. As an example, Fig. 6 displays average  
5 abundances during two selected periods (17 to 21 August 2012 and 16 to 27 January 2013),  
6 where the organic fraction is further distinguished into the PMF factors. Nitrate and organics  
7 are still the dominant species, while the primary aerosol components (BC, HOA, BBOA) have  
8 even less influence than averaged over the respective season. An exception is seen from  
9 BBOA, which contribution is reasonably higher during the latter pollution event with very  
10 low temperatures, when domestic heating sources most likely increased. But even at this time,  
11 primary organics do not exceed 11% of total mass on average.

12 Since the major inorganic components  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  are produced by atmospheric  
13 processes, they are considered as secondary aerosols. Together with the high abundance of  
14 SOA (OOA, HULIS), chemically aged aerosol components have the largest impact on total  
15 particulate mass (up to 90%) at Cabauw. The largest effect on a potential reduction of  
16 particulate mass can therefore be achieved by reducing  $\text{NO}_x$  and/or  $\text{NH}_3$  emissions, the  
17 anthropogenic precursors of particulate  $\text{NH}_4$  and  $\text{NO}_3$ . Indeed, on 16 January 2013 highest  
18  $\text{NO}_x$  values were observed compared to the whole campaign (daily mean:  $96 \mu\text{g m}^{-3}$ ; seasonal  
19 average:  $29 \mu\text{g m}^{-3}$ ). Also the highest  $\text{NH}_3$  values were obtained between 17 and 19 August  
20 2012 (daily means:  $26\text{--}28 \mu\text{g m}^{-3}$ ; seasonal average:  $10 \mu\text{g m}^{-3}$ ). These ammonia values are  
21 higher than previously reported for Cabauw, e.g. by Derksen et al. (2011) in May 2008  
22 (approximately  $20 \mu\text{g m}^{-3}$ ). Lolkema et al. (2015) gave an annual average of  $5.3 \mu\text{g m}^{-3}$  for  
23 2013 in this region.

24

## 25 **4 Conclusions**

26 This work provides chemical composition data of atmospheric aerosols acquired during one  
27 year at the CESAR tower in Cabauw, the Netherlands, which is a representative rural site for  
28 North Western Europe. The concentration of submicron particles from combined ACSM and  
29 MAAP data showed 12 exceedances from the WHO  $\text{PM}_{2.5}$  daily mean limit. The respective  
30 campaign average of  $9.5 \mu\text{g m}^{-3}$  approached the WHO  $\text{PM}_{2.5}$  annual mean limit. Taking  
31 MARGA  $\text{PM}_{2.5}$  into account the number and proportions of these exceedances are even  
32 higher, emphasizing the importance of these high ACSM  $\text{PM}_1$  results shown here which

1 represent lower limits. As carbonaceous compounds are estimated to be five times more toxic  
2 than inorganic particles (Lelieveld et al., 2015) MARGA data alone would not give  
3 sufficiently possible implications regarding adverse health effects. While few people live in  
4 the direct vicinity of the measurement site, the high aerosol concentration measured at the site  
5 can be considered to represent the regional background. This regional background is adding to  
6 local aerosol contributions in high populated urban sites (Pandis et al., 2013), namely the 4  
7 largest cities of the Netherlands which have a distance of 40 km or less from the CESAR  
8 tower.

9 Particulate mass loadings found at this rural site are dominated by secondary aerosol  
10 formation through atmospheric gas phase chemistry and particle phase aging. It is shown that  
11 particulate ammonium nitrate is the major aerosol component (39% on average) and  
12 represents the more hygroscopic aerosol fraction. Since the human respiratory system is  
13 characterized by high humidity more hygroscopic aerosols have a higher deposition tendency  
14 within the human lung than less water soluble particle compounds (Asgharian, 2004; Broday  
15 and Georgopoulos, 2001). With special regard to adverse health effects this is very crucial  
16 because Asgharian (2004) also found that especially hygroscopic submicron particles can  
17 deposit in the entire lung. The high ammonium nitrate fraction also implies that inorganic SA  
18 reduction in Cabauw can be most efficiently achieved through the reduction of gaseous  
19 ammonia emissions in the area.

20 As indicated by model results for the South Western United States from Zhang and Wu  
21 (2013), the reduction of  $\text{NH}_3$  emissions, in conjunction with already implemented  $\text{SO}_2$  and  
22  $\text{NO}_x$  emission reductions, can further reduce  $\text{PM}_{2.5}$  than reducing  $\text{SO}_2$  and  $\text{NO}_x$  emissions  
23 alone, particularly for regions with high emissions of  $\text{NH}_3$  from agricultural sources. The  
24 latter is clearly the case for Cabauw with its high number of animal husbandry and the use of  
25 nitrogen containing fertilizers around the CESAR tower. Banzhaf et al. (2013) derived similar  
26 conclusions for  $\text{PM}_{10}$  using different emission scenarios within domains covering Germany  
27 and Europe. Applying a 3d chemical transport model over Europe Megaritis et al. (2014)  
28 found that a reduction of  $\text{NH}_3$  emissions by 50% would have a much higher effect on  
29 reducing  $\text{PM}_{2.5}$  than decreasing  $\text{NO}_x$  emissions by 50%. The latter scenario would even result  
30 in negative side effects such as higher tropospheric ozone concentrations (especially in  
31 summertime 4% over Western Europe and up to 40% in major urban areas) and higher  
32 amounts of particulate sulfate and OA by 8% and 12%, respectively, in winter.



1 The local mitigation of organic aerosol mass (29% contribution on average) is more  
2 challenging, as secondary organic aerosols are highly abundant at the Cabauw site (74% and  
3 22% of OA and total PM<sub>1</sub> on average, respectively). The presented data set shows a large and  
4 ubiquitous HULIS fraction (37%) which based on diurnal patterns and a lack of correlation  
5 with wind direction can be considered as long-range background aerosol formed from  
6 atmospheric aging processes. In turn, primary organic aerosols emitted mainly from traffic  
7 and biomass burning (12% and 13% of OA on average) have only minor importance. For a  
8 more detailed identification of the SOA sources compound specific measurements of OA as  
9 well as routine VOC monitoring are needed.

10 Finally, the presented data set and interpretations provide an important contribution to the  
11 EU-FP7-ACTRIS project which supported building of new knowledge as well as policy  
12 issues on climate change, air quality, and long-range transport of pollutants on a European  
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14

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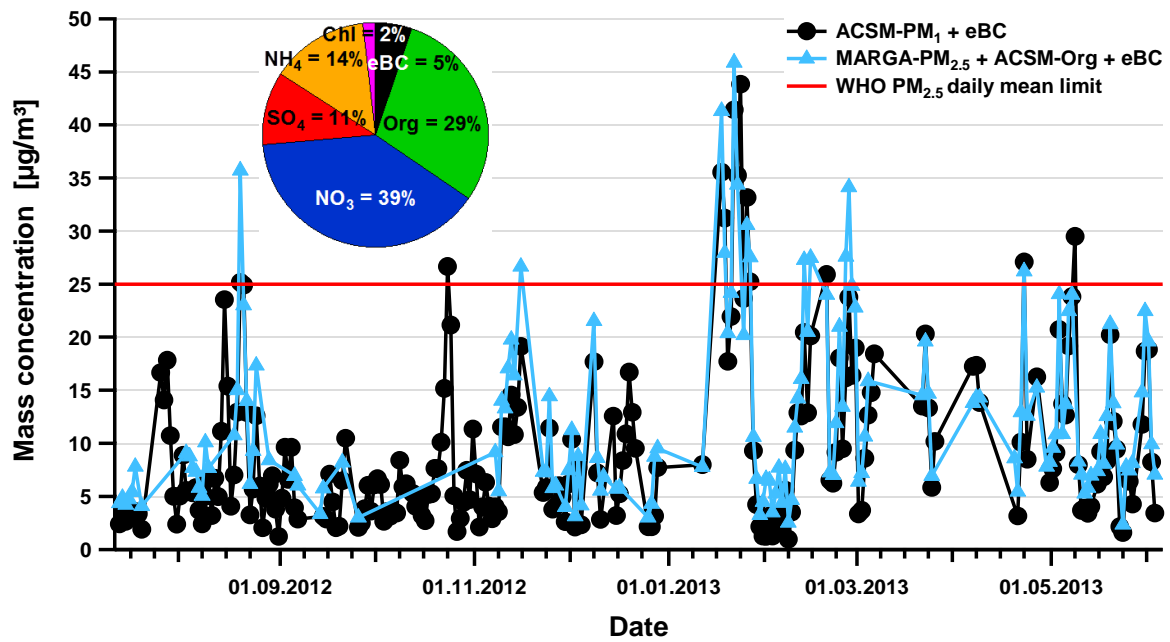
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1 Table 1: Results of the ACSM to MARGA and ACSM to AMS comparisons for individual  
 2 species and the respective total masses. Note that for comparison with the MARGA total mass  
 3 concentrations, only the ACSM inorganic species were considered.

		Slope	intercept [ $\mu\text{g m}^{-3}$ ]	$R^2$
Chl	MARGA	$0.49 \pm 0.02$	$0.11 \pm 0.01$	0.24
	AMS	$0.67 \pm 0.01$	$-0.01 \pm 0.01$	0.31
$\text{NH}_4$	MARGA	$0.88 \pm 0.01$	$0.07 \pm 0.01$	0.93
	AMS	$0.82 \pm 0.03$	$0.01 \pm 0.02$	0.71
$\text{SO}_4$	MARGA	$0.63 \pm 0.01$	$-0.08 \pm 0.01$	0.86
	AMS	$0.49 \pm 0.02$	$-0.18 \pm 0.02$	0.76
$\text{NO}_3$	MARGA	$1.23 \pm 0.01$	$-0.37 \pm 0.03$	0.96
	AMS	$1.17 \pm 0.02$	$-0.04 \pm 0.02$	0.89
Organics	AMS	$1.03 \pm 0.04$	$0.07 \pm 0.04$	0.73
Total	MARGA	$1.05 \pm 0.01$	$-0.70 \pm 0.06$	0.93
	AMS	$0.90 \pm 0.02$	$-0.02 \pm 0.07$	0.84

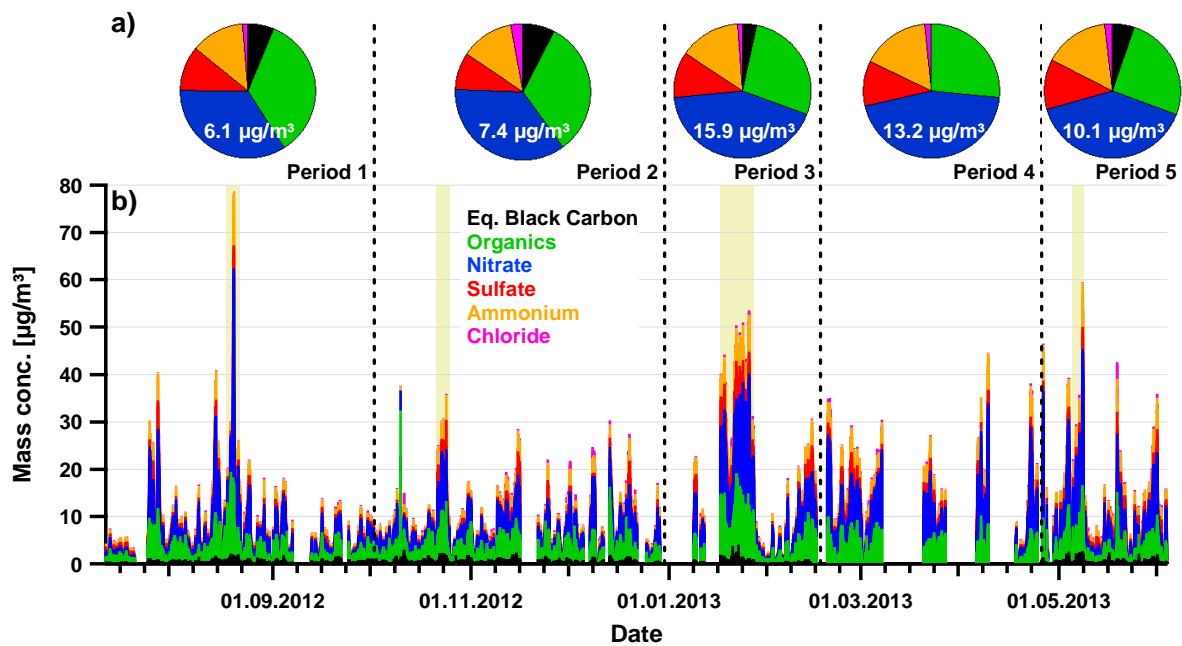
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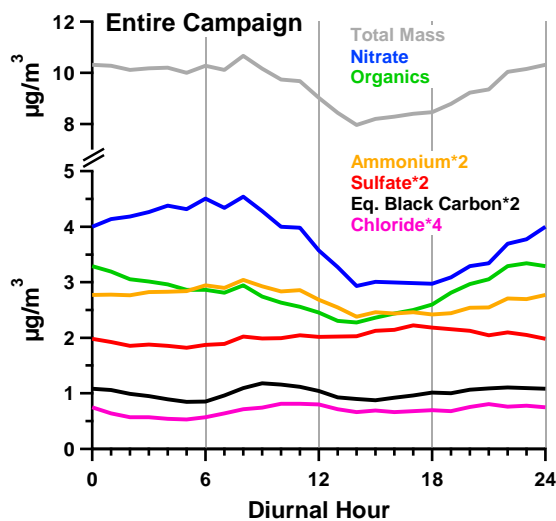
2 Figure 1: Time series of the daily mean. The black line represents the sum of eBC and all  
 3 ACSM species, the blue line the sum of eBC, ACSM organics and all MARGA-PM<sub>2.5</sub>  
 4 species. The pie chart shows the fractional abundances of individual eBC and ACSM species  
 5 averaged over the whole campaign. For the determination of the daily means missing eBC  
 6 data was filled with zero values, thus deriving lower concentration limits.

7



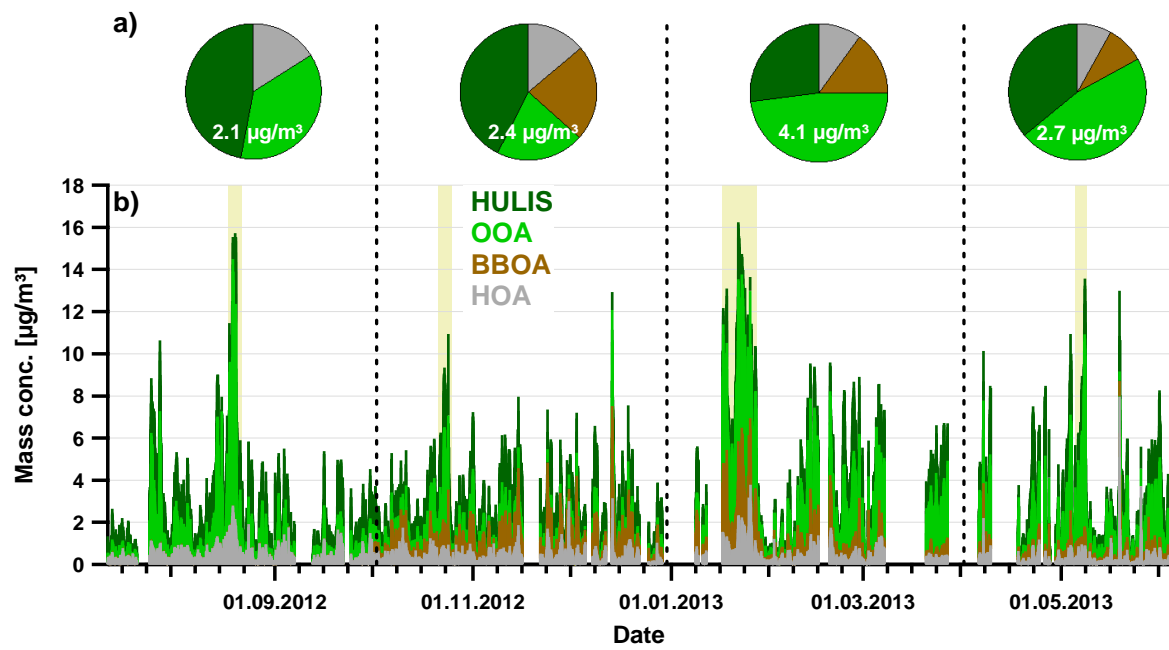
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 2 Figure 2: Overview of the ACSM campaign: a) Pie charts of average fractional abundances of  
 3 aerosol species, separated in five periods. The respective average total mass concentration is  
 4 written inside the pie chart. b) Stacked time series of mass concentrations of aerosol species.  
 5 Pollution events are indicated by shaded areas.

6

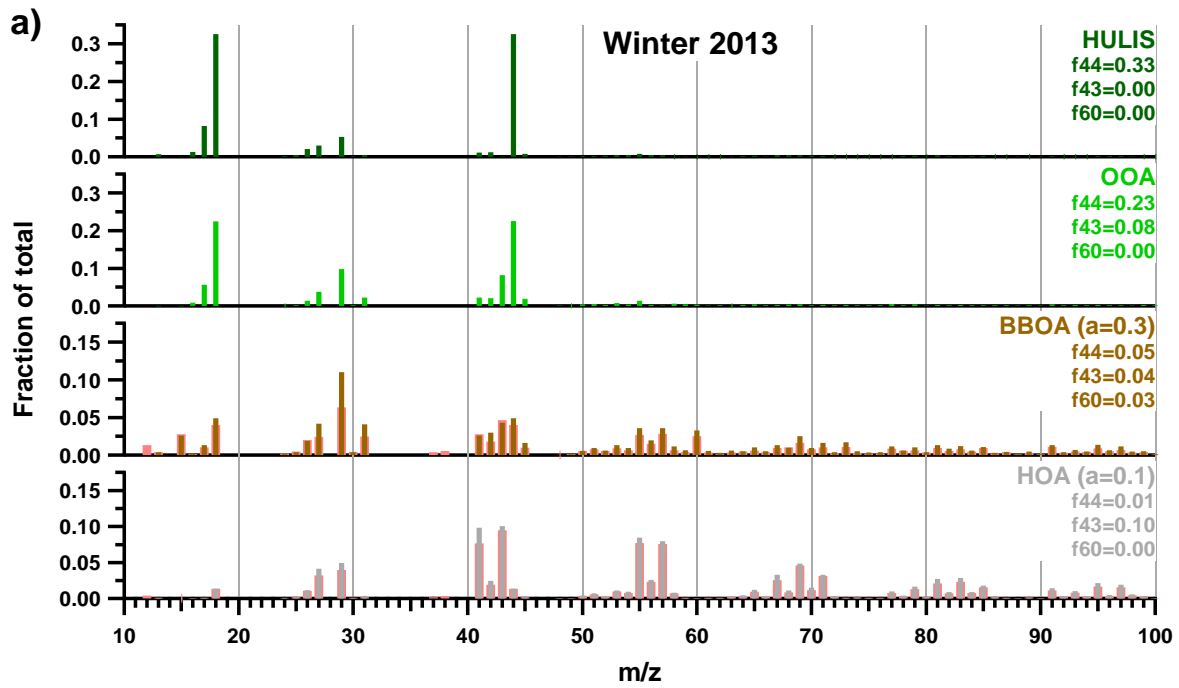


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 8 Figure 3: Diurnal variation (local time, LT) of individual species and the total mass, averaged  
 9 over the whole ACSM campaign

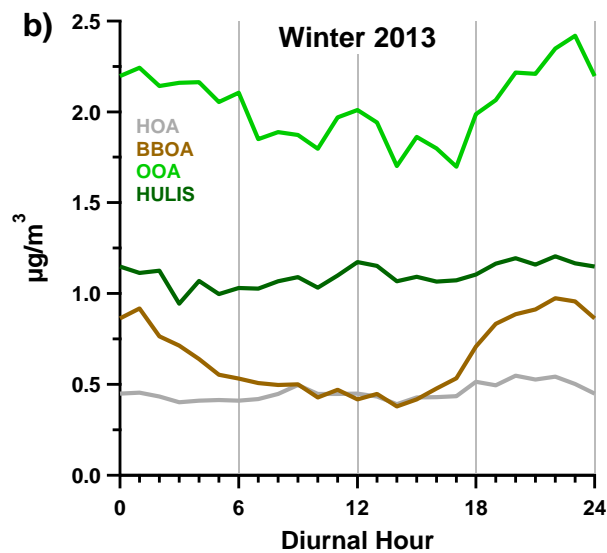
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1  
 2 Figure 4: Overview of ACSM PMF factors: a) Seasonal pie charts of the factor contributions.  
 3 The respective average total organic concentration is written inside the pie chart. b) Stacked  
 4 time series of mass concentrations. Shaded areas represent highly polluted events.  
 5



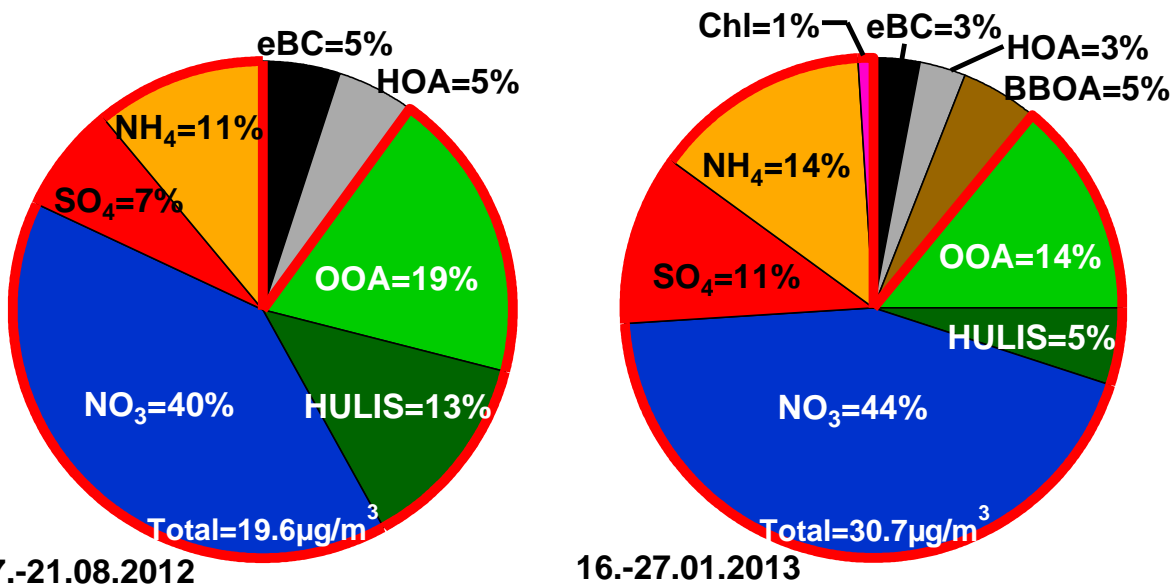
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3 Figure 5: a) Mass spectra of ACSM PMF factors and b) average diurnal variations (LT) of  
 4 ACSM factors found in Winter 2013. For the constrained profiles HOA and BBOA, the  
 5 applied a-value is written in brackets. Corresponding reference spectra are shown by red bars.  
 6 Note that the y-axis scales of the POA profiles are zoomed by a factor of 2 comparing to SOA  
 7 profiles.

8



1 17.-21.08.2012 16.-27.01.2013

2 Figure 6: Average contributions of individual aerosol species and PMF factors during selected

3 pollution events. Surrounded red regions represent the secondary aerosol fraction.