Responses to anonymous referee #1

Received and published: 18th January 2016

We thank the reviewer for the careful review of our manuscript; the comments and suggestions are greatly appreciated. All the comments have been addressed. In the following please find our responses to the comments one by one and the corresponding changes made to the manuscript. The original comments are shown in italics.

1) The scientific quality and presentation of the manuscript are good. The manuscript will need copy-editing because there are numerous grammatical errors, although the text is still clear. There is agreement between the various instruments utilised at the site (ACSM vs SMPS vs MARGA), and the PMF analysis follows established procedures. I do have questions about the determination of organic nitrates and about the correlations between the OA components and tracers, and these questions are given below. On the other hand, the scientific significance of the manuscript is not clear. Aerosol mass spectrometry (AMS) including ACSM measurements are fairly standard now, and AMS measurements were previously carried out at this site, as indicated in the manuscript. I acknowledge that the long duration of the measurements in this manuscript is somewhat novel, but it is not clear how having simply more measurements provides new significant insight into atmospheric chemistry. This concern will need to be addressed before final publication, in addition to the comments provided below.

Response:

Fortunately, copy-editing is standard in ACP. We are relieved though, that despite some language issues the manuscript is understandable and clear.

The reviewer is right that a publication just presenting longer records obtained with AMS or ACSM is not per se novel enough to warrant publication in a quality journal such as ACP, also considering that two AMS campaigns were previously performed in Cabauw. We emphasize here that the focus of this work extends beyond the presentation of a larger data set for this site:

In this study, we showed that the major fraction of atmospheric aerosol at this site is comprised of secondary aerosol (SA) which is chemically formed in the atmosphere. SA also dominates the high mass loadings during the pollution episodes exceeding air quality standards. The long term aerosol mass spectrometric data provided by this work is important for the understanding of the chemical processes leading to such high aerosol masses which are unexpected for a rural site like Cabauw. This information is necessary for potential mitigation of particle masses. The findings presented here were not seen in previous studies due to their limited time of sampling.

General Comments:

2) Organic nitrates: The difference in the concentration of nitrate measured by the ACSM and MARGA is not a direct means of identifying and quantifying the presence of organic nitrates. Is there other evidence from the ACSM or other instruments to support the conclusion that these compounds are present and account for 9% of the total ACSM NO3? If not, then this conclusion is rather weakly supported by the data.

Response:

We followed a procedure given by Xu et al. (2015) who calculated the organic nitrate fraction by subtracting the inorganic nitrate concentrations measured by a particle-into-liquid sampler (PILS, see Orsini et al. (2003)) from ToF-AMS total nitrate concentrations. Those instruments have similar uncertainties as the respective instruments reported here. In the revised manuscript we provide following additional evidence for the presence of $OrgNO_3$ in the aerosol: the use of external data from the MARGA to determine the inorganic nitrate in the ACSM data set improved the agreement of measured against predicted ACSM-NH_4, resulting in a nearly 1:1 regression line without a significant offset. This is in agreement with the MARGA internal ion balance which also indicates neutralized inorganic aerosols. All evidence together makes a strong case that the difference of AMS total nitrate to MARGA nitrate is most likely due to the presence of organic nitrates. These findings and the previously reported relatively high AMS organic nitrate fractions by Mensah (2011) in May 2008 (0.5 µg m^{-3}, 35% of total nitrate, 5.2% of total aerosol mass) and March 2009 (0.2 µg m^{-3}, 10% of total nitrate, 3.6% of total aerosol mass) in Cabauw show strong evidence of the presence of organic nitrates during this campaign and the reliability of its estimation as presented in the manuscript.

To provide a more detailed description this part was changed in the revised manuscript as follows:

"This assumption is acceptable, as shown by using the MARGA-NO_3 instead of the ACSM-total-NO_3 for the ion balance of ACSM data (including ACSM-SO_4, -Chl and -NH_4), following a procedure given by Xu et al. (2015) who calculated the organic nitrate fraction by subtracting the inorganic nitrate concentrations measured by a particle-into-liquid sampler (PILS, see Orsini et al. (2003)) from ToF-AMS total nitrate concentrations. In the Cabauw data set, the correlation of measured against predicted NH_4 resulted in a nearly 1:1 regression line without a significant offset (Fig. S10). This is in agreement with the MARGA internal ion balance which also indicates neutralized inorganic aerosols. Therefore, the mass concentration of nitrate groups associated with organic molecules (hereafter called organic nitrate or $OrgNO_3$), can be estimated by subtracting the MARGA-nitrate from the ACSM-nitrate concentration. The $OrgNO_3$ time series using this approach is plotted in Fig. S11, the respective diurnal variation averaged over the whole campaign in Fig. S12. An average mass fraction of 9% was calculated for $OrgNO_3$ (average concentration: 0.43 µg m^{-3}) in respect to total ACSM-NO_3. The organic nitrate fraction shows a maximum concentration in the night, followed by a decrease during the day. These findings are in agreement with previously reported relatively high AMS organic nitrate fractions by Mensah (2011) in May 2008 (0.5 µg m^{-3}, 35% of total nitrate, 5.2% of total aerosol mass) and March 2009 (0.2 µg m^{-3}, 10% of total nitrate, 3.6% of total aerosol mass) in Cabauw."

3) Correlation of PMF time series with tracers: The correlations of the PMF factors with the tracer time series seems very low for HOA, BBOA and HULIS, and the correlation coefficients (R2) are all below 0.5 for all the tracers used in this study. For example, the HULIS factor, which is presumably secondary in nature, exhibits the highest correlation with BC rather than one of the primary combustion factors (i.e. HOA and BBOA). This lack of correlation indicates that PMF is not identifying OA components that can be unambiguously associated with specific sources. The lack of correlation should be examined in more detail as it calls into question the validity of the PMF results.

Response:

As mentioned in the manuscript the HULIS factor was found as high oxygenized background aerosol in Cabauw, which is characterized by the low temporal variation and therefore reasonably low correlation coefficients with most of the tracers. On the other hand the reviewer noticed correctly that the correlation results given as Pearson-R^2 in case of the POA factors with BC data don't seem to be as high as seen in previous studies showing PMF/ME-2 data. This has several reasons:

The black carbon data used in this study derived from a MAAP, which measures simultaneously the radiation penetrating through and scattered back from a particle-loaded fiber filter. Andreae and Gelencser (2006) pointed out that non-BC light-absorbing carbonaceous matter like brown carbon can interfere with BC measurements using this instrument. They also stated that filters loaded with macroscopic amounts of humic like substances (HULIS) samples look very dark brown or nearly black. This would imply a possible interference of HULIS with BC. Consequently this may explain why the HULIS factor has a relatively high correlation with BC. In summary, black carbon measured by the MAAP can have three main sources: traffic and biomass burning, represented by the HOA and BBOA factors, respectively, and the interference with HULIS. All three sources are independent from each other, leading to the observed correlation results. The use of instruments like an aethalometer or a particle soot absorption photometer as used in other studies would reduce these interferences (Andreae and Gelencser, 2006; Petzold et al., 2013), but were not available during the campaign.

As expected, the gaseous tracers NO_x and CO exhibited the highest R^2 values with HOA, and higher correlations with BBOA than with both SOA factors.

In the revised manuscript the respective part was changed to:

“Note that the correlation (Pearson-R^2) of the POA factors with eBC data is relatively low ($R^2 = 0.38$ and 0.39 with HOA and BBOA, respectively), while in turn HULIS shows a higher correlation with eBC, $R^2 = 0.47$. This can be understood in the light of a study by Andreae and Gelencser (2006) who pointed out that the fiber filters, as used by the MAAP, loaded with macroscopic amounts of humic like substances samples look very dark brown or nearly black. This implies an interference of HULIS with BC measurements and in consequence explains why the HULIS factor, in contrast to the POA factors, has a relatively high correlation coefficient with BC data.”

Specific Comments:

4) P35121, L20: What is the difference between intensively and extensively managed grassland?

Response:

The phrase “intensively managed” agricultural land refers to the extended use of fertilization, irrigation or drainage techniques. In case of grasslands this definition is also applied to fields where, with respect to the agricultural area, a relatively high amount of farm animals are hold in order to optimize the respective production. Consequently, “extensively managed” areas refer to the opposite: keeping the pasture area in their natural conditions and using them with less numbers of animals. Since these phrases are common agricultural definitions, the authors decided to not explain them in detail.

5) P35122, L2: Remote sensing is a very general term. The manuscript should specify exactly which remote sensing measurements are made at the tower site.

Response:

In the revised manuscript, we have modified this sentence as follows:

“In addition, other meteorological data like precipitation, radiation and remote sensing, including lidar, radar and radiometer techniques, are acquired at the tower and submitted to the CESAR data base.”

6) Page 35123, L27: In contrast with what is implied in the text, I believe that the Middlebrook et al. (2012) CE correction algorithm also accounts for high ammonium nitrate.

Response:

We agree with the reviewer that the ammonium nitrate mass fraction (ANMF) is used as a parameter within the algorithm published by Middlebrook et al. (2012). Specifically ANMF is used when the ratio of measured to predicted NH_4 is higher than 0.75. Otherwise a different equation using just this ratio is applied to determine the CE in the Middlebrook algorithm. For the Cabauw ACSM data set, where $OrgNO_3$ could only be determined from the combined ACSM and MARGA datasets, the ratio of measured to predicted NH_4 varies around 0.75, which lead to unreasonable discontinuities of CE values when applying the Middlebrook algorithm. The authors agree that the current explanation is misleading. In the revised manuscript the respective part was changed to:

“In contrast to the commonly used constant value of 0.5 this CE correction accounts for the high ammonium nitrate mass fraction (ANMF) found at this site and is thus more suitable for the data presented here. Another algorithm for composition dependent CE determination (Middlebrook et al., 2012) was also tested for its validity. It uses a threshold ratio of measured to predicted NH_4 to switch between two different equations to determine the CE. The threshold value of 0.75 is close to the observed ratio of measured over predicted NH4 of this data set, resulting in large discontinuities of CE values and in consequence, discontinuous changes in aerosol mass concentrations. In other words, the Middlebrook algorithm is not suitable for data sets showing at the same time low ratios of measured to predicted NH_4 and high AMNF's."

7) Page 35124, L5 – L8: Why was the detection limit not calculated during the measurement period or afterwards using data from the measurement period? Data from periods when the instrument was sampling behind a particle filter could be used for this analysis.

Response:

Unfortunately, there were no ACSM measurements done during the presented campaign where a separate particle filter was introduced in the sample line, in addition to the filter included in the gas-phase background filter cycle as described by Ng et al. (2011). Furthermore, the ACSM software version used in this study could not show data acquired during the filter cycle measurements (e.g. closed mass spectra/time series), which would be needed for the determination of the detection limits. The software could only show the differential mass spectra/time series.

8) Page 35125, L23 – 29: The correction for the wall loses in the 60 m sampling line is a critical point for the manuscript. However, the description of how the losses were calculated or estimated is not sufficient. Only a reference to a personal communication is provided. Given that this correction can impact the aerosol measurements substantially – by 33% as indicated by the authors – the manuscript must contain a detailed explanation of how the aerosol losses in the sampling line are determined.

Response:

We agree with the reviewer that the correction and explanation for these losses is not sufficient enough.

In the revised manuscript we used now the particle density deriving from the chemical composition not as the campaign average but time resolved for each data point. In addition we introduced SMPS data which is now size dependently corrected as published by Henzing (2011). The description of the sampling losses of the 60 m inlet for eBC given in the manuscript derived from a series of measurements at the Cabauw tower performed in a previous campaign. Unfortunately these results are not published yet. To clarify how these losses were determined in the revised manuscript and to account for a comment from referee #2, the loss description was changed as follows:

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

Please note that these losses influenced only data acquired by the MAAP and SMPS. Since the contribution of eBC is rather low (average: 5%) a potential overall error for total aerosol masses is low and would not significantly alter one quintessence of the paper, namely total mass concentrations above the air quality limits.

As a consequence of the newly evaluated SMPS data the correlation values between ACSM+MAAP data with SMPS data changed as seen in Fig. S3 and S4 in the revised supplement. Nevertheless, the overall qualitative and quantitative agreement is still given except that the ACSM+MAAP data is now overestimating the total PM_1 mass by 16%, excluding the eBC data the ACSM overestimates total mass by 12%. As seen in Fig. S3 the difference between both systems is significantly higher during the pollution events 16 to 27 January 2013 and 5 to 8 May 2013. Since the quantitative agreement with the MARGA is much higher at these times the discrepancy to the SMPS is likely due to the fact that the losses within the 60 m inlet could not be corrected for individual species as mentioned above. Therefore the following paragraph was added at the end of the cross validation chapter in the revised manuscript:

"Major discrepancies to the SMPS especially during some of the pollution events like 16 to 27 January 2013 and 5 to 8 May 2013 (see below) can be explained by the correction of losses through the 60 m inlet line which was done size dependently and did not account for losses of individual species as mentioned in chapter 2.3. As the quantitative agreements of individual inorganic species as well as of total inorganics between the ACSM and the MARGA during these periods are much higher, the mass loadings determined from these instruments are more reliable than the SMPS data."

9) Page 35126, L13 – L16: During the measurements with the MARGA system, a polyethylene tube was used as the sampling line. Could the use of a non-conducting material for the line lead to substantial electrostatic deposition of the particles to the walls of the tube?

Response:

Indeed, a polyethylene (PE) tube can potentially enhance wall losses of particles comparing to stainless steel tubes. The MARGA-inlet system at the Cabauw tower as used for this study was previously described by Schaap et al. (2011). It actually did not only consist of PE tubes but of a series of components reducing particle losses. They investigated wall losses on a similar system and found only minor concentration losses for several compounds of 2% and less. A more detailed description was added in the revised manuscript:

"The sample air was transferred into the instrument within a polyethylene („Polyflo") tube with an inner diameter of 0.5" (= 1.27 cm) and a sample flow of 16.7 L min^{-1}, which is either directed through a PM_1 or a $PM_{2.5}$ size selective head. A detailed description of the MARGA inlet system at the Cabauw tower was previously described by Schaap et al. (2011). There, wall losses were investigated and found to be less than 2% for several gaseous and particulate compounds."

10) Page 35129, L7: Why is SO2 included in the MARGA PM2.5 mass? In the atmosphere, this compound is found in the gas phase.

Response:

We thank the reviewer for pointing out this mistake. Not only SO_2 but all gas phase compounds HNO_2, HNO_3 and HCl were mistakenly added to total aerosol masses. Nevertheless, the conclusions deriving from these calculations did not change. In the revised manuscript, the resulting time series "MARGA $PM_{2.5}$ + ACSM-Org + eBC" in Fig. 1 was exchanged and the sentence was changed to:

Nevertheless, the average total mass derived from the combination of the MARGA $PM_{2.5}$ data (including all water soluble inorganic components NO_3, NH_4, SO_4, Cl, Na, K, Mg, and Ca), MAAP eBC and ACSM PM_1 organics resulted in 12.5 µg m^{-3} during this time, clearly exceeding the WHO $PM_{2.5}$ annual mean limit (10 µg m^{-3}) by 25%.

The reader may now notice that the concentration values of MARGA $PM_{2.5}$ + MAAP eBC + ACSM PM_1 Organics (light blue time series in Fig. 1) decreased reasonably because the mentioned gas phase data was excluded. On the other hand, more data points are now seen. This is due to the fact that data coverage of the MARGA $PM_{2.5}$ data is better than for the MARGA gas phase data.

11) Page 35129, L9: It appears that there is an error on this line and the concentration for the annual mean limit should be 10 µg m-3 rather than 25 µg m-3 as is currently written.

Response:

The value is indeed wrong. In the revised manuscript it was changed from 25 to 10 µg m^{-3}.

12) Page 35130, L6 – L9: This sentence is confusing. First, it is written that the pollution events are highlighted in green, but (to my eye) the highlighting is grey. Second, there are four periods that are highlighted in Figure 2, but only three periods are listed in the text. The dates for the missing period should be given as well.

Response:

The authors agree that the color used for highlighting cannot be designated unambiguously. To keep it simple, we renamed it as just “shaded”. Figure 2 is the only figure where two different colors were used for shaded areas. Therefore, the shading for the period where ACSM and AMS data were overlapping was removed in this figure in the revised manuscript. Consequently, the captions from Figures 1 and 4 as well as from several figures in the revised supplement file were changed by calling the “green shaded” areas as just “shaded” instead of giving them a certain color. Furthermore and accounting for a comment from referee #2, the sentences on page 35130, lines 6-8, were changed in the revised manuscript to:

“The most significant pollution events (17 to 21 August 2012, 21 to 25 October 2012, 16 to 27 January 2013, and 5 to 8 May 2013) are highlighted with shaded backgrounds in Fig. 2. During the last three periods, northerly and north-easterly winds dominated.”

13) Page 35132, L21: From Figure S10, it appears that the intercept is negative rather than positive (i.e. –0.80 versus 0.80). The sign is important as there is likely a small amount of dust and perhaps sea salt which is measured by the SMPS and not the ACSM that is responsible for the non-zero intercept value.

Response:

Indeed, the value in the main text has a wrong algebraic sign. As described in the respond to comment #8 we introduced newly evaluated SMPS data in the revised manuscript by which the values changed. The intercept is now -1.05 ± 0.06 but still negative. We thank the reviewer for pointing out that a negative offset infers influence from sea salt or dust aerosols, which can be detected well by the SMPS and MARGA but not by the ACSM with a sufficient sensitivity. Therefore we added a small discussion to this section in the revised manuscript:

"The negative offset can be explained by minor influences of sea salt and dust particles, which can be detected well by the SMPS and MARGA but not by the ACSM with a sufficient sensitivity. But the low value of the intercept shows already that the uncertainty introduced by these aerosol components is rather low in general. This can also be explained by the low concentrations of Mg, Na, K and Ca as measured by the MARGA (see below) and the assumption that the majority of dust particles is most likely found in particles with diameters larger than 1 or even 2.5 µm (Finlayson-Pitts and Pitts (2000) and references therein)."

14) Page 35133, L18 – 20: Why couldn't the fragmentation table be adjusted? Adjustment of the fragmentation table is fairly standard during analysis of AMS data. If it is believed that the fragmentation table may be responsible for the underestimation of SO4, then the authors should explore making possible adjustments of the values in the table.

Response:

We agree with the reviewer that for AMS data a proper adjustment of the fragmentation table is recommended especially for unit mass resolution data, which is produced by the ACSM, too. Unfortunately, the ACSM software used in this study did not allow plotting time series for specific fragments apportioned by the frag table, e.g. "frag_sulphate[48]" like it is commonly done in the AMS analysis toolkits SQUIRREL or PIKA. Without exploring the resulting changes of these time series by adjusting the fragmentation table it did not make sense to vary the fragmentation table entries. To clarify that the revised manuscript was adjusted to:

Additionally, the ACSM fragmentation table could not be adjusted for interferences of ions from different aerosol species on the same m/z properly because ACSM software used in this study did not allow plotting time series for specific fragments apportioned by the fragmentation table. Thus, the standard table had to be used.

15) Figure 1: Using zeros to fill in the missing values for black carbon for periods when measurements are not available is not a standard approach (to my knowledge). It would be preferable if the existing BC data was simply just averaged. It is already very clear from the manuscript that data is missing in certain periods, so a reader can take this into account when evaluating the data. Alternatively, the pie chart could be modified to include only the ACSM data for when the MAAP was functional.

Response:

Unfortunately, the figure caption here was misleading: Missing values of eBC data was only filled with zeros for the calculation of the time series of the daily means. For the calculation of the pie chart values eBC data was just averaged as suggested by the reviewer. In the revised manuscript, the caption for this figure was changed to:

Figure 1: Time series of the daily mean. The black line represents the sum of eBC and all ACSM species, the blue line the sum of eBC, ACSM organics and all MARGA-$PM_{2.5}$ species. The pie chart shows the fractional abundances of individual eBC and ACSM species averaged over the whole campaign. For the determination of the daily means missing eBC data was filled with zero values, thus deriving lower concentration limits.

We thank the reviewer to bring up this ambiguity.

16) Figure 4: I assume the authors mean to say "grey shaded areas" rather than "green shaded areas".

Response:

Please see the response for author's comment #12 above.

Supporting Information:

17) Page 2, L3: I think this equation should be MFNO3 $\geq$ 0.78.

Response:

Indeed. In the revised manuscript, this equation was corrected.

18) Figure S1: The figure legend text is very small and hard to read. The font size should be increased to improve readability.

Response:

In the revised supplement material, this picture is enlarged to enhance the readability of the legend. The picture of the tower itself was removed.

19) Figure S2: I assume the authors mean to say "gray shaded areas" rather than "green shaded areas".

Response:

Please see the response for author's comment #12 above.

20) Figure S6: Similar to the previous comments, the shaded areas look grey to me rather than green. Perhaps there is a difference in how the colors are displayed by the author's monitor and my monitor? There are subsequent figures were this comment applies as well, but I will not repeat it to avoid being overly repetitive.

Response:

Please see the response for author's comment #12 above.

21) Figure S13: It would improve the presentation of the results if all the bar graphs were plotted with the same format. The size of the bars is not consistent.

Response:

In the revised manuscript, the format of all four graphs is similar.

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Responses to anonymous referee #2

Received and published: 19th February 2016

We thank the reviewer for the careful review of our manuscript; the comments and suggestions are greatly appreciated. All the comments have been addressed. In the following please find our responses to the comments one by one and the corresponding changes made to the manuscript. The original comments are shown in italics.

General Comments:

1) Order of sections: Please exchange 3.1. and 3.2 (data quality assurance should be before the results). You might even consider moving section 3.2 to chapter 2. Also in the PMF results section, the applied contraints should be described first, and then the results should be discussed. See also my comments below. With respect to the discussion on organic nitrate, I am very sceptical that the data support the conclusions. The uncertanties of both instruments are too large for an estimation of organic nitrate from the difference between ACSM and MARGA.

Response:

The authors agree with the reviewer that the cross validation chapter should be placed before the presentation of the results themselves. In the revised manuscript chapter 3.1 and 3.2 were exchanged.

We also accept the suggestion from the reviewer to move the description for the applied a values to the beginning of chapter 3.3 in the revised manuscript. Referring to comments #12 and #14 from the reviewer, we added a sentence describing that the choice for the a-values resulted from a series of sensitivity tests:

“Figure 4 summarizes the time series of PMF factor classes (two POA factors: HOA and BBOA; and two SOA factors: OOA and a humic-like substances (HULIS) related factor, see below for descriptions) found for all seasons, except for BBOA in Summer 2012. A corresponding graph dividing these PMF results into the five periods according to Fig. 2 is shown in Fig. S13. The POA profiles were constrained within ME-2 using the HOA and BBOA mass spectra found by ME-2 operated PMF analyses by Crippa et al. (2014) at the CESAR tower in Cabauw in March 2009. For the HOA profile, a constant a-value of 0.1 was found to be most suitable for every season. If observed, the BBOA a-value was set to either

0.2 (Autumn 2012) or 0.3 (Winter and Spring 2013). The a-values based on different sensitivity tests for each season as described by Canonaco et al. (2013)."

Organic nitrate related aspects are answered in the specific comments below.

__Specific Comments:__

2) Abstract: Please mention the height above ground of the ACSM. Until the end of section 2.2 the reader thinks that the ACSM was located on top of the tower.

Response:

The first sentence of the abstract was changed in the revised manuscript to:

"Intensive measurements of submicron aerosol particles and their chemical composition were performed with an Aerosol Chemical Speciation Monitor (ACSM) at the Cabauw Experimental Site for Atmospheric Research (CESAR) in Cabauw, NL, sampling at 5 m height above ground."

Section 2.2: Instrument description (second paragraph of this section) should be placed before the statements on the agreement between different ACSMs and the ACTRIS comparisons.

Response:

In the revised manuscript we accepted the suggestion of the reviewer and placed the instrument description before the statements on the agreement between different ACSMs and the ACTRIS comparisons.

3) Page 35124, line 5-8: Detection limits? It is not clear to me why they were not determined? As far as I understand, a blank filter measurement is done on a routine time schedule by an ACSM, and then the detection limit can be calculated as three times the average noise level.

Response:

As responded to a similar comment from referee #1, there were no measurements done with this ACSM during the presented campaign, where a separate particle filter was introduced in the sample line, in addition to the filter including in the gas-phase background filter cycle as described by Ng et al. (2011). Furthermore, the ACSM Local software version used in this study could not show data acquired during the filter cycle measurements (e.g. closed mass spectra/time series), which would be needed for the determination of the detection limits. The software could only show the differential mass spectra/time series.

4) Page 35124, line 12-15: Particle losses: I recommend using the PLC by von der Weiden et al (AMT, 2009) to estimate the losses in such long a sampling line (all vertical or horizontal?) www.atmos-meas-tech.net/2/479/2009/ http://www.mpchmainz. mpg.de/drewnick/PLC/

Response:

As responded to a similar comment from referee #1, we used now the particle density deriving from the chemical composition not as the campaign average but time resolved for each data point in the revised manuscript. In addition we introduced SMPS data which is now size dependently corrected as published by Henzing (2011). The description of the sampling losses of the 60 m inlet for eBC given in the manuscript derived from a series of measurements at the Cabauw tower performed in a previous campaign. Unfortunately these results are not published yet. To clarify how these losses were determined in the revised manuscript and to account for a comment from referee #2, the loss description was changed as follows:

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

Please note that these losses influenced only data acquired by the MAAP and SMPS. Since the contribution of eBC is rather low (average: 5%) a potential overall error for total aerosol masses is low and would not significantly alter one quintessence of the paper, namely total mass concentrations above the air quality limits. We think theoretical particle loss calculations would not add additional information in the context of this paper.

As a consequence of the newly evaluated SMPS data the correlation values between ACSM+MAAP data with SMPS data changed as seen in Fig. S3 and S4 in the revised supplement. Nevertheless, the overall qualitative and quantitative agreement is still given except that the ACSM+MAAP data is now overestimating the total PM_1 mass by 16%, excluding the eBC data the ACSM overestimates total mass by 12%. As seen in Fig. S3 the difference between both systems is significantly higher during the pollution events 16 to 27 January 2013 and 5 to 8 May 2013. Since the quantitative agreement with the MARGA is much higher at these times the discrepancy to the SMPS is likely due to the fact that the losses within the 60 m inlet could not be corrected for individual species as mentioned above. Therefore the following paragraph was added at the end of the cross validation chapter in the revised manuscript:

"Major discrepancies to the SMPS especially during some of the pollution events like 16 to 27 January 2013 and 5 to 8 May 2013 (see below) can be explained by the correction of losses through the 60 m inlet line which was done size dependently and did not account for losses of individual species as mentioned in chapter 2.3. As the quantitative agreements of individual inorganic species as well as of total inorganics between the ACSM and the MARGA during these periods are much higher, the mass loadings determined from these instruments are more reliable than the SMPS data."

5) Page 35124, lines 24 ff: MAAP: Please mention that a MAAP reports equivalent black carbon (eqBC), see Petzold et al., Atmos. Chem. Phys., 13, 8365-8379, doi:10.5194/acp-13-8365-2013, 2013

Response:

We thank the reviewer for the supportive remark and pointing out the reference. In the revised manuscript, the MAAP description was written in more detail as follows:

"The MAAP instrument has been introduced by Petzold and Schönlinner (2004) and Petzold et al. (2005). It is designed for the determination of the black carbon (BC), which is a product of incomplete combustion. There is in the scientific community a general consensus over what black carbon is in terms of properties (Bond et al., 2013) The MAAP measures the strong visible light absorption property of BC by simultaneous measurements of the radiation penetrating through and scattered back from a particle-loaded fiber filter. According to Petzold et al. (2013), optical BC determined by MAAP is to be referred to as equivalent black carbon (eBC). One property of BC is that it is highly refractory with a vaporization temperature near 4000K (Schwarz et al., 2006), thus BC is not vaporized at 600°C and cannot be measured by the ACSM. The MAAP achieves a time resolution of 5 minutes with an uncertainty of 12% (Petzold and Schönlinner, 2004)."

In addition, we used the term equivalent black carbon or its abbreviation (eBC) in the revised manuscript and supplement including tables and figures, whenever its measured values are given, since eBC represents the actual quantitative the MAAP is acquiring.

6) Page 35125, lines 23-29: For the 60 m inlet the sampling losses were calculated. So why not for the ACSM inlet?

Response:

As pointed out in the response to the reviewer's comment #4, the losses in the 60 m sampling line were measured on site in a previous campaign. These measurements could reasonably not be done for the ACSM inlet within the scope of the presented study.

7) Page 35127, line 15: 38Cl should read H37Cl, I assume? There is no 38Cl isotope

Response:

Indeed, the interference on m/z 38 is due to the $H^{37}Cl$ ion. The respective sentence was changed in the revised manuscript to:

"This was done because the signal at these masses showed high interferences with the chloride related ions ^{37}Cl and $H^{37}Cl$."

8) Page 35128, line 9-11: "Even when only considering the ACSM + MAAP PM1 concentration, where a campaign average of 9.5 µg m^{-3} was determined, the WHO PM2.5 limit was approximated." I suggest rephrasing as: Even the PM1 concentration inferred from ACSM + MAAP data (campaign average 9.5 µg m^{-3}) approached the WHO PM2.5 limit.

Response:

We accepted the suggestion of the reviewer and changed this part accordingly in the revised manuscript.

9) Page 35131 line 29 – page 35132, line 8: You calculate organic nitrate from the difference of ACSM and MARGA. I think that bears quite some uncertainty considering the large uncertainties of the instruments. At least you should provide an error estimation. What about looking at ion ratios, e.g., 30/46? This is known to differ between inorganic and organic nitrates? Can you plot 30/46 vs. the difference between MARGA-nitrate and ACSM-nitrate? Later on, on page 35133, lines 6-7, you state that the uncertainties are 30% for ACSM-nitrate and 10% for MARGA-nitrate. Thus, how can you infer 9% organic NO3?

Response:

As responded to the similar comment from referee #1, there are strong evidences for the existence of particulate organic nitrates during this campaign despite the uncertainties of both instruments. We agree with the reviewer that these explanations are contradictory to those given in the cross-validation chapter on the comparison of ACSM and MARGA total nitrates. The latter part (page 35133, lines 4-12) was changed in the revised manuscript to:

"The quantitative difference to the AMS-organics is also very low, and the discrepancies in case of ammonium and nitrate are within the stated ± 30% accuracy of the AMS and ACSM (Ng et al., 2011) and the ± 10% for the MARGA–NO_3, respectively (Makkonen et al., 2012). Similar variations were also found by Crenn et al. (2015) as well as Budisulistiorini et al. (2014). The latter reported of a comparison between two collocated ACSM's (± 27%, $R^2 = 0.21$ for Chl, $R^2 > 0.8$ for the other species) and between these ACSM's and a continuous Tapered Element Oscillating Microbalance (TEOM, $PM_{2.5}$) instrument. Note that the major ions used for nitrate detection in AMS and ACSM (NO^+ and NO_2^+) are produced from both inorganic and organic nitrate (e.g. Farmer et al. (2010)). The higher ACSM nitrate compared to MARGA nitrate can therefore also be explained by the presence of organic nitrates. In case of nitrate the ASCM and MARGA comparison cannot be seen as independent"

As the reviewer pointed out correctly, the ratio of m/z46 (NO_2^+) to m/z30 (NO^+) can be used as a parameter to determine to organic and inorganic nitrate fractions. To do that, the 46/30 ratios of purely inorganic and pure organic nitrates need to be known. The value of purely inorganic nitrate for individual instruments can be taken from ammonium nitrate measurements during IE calibrations. For AMS instruments this ratio was commonly seen to be around 0.4 (Fry et al., 2011; Fry et al., 2009; Mensah, 2011). The corresponding ratio of purely organic nitrates (R_{OrgNO3}) was found to be approximately 0.1 in chamber experiments, measuring SOA from the reactions of BVOC's with NO_3 radicals with an HR-ToF-AMS (Fry et al., 2011; Fry et al., 2009; Mensah, 2011). Analogous experiments were not yet published for ACSM instruments. During the presented campaign in Cabauw, a 46/30 ratio of around 0.2 was observed during the response factor calibrations of the ACSM. Crenn et al. (2015) reported a similar value (0.23) for this particular ACSM and that this ratio is strongly varying between the investigated ACSM's (0.20-0.58). That implies that it is highly uncertain that the 46/30 ratio of 0.1 for organic nitrates should be used for ACSM data, at least for the campaign presented here. Furthermore, as stated in the response to a comment from referee #1, the fragmentation table of the ACSM Local software used here could not be user defined. Thus possible interferences on m/z30 and m/z46 between nitrate and organic fragments could not be corrected. Those interferences would in turn increase the uncertainty of the NO_2^+/NO^+ ratio determination from unit mass resolution data.

10) Page 35132, line 10-12: What value was assumed for the density of organics?

Response:

As mentioned on page 35125, line 12, a density of 1.4 g cm^{-3} for organics was assumed.

11) Page 35133, line 12 ff: There seems to be a problem with sulfate here. The ACSM appears to underestimate SO4 by a factor of two compared to the HR-ToF-AMS. In the paper by Crenn et al (Atmos. Meas. Tech., 8, 5063–5087, 2015, www.atmos-meastech.net/8/5063/2015/ doi:10.5194/amt-8-5063-2015) it looked much better. How were the RIEs for the ACSM and for the HR-ToF-ASM determined? How often for the ACSM? Did all sulfate calibrations suffer from high background signals?

Respond:

The RIE of sulfate was calculated using a common procedure for AMS and ACSM instruments (e.g. Budisulistiorini et al. (2014) and Elser et al. (2015)). Monodisperse ammonium sulfate particles were measured right after the measurement of monodisperse ammonium nitrate. Using the RIE of ammonium deriving from the ammonium nitrate data, the RIE of sulfate was determined by an ion balance of data derived by the ammonium sulfate measurements. For the ACSM, this was done every 1-2 months (AMS: once per week) with relatively stable results (RIE_{SO4} = 0.81 ± 0.10). Close after the sampling of ammonium sulfate (up to 120 µg m^{-3}), a largely increased background of sulfate was observed during all calibrations, leading to the conclusions mentioned in the manuscript.

As mentioned in Crenn et al. (2015), the accuracy of AMS- and ACSM-sulfate measurements is still under debate. In their work, RIE calibrations were done for all instruments, including the particular ACSM used here. For the inter-comparison of the ACSM data sets with the collocated HR-ToF-AMS, Crenn et al. (2015) took the default RIE_{SO4} of 1.2 for all ACSM's, although the calibration results were partly much lower with strongly varying values of RIE_{SO4} between 0.48 and 0.97, while for the AMS the experimental RIE_{SO4} was applied (Fröhlich et al., 2015). Unfortunately, Crenn et al. (2015) did not publish comparison results with the AMS for individual ACSM's. Overall we think that in the case of sulfate it is difficult to generalize from Crenn et al. (2015) on AMS-ACSM comparisons for the presented work.

The reader should also take into account that the overlap period of the AMS and ACSM comprises only one week (294 common data points) in the beginning of the ACSM campaign during a time with low mass concentrations, while the comparison with the MARGA PM_1 data could be done over the whole ACSM data set (1943 common data points), leading to more representative correlation results. There, a better quantitative and qualitative agreement in case of sulfate was found comparing to the ACSM-AMS cross-validation.

12) Section 3.3 Factor analysis:

You prefer the 4-piece separate analysis over the one-year analysis, but I don't see an objective reason for this. To my opinion this discrepancy reflects the uncertainty of the factor analysis. I appreciate that you openly show and discuss the differences, but the conclusion that the 1-year analysis "overestimates" something is not backed up by any data, or am I wrong? If you argue that BBOA is overestimated because of the high degree of freedom (a = 0.3), why didn't you restrict it more (a = 0.1) as the HOA? You should state the reasons for choosing a certain a value at the beginning for the section. If the 1-year analysis would be run with a=0.1, would it be better? In general I would describe first the constraints, then the factors, then the alternative 1-year solution, and then conclude that latter cannot be correct (no m/z 60 in summer).

Response:

As described in the response to comment #1 of the reviewer, we added an explanation that the a-values were determined by a standardized procedure described in detail by Canonaco et al. (2013) and Crippa et al. (2014), in addition to the description of the source apportionment as applied in this work in chapter 2.4 (specifically page 35128, lines 1-13). In contrast to unconstrained PMF commonly published for AMS data, a higher amount of exploration runs including sensitivity tests are necessary to choose the most suitable a-values for constrained factors and overall the most suitable solution for a data set within a ME-2 analysis. It is not feasible to report all these runs with individual explanations on choices of solutions.

We agree with the reviewer that the conclusion of a possible overestimation of BBOA in summer due to the high degree of freedom cannot be sufficiently proven. Further PMF analyses with a constrained BBOA and a-values lower than 3 gave the same results with only very minor differences regarding profiles and time series. As suggested by the reviewer, the description of the 1-year PMF was moved to the end chapter 3.3 in the revised manuscript and changed as follows:

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

13) Page 35136 line 16: Typo: it's -> its

Response:

This part was corrected in the revised manuscript.

14) Page 35137 line 10: Explain humic-like substances (HULIS) on first occurrence

Response:

To clarify the HULIS term, the introductory sentence on page 35134, line 18, was changed in the revised manuscript to:

"Figure 4 summarizes the time series of PMF factor classes (two POA factors: HOA and BBOA; and two SOA factors: OOA and a humic-like substances (HULIS) related factor, see below for descriptions) found for all seasons, except for BBOA in Summer 2012."

15) Conclusions: This section is too short and too weak and should be expanded.

Response:

To meet this suggestion by the reviewer we restructured the conclusions section and moved some concluding statements from previous sections to this part. The conclusions now emphasize the important finding that NH_3 emission control can significantly decrease PM loading at this rural site. Furthermore the high SOA fraction in the aerosol challenges mitigation strategies in particular when large background fractions are observed as is the case with HULIS here. To account for comments from other reviewers as well the revised section now reads:

This work provides chemical composition data of atmospheric aerosols acquired during one year at the CESAR tower in Cabauw, the Netherlands, which is a representative rural site for North Western Europe. The concentration of submicron particles from combined ACSM and MAAP data showed 12 exceedances from the WHO $PM_{2.5}$ daily mean limit. The respective campaign average of 9.5 $\mu g\ m^{-3}$ approached the WHO $PM_{2.5}$ annual mean limit. Taking MARGA $PM_{2.5}$ into account the number and proportions of these exceedances are even higher, emphasizing the importance of these high ACSM PM_1 results shown here which represent lower limits. As carbonaceous compounds are estimated to be five times more toxic than inorganic particles (Lelieveld et al., 2015) MARGA data alone would not give sufficiently possible implications regarding adverse health effects. While few people live in the direct vicinity of the measurement site, the high aerosol concentration measured at the site can be considered to represent the regional background. This regional background is adding to local aerosol contributions in high populated urban sites (Pandis et al., 2013), namely the 4 largest cities of the Netherlands which have a distance of 40 km or less from the CESAR tower.

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

As indicated by model results for the South Western United States from Zhang and Wu (2013), the reduction of NH_3 emissions, in conjunction with already implemented SO_2 and NO_x emission reductions, can further reduce $PM_{2.5}$ than reducing SO_2 and NO_x emissions alone, particularly for regions with high emissions of NH_3 from agricultural sources. The latter is clearly the case for Cabauw with its high number of animal husbandry and the use of nitrogen containing fertilizers around the CESAR tower. Banzhaf et al. (2013) derived similar conclusions for PM_{10} using different emission scenarios within domains covering Germany and Europe. Applying a 3d chemical transport model over Europe Megaritis et al. (2014) found that a reduction of NH_3 emissions by 50% would have a much higher effect on reducing $PM_{2.5}$ than decreasing NO_x emissions by 50%. The latter scenario would even result in negative side effects such as higher tropospheric ozone concentrations (especially in summertime 4% over Western Europe and up to 40% in major urban areas) and higher amounts of particulate sulfate and OA by 8% and 12%, respectively, in winter.

The local mitigation of organic aerosol mass (29% contribution on average) is more challenging, as secondary organic aerosols are highly abundant at the Cabauw site (74% and 22% of OA and total PM_1 on average, respectively). The presented data set shows a large and ubiquitous HULIS fraction (37%) which based on diurnal patterns and a lack of correlation with wind direction can be considered as long-range background aerosol formed from atmospheric aging processes. In turn, primary organic aerosols emitted mainly from traffic and biomass burning (12% and 13% of OA on average) have only minor importance. For a more detailed identification of the SOA sources compound specific measurements of OA as well as routine VOC monitoring are needed.

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

Figures:

16) Figure S2: Wind speed is hard to see. Please make extra graph.

Response:

As suggested by the reviewer, the wind speed is now shown in a separate graph in Fig. S2 in the revised supplement material

17) Figure S11: Mention in figure caption that MARGA data are PM1.

Response:

In the revised supplement material the figure caption was changed to:

"Figure S11: Correlation graphs of Chl, NH_4, SO_4, NO_3, and total inorganic mass concentrations from ACSM and MARGA PM_1 data"

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Responses to anonymous referee #3

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We thank the reviewer for the careful review of our manuscript; the comments and suggestions are greatly appreciated. All the comments have been addressed. In the following please find our responses to the comments one by one and the corresponding changes made to the manuscript. The original comments are shown in italics.

1) This paper is well written. Figures are clear and provide important information. The supporting information is also well presented. The source apportionment study is very well conducted in terms of methodology and scientific interpretation. Out of this, the scientific interest for this paper remains (too) limited with no clear addedvalue compare to previous AMS studies performed at Cabauw. Providing a 1-year continuous observation of NR-PM1 with Q-ACSM (with source apportionment) is not any more self-sufficient for a scientific paper. Scientific interpretation is often set here at the minimum with poor perspectives; lack of comparison neither with previous studies related to Cabauw nor Q-ACSM measurements and source apportionment studies. The scientific motivation is not convincing enough. Air Quality issues related to PM are important in densely populated regions (with high exposure to particulate pollution), much less in a rural area like Cabauw. In this AQ context, it would have been more meaningful to use this background (Cabauw) PM dataset to interpret the contribution of regional pollution to PM in Dutch cities. You missed the point that this dataset remains an important contribution to a larger one obtained at the European scale within theEU-FP7-ACTRIS project (ACTRIS Q-ACSM network).

Response:

As responded to a similar comment from referee #1, it is correct that a publication just dealing with AMS or ACSM measurements as well as the presentation of their data sets are not novel enough for ACP, also considering that two AMS campaigns were previously performed in Cabauw. We emphasize here that the focus of this work extends beyond the presentation of a larger data set for this site:

In this study, we showed that the major fraction of atmospheric aerosol at this site is comprised of secondary aerosol (SA) which is chemically formed in the atmosphere. SA also dominates the high mass loadings during the pollution episodes greatly exceeding air quality standards. The long term aerosol mass spectrometric data provided by this work is important for the understanding of the chemical processes leading to such high aerosol masses which are unexpected for a rural site like Cabauw. This information is necessary for potential mitigation of particle masses. The findings presented here were not seen in previous studies due to their limited time of sampling.

It is true that Cabauw is categorized as rural. However one should note that this term is not indicative that is has not significant impact on the population. The Netherlands is the 24th most densely populated country in the world (average population density 502 persons per km^2, UN (2015)), exceeding e.g. population densities of India (391) or Japan (335). The measurement site is located in the part of the municipality of Lopik which lies within or near the three most populated provinces: Noord-Holland, Zuid-Holland and Utrecht (976, 1227, 851 persons per km^2). The population of the statistical district Cabauw, covering the village center and the farms along the canal, has a population of around 690 (CBS, 2004). This number is indeed small, but on the other hand the centers of the four largest and most populated cities of the Netherlands are located within a surrounding of maximum 40 km air-line from the CESAR tower (Amsterdam and The Hague ca. 40 km, Rotterdam 25 km, and Utrecht 20 km), covering around 2.3 million inhabitants. Pandis et al. (2013) stated that high organic mass loadings found in rural sites clearly influence the background of urban areas, as mentioned by the reviewer. Skyllakou et al. (2014) applied the particulate matter source apportionment technology (PSAT) together with PMCAMx, a regional chemical transport model for the Megacity of Paris. They showed that only 13% of the $PM_{2.5}$ fraction originated from the urban agglomeration (an area of around 50 km around the city center), 36% coming from mid-range (50–500 km from the center of the Paris) sources and 51% from long range transport (more than 500 km from Paris). In this context the high aerosol mass loadings found in this work have a strong impact on the air quality not only for the area close to the measurement site but also for a huge number of inhabitants within a surrounding of less than 40 km, justifying the comparison with the WHO air quality limits.

To emphasize the influence of the findings from this site to urban areas we added the following sentence to first paragraph of the conclusions chapter:

“While few people live in the direct vicinity of the measurement site, the high aerosol concentration measured at the site can be considered to represent the regional background. This regional background is adding to local aerosol contributions in high populated urban sites (Pandis et al., 2013), namely the 4 largest cities of the Netherlands which have a distance of 40 km or less from the CESAR tower.”

We thank the reviewer to point out that this work is also an important contribution within the framework of ACTRIS. As suggested by the reviewer we added the following paragraph into the conclusion chapter:

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

<u>Specific Comments:</u>

2) Hyphen is often missing (gas-to-particle, long-term, time-resolved, water-soluble, etc)

Response:

Fortunately, copy-editing is standard in ACP. Thus minor errors will be eliminated later on.

3) Page 35119, line 10: Why are you focusing only on WHO and not on EU-regulated PM2.5? Because PM2.5 at Cabauw may exceed WHO AQ guidelines? (and not EUregulated PM2.5)

Response:

The air quality guideline of the European Union (EU) only provides a "target value" for the annual $PM_{2.5}$ limit of 25 μg m^{-3} (EU, 2008), which is indeed higher than the respective WHO limit. As the WHO gives additionally a daily mean limit the conclusions of this work with respect to air quality could be aimed with a much higher time resolution. It could be shown which conditions, compounds and sources are responsible for high particle mass loading during times of exceedances. That is why the authors focused on the WHO limits.

Furthermore, the WHO limits are based on the now extensive body of scientific evidence relating to air pollution and its health consequences. Although this information base has gaps and uncertainties, it offers a strong foundation for the recommended guidelines (WHO, 2006). EU standards in contrast vary according to the approach adopted for balancing health risks, technological feasibility, economic considerations and various other political and social factors. This in turn will depend on, among other things, the level of development and national capability in air quality management in each member state. Since it is not in the scope of the manuscript to discuss these issues in detail, the authors decided to just provide the target value for the annual $PM_{2.5}$ limit according to the EU in the introduction chapter of the revised manuscript as follows:

"The European Union Air Quality Directive 2008/50/EC provides only a target value of the annual mean limit of $PM_{2.5}$ of 25 µg m^{-3} (EU, 2008)."

4) Page 35120, line 16: it should be NR-PM1 (and not ambient aerosol).

Response:

In the revised manuscript, this part was changed to:

"The Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc., Billerica, MA, USA) is a powerful instrument to quantitatively measure the chemical composition of the Non-Refractory fraction of PM_1 (NR-PM_1) with high time and mass resolution."

5) Page 35120, line 25: Please state that it is a Q-ACSM (Q=Quadripole).

Response:

In the revised manuscript, this part was changed to:

"The Quadrupol-ACSM (Q-ACSM) is specially designed for long-term continuous and real-time measurements of mass concentrations and composition of NR-PM_1 species (Ng et al., 2011)."

6) Page 35122, line 20: Remove Fröhlich et al. (2015) which is focused on Source apportionment intercomparison only.

Response:

In the revised manuscript, the reference Fröhlich et al. (2015) was removed.

7) Page 35123, line 23: Did you install a dryer at the inlet? If so, please specify. Otherwise, you should address the impact of sampling aerosols at ambient RH.

Response:

On page 35123, line 23 in the manuscript, there is no description of any inlet so far. On page 35124, line 14 and page 35125, line 17 the nafion dryers for the ACSM and for the

MAAP/SMPS inlet are mentioned, respectively. As described in line 6 on page 35126, the MARGA samples at ambient RH.

8) Page 35124, line 15: 3LPM is supposed to be the nominal flow in the Q-ACSM for isokinetic sampling. Why did you use 1LPM. Impact?

Response:

The flow rate of 1 liter per minute at this part of the inlet was set due to a restriction of the nafion dryer. At higher flow rates this dryer may not dry the sample air sufficient enough. Since the length of this inlet section was rather small (less than 2 m) we don't expect a significant impact, e.g. enhanced wall losses, comparing to a flow of 3 liter per minute.

9) Page 35124, 17: "The" before "following"

Response:

In the revised manuscript, this part was changed to:

"The following collocated aerosol instruments were used for cross-validation of the ACSM data:"

10) Page 35125, line 1-2: MAAP provides absorption data and uncalibrated BC. You did not mention here how you address this issue.

Response:

In this work, the factory default inversion and calibration was used to determine the eBC concentrations from MAAP data. We agree that this information should be added in the revised manuscript. In addition to other changes due to comments from other referees, the MAAP description was changed as follows:

"The MAAP instrument has been introduced by Petzold and Schönlinner (2004) and Petzold et al. (2005). It is designed for the determination of the black carbon (BC), which is a product of incomplete combustion. There is in the scientific community a general consensus over what black carbon is in terms of properties (Bond et al., 2013) The MAAP measures the strong visible light absorption property of BC by simultaneous measurements of the radiation penetrating through and scattered back from a particle-loaded fiber filter. According to

Petzold et al. (2013), optical BC determined by MAAP is to be referred to as equivalent black carbon (eBC). One property of BC is that it is highly refractory with a vaporization temperature near 4000K (Schwarz et al., 2006), thus BC is not vaporized at 600°C and cannot be measured by the ACSM. The MAAP achieves a time resolution of 5 minutes with an uncertainty of 12% (Petzold and Schönlinner, 2004). A mass absorption cross section (MAC) of 6.6 m^2 g^{-1} for a wavelength of 637 nm (Müller et al., 2011) was chosen to convert the measured particle absorption coefficient to eBC mass concentrations."

11) Page 35125, line 23: The number here (33% of particle loss) is very high and not address correctly in the paper. It should be a function of size. Brownian diffusion (and associated losses) may be an important issue for number concentration in the nanometer range; not sure it is an important issue for PM calculation using SMPS. More information should be provided here.

Response:

As responded to a similar comment from referee #1, we used now the particle density deriving from the chemical composition not as the campaign average but time resolved for each data point in the revised manuscript. In addition we introduced SMPS data which is now size dependently corrected as published by Henzing (2011) The description of the sampling losses of the 60 m inlet for eBC given in the manuscript derived from a series of measurements at the Cabauw tower performed in a previous campaign. Unfortunately these results are not published yet. To clarify how these losses were determined in the revised manuscript and to account for a comment from referee #2, the loss description was changed as follows:

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

Please note that these losses influenced only data acquired by the MAAP and SMPS. Since the contribution of eBC is rather low (average: 5%) a potential overall error for total aerosol masses is low and would not significantly alter one quintessence of the paper, namely total mass concentrations above the air quality limits.

As a consequence of the newly evaluated SMPS data the correlation values between ACSM+MAAP data with SMPS data changed as seen in Fig. S3 and S4 in the revised supplement. Nevertheless, the overall qualitative and quantitative agreement is still given except that the ACSM+MAAP data is now overestimating the total PM_1 mass by 16%, excluding the eBC data the ACSM overestimates total mass by 12%. As seen in Fig. S3 the difference between both systems is significantly higher during the pollution events 16 to 27 January 2013 and 5 to 8 May 2013. Since the quantitative agreement with the MARGA is much higher at these times the discrepancy to the SMPS is likely due to the fact that the losses within the 60 m inlet could not be corrected for individual species as mentioned above. Therefore the following paragraph was added at the end of the cross validation chapter in the revised manuscript:

"Major discrepancies to the SMPS especially during some of the pollution events like 16 to 27 January 2013 and 5 to 8 May 2013 (see below) can be explained by the correction of losses through the 60 m inlet line which was done size dependently and did not account for losses of individual species as mentioned in chapter 2.3. As the quantitative agreements of individual inorganic species as well as of total inorganics between the ACSM and the MARGA during these periods are much higher, the mass loadings determined from these instruments are more reliable than the SMPS data."

12) Page 35126, line 23: "Source apportionment : : : was performed" (and not "were performed").

Response:

In the revised manuscript, this part was changed to:

"Source apportionment of organic aerosol components was performed using Positive Matrix Factorization…"

13) Page 35127, line 23: BBOA is not 100% POA. But if you want to go in this direction, you may specify here "pBBOA" (primary BBOA).

Response:

We agree with the reviewer that some secondary organic aerosols originate from biomass burning. Nevertheless, BBOA is related to the profiles found by PMF analysis using a BBOA mass spectrum found by Crippa et al. (2014) at the same site. In this and a number of other publications BBOA factors as found by PMF explorations from AMS or ACSM measurements are described as POA (Canonaco et al., 2015; Elser et al., 2016; Fröhlich et al., 2015; Ripoll et al., 2015; Sun et al., 2012) as well as this particular section of this manuscript does. This is mainly due to the fact that this factor is usually partly identified by the correlation with external primary emitted tracers like BC or CO. That is why BBOA as found by the PMF analysis using ACSM data is considered here as POA.

14) Page 35129, line 2: You want to address here risk assessment (WHO air quality guideline); but for a rural site having few inhabitants. This is not very relevant.

Response:

We hope that this comment is answered in detail by the responds to the referee's comments #1 and #3.

15) Page 35129, line 7: You state here that MARGA PM2.5 is calculated as the sum of chemical compounds in the aerosol phase (NO3, NH4, SO4, Cl, Na, K, Mg, Ca) AND in the gas phase (SO2, HCl, HNO3, HNO2). Are you sure? (if so MARGA PM2.5 data is not correct).

Response:

We thank the reviewer for pointing out this mistake as well as referee #1 did in a similar comment. The gas phase compounds SO_2, HNO_2, HNO_3 and HCl were mistakenly added to total aerosol masses. Nevertheless, the conclusions deriving from these calculations did not change. In the revised manuscript, the resulting time series "MARGA $PM_{2.5}$ + ACSM-Org + eBC" in Fig. 1 was exchanged and the sentence was changed to:

Nevertheless, the average total mass derived from the combination of the MARGA $PM_{2.5}$ data (including all water soluble inorganic components NO_3, NH_4, SO_4, Cl, Na, K, Mg, and Ca), MAAP eBC and ACSM PM_1 organics resulted in 12.5 µg m^{-3} during this time, clearly exceeding the WHO $PM_{2.5}$ annual mean limit (10 µg m^{-3}) by 25%.

The reader may now notice that the concentration values of MARGA $PM_{2.5}$ + MAAP eBC + ACSM PM_1 Organics (light blue time series in Fig. 1) decreased reasonably because the mentioned gas phase data was excluded. On the other hand, more data points are now seen. This is due to the fact that data coverage of the MARGA $PM_{2.5}$ data is better than for the MARGA gas phase data.

16) Page 35129 : You have 30-min time resolution data and you interpret seasonal variability (averaging data over typically 3 months). Why don't you go for monthly mean variability? You may better see some trends here with 12 points instead of 4.

Response:

The presentation of 3-months-averaged data was mainly due to the season-wisely separation of the data set prior to PMF analysis. Furthermore, some months have larger lacks of data coverage either from the ACSM or MAAP, especially in periods 3 and 4. That is why it was more representative to average the data over 2-3 months than for each month. We agree with the reviewer that this sentence is misleading since there was no actual further analysis performed using 3-months-averaged data of the aerosol species apart from the calculation of the pie charts in Fig. 2a. The variation of each species across the whole campaign can be much better observed by the 30 minutes resolution data shown in Fig. 2b. Therefore this part was changed in the revised manuscript to:

"To determine properly average species contributions for each pie chart the campaign was therefore not divided strictly season-wise, but into five periods."

In addition, Table S2 shows now the contribution and total mass concentrations averaged over each month instead over the whole season/period. Another column was introduced to show the number of data points acquired each month and used for averaging.

17) Page 35130, line 10: You state here that you may observe some inversions a low altitudes (typically below 60m). How often? Then you would assume that concentrations below/above the inversion layer are disconnected. If so, how are you dealing with SMPS and BC data which are sampled at 60m height?

Response:

We agree with the reviewer that a temperature inversion between the inlet of the ACSM (at 5 m) and the inlet of the MAAP and SMPS (at 60 m) would infer that the instruments sample from different atmospheric layers. In fact, such distinct inversions between the temperature sensors at 2 m and 80 m height happened only few times across the whole campaign (in total 18 times with a duration of around 1-6 hours) and during periods with aerosol mass loadings not higher than 10 µg m^{-3}. An exception is the inversion of the morning on 25 January between 3 and 9 am where total mass concentrations of around 20 µg m^{-3} from both SMPS and ACSM+MAAP was determined, meaning that there no significant difference was seen from both instruments. On the other hand it is true that in some other cases the total mass concentrations of the SMPS and the ACSM differ from each other. But these differences are not higher than in some periods without a temperature inversion. That means that if the data points during temperature inversions would be cancelled out, it would not alter the correlation results from both instruments significantly as well as the main conclusions of this work. Therefore, the SMPS and BC data was untreated with respect to possible samplings from different atmospheric layers. In the morning of 16 January the temperature inversion is not relevant since there is no ACSM data existing, but is only beginning from the evening of 16 January. We admit that the current mention of this morning in the manuscript is unnecessary and misleading. Therefore it was deleted from this part in the revised manuscript to:

"The period 16 to 27 January 2013 showed also the lowest temperatures (average: -4°C) with respect to the whole campaign and a temperature inversion between 2 m and 40 m height in the morning 25 January 2013, where both instruments showed total mass concentrations of ca. 20 µg m^{-3}."

18) Page 35130, line 25: You are located at a rural site and you report diurnal BC variations with maxima at rush hours (evening/morning). What does it mean? You are locally influenced by traffic? Are you sure?

Response:

As mentioned in the respond to the referee's comments #1, this site is categorized as rural but should not be considered as very low dense populated. Thus it has significant influence from anthropogenic sources including traffic. With a low air-line distance of just 600 m from the CESAR Tower there is the nearest expressway (Dutch: Autoweg) N210, which connects the cities of Rotterdam and Ijsselstein and is only allowed for vehicles with a velocity of at least

50 km h^{-1}. Beside that the highway (Dutch: Autosnelweg) A27 has a distance of just 6 km in addition to the highly frequented highways A2 and A12, which have a distance of around 10 km each. Together with the observed clear traffic related diurnal pattern of the HOA factor and NO_x data, the authors are confident that this site is influenced by traffic emission.

19) Page 35131: the discussion on organic nitrates is not convincing at all. You show in SI that you have strong differences between SO4 (and NO3) between ACSM and MARGA. For me, it clearly shows that IENO3, RIESO4 and RIENH4 are not properly determined. As a result, I am not surprised to see that NH4 (measured vs predicted) is not matching well. And for that reason, I am not convinced that the difference is due to organic nitrates.

Response:

While comparisons between the ACSM and MARGA data show discrepancies which are interpreted in the manuscript, we cannot see how these could be explained based on wrong RIE's. From the way $OrgNO_3$ is derived (subtraction of MARGA inorganic nitrate from ACSM total nitrate) it is independent of RIE's. If the RIE_{NH4} were wrong, it would be wrong by a constant factor. The authors see no way how a time dependent correction to the total ACSM nitrate (which the $OrgNO_3$ is) would "happen by chance" to arrive at a closed ion balance.

As responded to a similar comment by referee #1, the presented determination of organic nitrates, which is in agreement with the procedure of Xu et al. (2015), improved the agreement of measured against predicted ACSM-NH_4, resulting in a nearly 1:1 regression line without a significant offset.

This is in agreement with the MARGA internal ion balance which also indicates neutralized inorganic aerosols. All evidence together makes a strong case that the difference of AMS total nitrate to MARGA nitrate is most likely due to the presence of organic nitrates. These findings and the previously reported relatively high AMS organic nitrate fractions by Mensah (2011) in May 2008 (0.5 µg m^{-3}, 35% of total nitrate, 5.2% of total aerosol mass) and March 2009 (0.2 µg m^{-3}, 10% of total nitrate, 3.6% of total aerosol mass) in Cabauw show strong evidence of the presence of organic nitrates during this campaign and the reliability of its estimation as presented in the manuscript.

To provide a more detailed description this part was changed in the revised manuscript as follows:

"This assumption is acceptable, as shown by using the MARGA-NO_3 instead of the ACSM-total-NO_3 for the ion balance of ACSM data (including ACSM-SO_4, -Chl and -NH_4), following a procedure given by Xu et al. (2015) who calculated the organic nitrate fraction by subtracting the inorganic nitrate concentrations measured by a particle-into-liquid sampler (PILS, see Orsini et al. (2003)) from ToF-AMS total nitrate concentrations. In the Cabauw data set, the correlation of measured against predicted NH_4 resulted in a nearly 1:1 regression line without a significant offset (Fig. S10). This is in agreement with the MARGA internal ion balance which also indicates neutralized inorganic aerosols. Therefore, the mass concentration of nitrate groups associated with organic molecules (hereafter called organic nitrate or OrgNO_3), can be estimated by subtracting the MARGA-nitrate from the ACSM-nitrate concentration. The OrgNO_3 time series using this approach is plotted in Fig. S11, the respective diurnal variation averaged over the whole campaign in Fig. S12. An average mass fraction of 9% was calculated for OrgNO_3 (average concentration: 0.43 µg m^{-3}) in respect to total ACSM-NO_3. The organic nitrate fraction shows a maximum concentration in the night, followed by a decrease during the day. These findings are in agreement with previously reported relatively high AMS organic nitrate fractions by Mensah (2011) in May 2008 (0.5 µg m^{-3}, 35% of total nitrate, 5.2% of total aerosol mass) and March 2009 (0.2 µg m^{-3}, 10% of total nitrate, 3.6% of total aerosol mass) in Cabauw."

20) Page 35133, line 25: You completely skip sea salt chloride (measured by MARGA and not by ACSM). Please revise your conclusions here which are not correct.

Response:

Sea salt chloride was meant to be included in the term "inorganic chloride". In the manuscript it is described as component which can be detected well by the MARGA but not by the ACSM with a sufficient sensitivity as mentioned by the reviewer. That means that to our best knowledge our conclusions remain correct with respect to the inter-comparison between MARGA- and ACSM-chloride.

For clarification, this part was changed in the revised manuscript to:

"It should also be noted, that chloride concentrations can originate from particulate organic and inorganic chloride components originating from e.g. sea salt. For the latter, the ACSM is much less sensitive than the MARGA. As described above, influences from sea salt can be considered rather low. In turn, the MARGA might be less sensitive to organic chlorides, as they are likely less water soluble than inorganic chlorides."

The changes refer now to an added discussion about a possible influence of sea salt and dust particles as suggested by referee #1 to the section of the inter-comparison between the SMPS and ACSM+BC:

"The negative offset can be explained by minor influences of sea salt and dust particles, which can be detected well by the SMPS and MARGA but not by the ACSM with a sufficient sensitivity. But the low value of the intercept shows already that the uncertainty introduced by these aerosol components is rather low in general. This can also be explained by the low concentrations of Mg, Na, K and Ca as measured by the MARGA (see below) and the assumption that the majority of dust particles is most likely found in particles with diameters larger than 1 or even 2.5 µm (Finlayson-Pitts and Pitts (2000) and references therein)."

21) Page 35134, line 3: "PM2.5 values were up to 33% higher than PM1". This is a very interesting statement that points out the lack of efficiency of Q-ACSM to properly characterize PM2.5 pollution events. This should be highlighted at least when addressing these pollution events. How far is the Q-ACSM from MARGA PM2.5 during these episodes? Consequences on the conclusions of the paper?

Response:

The reviewer is right that the ACSM is not able to properly characterize $PM_{2.5}$ pollution events due to its inlet design. The differences between the data sets are implicated in Fig. 1, where MARGA $PM_{2.5}$ data. This is why it is considered as PM_1 instrument as stated in the manuscript. We also pointed out that even the presented PM_1 data exceeded the WHO $PM_{2.5}$ daily mean limit several times and approached the respective annual mean limit. In our opinion the conclusions of the paper do not change due to the reasonable underestimation of the ACSM concentrations with respect to $PM_{2.5}$. But to emphasize that this data represents the lower limits and to highlight the importance of the ACSM measurements in this context, we changed the description of the pollution events in the revised manuscript as follows:

"The most significant pollution events (17 to 21 August 2012, 21 to 25 October 2012, 16 to 27 January 2013, and 5 to 8 May 2013) are highlighted with shaded backgrounds in Fig. 2. During these events, MARGA $PM_{2.5}$ data showed up to 33% higher (e.g. on 17 to 21 August 2012) total inorganic masses than ACSM PM_1 inorganics as implicated in Fig. 1. As mentioned above the number and proportions of exceedances of the WHO $PM_{2.5}$ daily mean limit is therefore even higher than when only PM_1 data is considered. During the last three events, northerly and north-easterly winds dominated."

Furthermore, we added a paragraph into the conclusion chapter when addressing the exceedances. The first paragraph is now written as follows:

"This work provides chemical composition data of atmospheric aerosols acquired during one year at the CESAR tower in Cabauw, the Netherlands, which is a representative rural site for North Western Europe. The concentration of submicron particles from combined ACSM and MAAP data showed 12 exceedances from the WHO $PM_{2.5}$ daily mean limit. The respective campaign average of 9.5 µg m^{-3} approached the WHO $PM_{2.5}$ annual mean limit. Taking MARGA $PM_{2.5}$ into account the number and proportions of these exceedances are even higher, emphasizing the importance of these high ACSM PM_1 results shown here which represent lower limits. As carbonaceous compounds are estimated to be five times more toxic than inorganic particles (Lelieveld et al., 2015) MARGA data alone would not give sufficiently possible implications regarding adverse health effects."

22) Page 35136; line 18: I am a little bit loss. You are using BC and CO as external tracers to constrain both HOA and BBOA. Based on HOA and BBOA concentration levels and using literature data, you may be able to give a range of BC originating from both sources. I am pretty sure you will find that BC is coming mainly from traffic and thus cannot be used to constrain BBOA as done in the paper.

Response:

We think that there is a misunderstanding regarding the use of BC data in this work due to a misleading expression in the manuscript. Source apportionment was only performed for organic aerosols, not for CO and BC data. HOA and BBOA profiles were constrained using reference mass spectra from the literature. The resulting time series were then compared with the external tracers CO and BC to verify their origins as primary organic aerosols. The respective sentence in the manuscript should not imply that in Winter these tracers are mainly emitted by biomass burning comparing to traffic emission but the contribution from biomass burning to these tracer concentrations are higher in Winter than from biomass burning averaged over the whole campaign. This is a result of reasonably enhanced amount of biomass burning due to enhanced domestic heating in winter. To clarify this issue, the respective part was changed in the revised manuscript as follows:

"In Winter, the correlations with eBC and CO were higher ($R^2 = 0.64$ and 0.57, respectively) than over the whole campaign ($R^2 = 0.39$ and 0.49, respectively), meaning that these compounds are reasonably more attributed to domestic heating during the colder periods comparing to the contribution of heating to BC and CO during the other seasons in this region."

23) Page 35137, line 19: It should be R2=0.39 for NO3 (not 0.47).

Response:

In the revised manuscript, this part was changed to:

"Also the comparison to the most important tracers (Table S4 in the supplement) showed no preferential attribution, either to a low-volatile (R^2 = 0.41 with SO_4), semi-volatile (R^2 = 0.39 with NO_3) or to primary organic aerosol (R^2 = 0.47 with eBC)."

24) Page 35138, line 15: BC is not POA!

Response:

We thank the reviewer for pointing out this mistake. In the revised manuscript the term "POA components" was replaced by the term "primary aerosol components"

25) Page 35140, line 6: Why do you want to speak about hygroscopicity ? It has never been addressed before in the paper and has nothing to do with AQ-regulated PM.

Response:

It is true that hygroscopicity was not discussed as an aerosol property throughout the manuscript. Here it was mentioned to highlight the importance of the findings with regard to adverse health effects of aerosols, as the manuscript focuses on the WHO air quality guidelines. To clarify and emphasize this issue the respective part was changed to:

"It is shown that particulate ammonium nitrate is the major aerosol component (39% on average) and represents the more hygroscopic aerosol fraction. Since the human respiratory system is water vapor saturated more hygroscopic aerosols have a higher deposition tendency within the human lung than less water soluble particle compounds (Asgharian, 2004; Broday and Georgopoulos, 2001). With special regard to adverse health effects this is very crucial because Asgharian (2004) also found that especially hygroscopic submicron particles can deposit in the entire lung. The high ammonium nitrate fraction also implies that inorganic SA reduction in Cabauw can be most efficiently achieved through the reduction of gaseous ammonia emissions in the area."

26) Page 35140, line 23: I think P. Croteau is from Aerodyne Research Inc., not from PSI.

Response:

In the revised manuscript, this part was changed to:

"We also thank Philip Croteau (Aerodyne Research) for his support during the measurements regarding the data acquisition and evaluation."

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Responses to anonymous referee #4

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We thank the reviewer for the careful review of our manuscript; the comments and suggestions are greatly appreciated. All the comments have been addressed. In the following please find our responses to the comments one by one and the corresponding changes made to the manuscript. The original comments are shown in italics.

<u>Specific Comments:</u>

1) P35123, L27: Contrary to what is implied, the Middlebrook parameterisation does take account of the nitrate mass fraction. More justification should be given in the main article on why it was not suitable here because it would be preferable to use the SMPS data for an independent validation, rather than informing the CE.

Response:

The SMPS was sampling from the inlet located at 60 m height while the ACSM sampled from the roof at 5 m height, resulting in a higher uncertainty comparing to the usual set-up where both instruments would sampling from inlets close together. In addition and as responded to the similar comment from referee #1, the application of the Middlebrook algorithm lead to unreasonable discontinuities of CE value. The algorithm used in the work originated from the comparison of a ToF-AMS with the same SMPS, both sampling from the 60 m-inlet, during a campaign in Cabauw in May 2008 (Mensah et al., 2012). But the authors agree that the current explanation is misleading. In the revised manuscript the respective part was changed to:

"In contrast to the commonly used constant value of 0.5 this CE correction accounts for the high ammonium nitrate mass fraction (ANMF) found at this site and is thus more suitable for the data presented here. Another algorithm for composition dependent CE determination (Middlebrook et al., 2012) was also tested for its validity. It uses a threshold ratio of measured to predicted NH_4 to switch between two different equations to determine the CE. The threshold value of 0.75 is close to the observed ratio of measured over predicted NH4 of this data set, resulting in large discontinuities of CE values and in consequence, discontinuous changes in aerosol mass concentrations. In other words, the Middlebrook algorithm is not suitable for data sets showing at the same time low ratios of measured to predicted NH_4 and high AMNF's."

2) P34124, L25: Was the factory default inversion and calibration of the MAAP used? If so, this should be specified.

Response:

Indeed, the factory default inversion and calibration was used to determine the eBC concentrations from MAAP data. We agree that this information should be added in the revised manuscript. In addition to other changes due to comments from other referees, the MAAP description was changed as follows:

"The MAAP instrument has been introduced by Petzold and Schönlinner (2004) and Petzold et al. (2005). It is designed for the determination of the black carbon (BC), which is a product of incomplete combustion. There is in the scientific community a general consensus over what black carbon is in terms of properties (Bond et al., 2013) The MAAP measures the strong visible light absorption property of BC by simultaneous measurements of the radiation penetrating through and scattered back from a particle-loaded fiber filter. According to Petzold et al. (2013), optical BC determined by MAAP is to be referred to as equivalent black carbon (eBC). One property of BC is that it is highly refractory with a vaporization temperature near 4000K (Schwarz et al., 2006), thus BC is not vaporized at 600°C and cannot be measured by the ACSM. The MAAP achieves a time resolution of 5 minutes with an uncertainty of 12% (Petzold and Schönlinner, 2004). The eBC mass concentration was determined using the factory default inversion and calibration."

3) P35125, L3: The model numbers of the SPMS and CPC should be given.

Response:

The SMPS used in this work is actually a combination of a DMA and a CPC in one instrument. We agree that the model number of this instrument should be given. In the revised manuscript, this part was therefore changed to:

"The SMPS (TSI, Model 3034) is a sequential combination of several integrated components: an impactor, a neutralizer, a differential mobility analyzer and a condensation particle counter. It determines the size distribution of particles in a range of 10 nm to 487 nm (electro-mobility diameter)."

4) P35125, L23: More detail should be given regarding how the losses down the inlet pipe were calculated, given the magnitude of the correction. In particular, if diffusional losses were significant, whether this correction should be size-dependent should be commented on.

Response:

As responded to a similar comment from referee #1, we used now the particle density deriving from the chemical composition not as the campaign average but time resolved for each data point in the revised manuscript. In addition we introduced SMPS data which is now size dependently corrected as published by Henzing (2011) The description of the sampling losses of the 60 m inlet for eBC given in the manuscript derived from a series of measurements at the Cabauw tower performed in a previous campaign. Unfortunately these results are not published yet. To clarify how these losses were determined in the revised manuscript and to account for a comment from referee #2, the loss description was changed as follows:

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

Please note that these losses influenced only data acquired by the MAAP and SMPS. Since the contribution of eBC is rather low (average: 5%) a potential overall error for total aerosol masses is low and would not significantly alter one quintessence of the paper, namely total mass concentrations above the air quality limits. We think theoretical particle loss calculations would not add additional information in the context of this paper.

As a consequence of the newly evaluated SMPS data the correlation values between ACSM+MAAP data with SMPS data changed as seen in Fig. S3 and S4 in the revised supplement. Nevertheless, the overall qualitative and quantitative agreement is still given except that the ACSM+MAAP data is now overestimating the total PM_1 mass by 16%, excluding the eBC data the ACSM overestimates total mass by 12%. As seen in Fig. S3 the difference between both systems is significantly higher during the pollution events 16 to 27 January 2013 and 5 to 8 May 2013. Since the quantitative agreement with the MARGA is much higher at these times the discrepancy to the SMPS is likely due to the fact that the losses within the 60 m inlet could not be corrected for individual species as mentioned above. Therefore the following paragraph was added at the end of the cross validation chapter in the revised manuscript:

“Major discrepancies to the SMPS especially during some of the pollution events like 16 to 27 January 2013 and 5 to 8 May 2013 (see below) can be explained by the correction of losses through the 60 m inlet line which was done size dependently and did not account for losses of individual species as mentioned in chapter 2.3. As the quantitative agreements of individual inorganic species as well as of total inorganics between the ACSM and the MARGA during these periods are much higher, the mass loadings determined from these instruments are more reliable than the SMPS data.”

5) P35126, L13: Polyethylene is not a conductive polymer, so electrostatic losses of particles should be expected. Has this inlet line been characterised for this?

Response:

As responded to the similar comment from referee #1 a polyethylene (PE) tube can indeed potentially enhance wall losses of particles comparing to stainless steel tubes. The MARGA-inlet system at the Cabauw tower as used for this study was previously described by Schaap et al. (2011). It actually did not only consist of PE tubes but of a series of components reducing particle losses. They investigated wall losses on a similar system and found only minor concentration losses for several compounds of 2% and less. A more detailed description was added in the revised manuscript:

“The sample air was transferred into the instrument within a polyethylene („Polyflo“) tube with an inner diameter of 0.5” (= 1.27 cm) and a sample flow of 16.7 L min^{-1}, which is either directed through a PM_1 or a $PM_{2.5}$ size selective head. A detailed description of the MARGA inlet system at the Cabauw tower was previously described by Schaap et al. (2011). There, wall losses were investigated and found to be less than 2% for several gaseous and particulate compounds.”

6) P35126, L15: The method of size selection (e.g. impaction, cyclone) should be specified.

Response:

The size selection was done using size selective cyclones. We agree that this should be specified. This part was changed in the revised manuscript to:

"The sample air was transferred into the instrument within a polyethylene („Polyflo") tube with an inner diameter of 0.5" (= 1.27 cm) and a sample flow of 16.7 L min^{-1}, which is either directed through a PM_1 or a $PM_{2.5}$ size selective cyclone."

7) P35133, L3: I don't see how the sulphate comparison can be regarded as "high quantitative agreement" given that it is of the order of 50% out. Given that historically, comparisons regarding sulphate generally tend to be quite favourable, this is quite surprising. It is also a little worrying that the ACSM measures more than both the AMS and the MARGA. The authors should investigate this further.

Response:

The "very high qualitative and quantitative agreements" is just referring to the comparison of the total inorganic masses from both instruments as shown in the last plot of Fig. S11 (which changed to Fig. S5 in the revised supplement). The authors agree that the current description is misleading because the word "agreements" is written in the plural form. In the revised manuscript, this word was changed to its singular form "agreement".

As seen by the last plots in Fig. S11 and S12 (which changed to Fig. S5 and S6, respectively, in the revised supplement), the ACSM actually measures the same or even little less than the MARGA and AMS, respectively, in terms of total concentrations (slopes of the regression lines are 1.05 and 0.90, respectively). The ACSM showed higher concentrations only in case of nitrate. This issue and the discrepancies regarding other aerosol species is explained in detail in the manuscript and in the responds to similar comments from referees #1 and #2.

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

P. Schlag[1,2], A. Kiendler-Scharr [2], M. J. Blom[3], F. Canonaco[4], J. S. Henzing[5], M. Moerman[5], A. S. H. Prévôt[4] and R. Holzinger [1]

[1]Institute for Marine and Atmospheric Research Utrecht (IMAU), Utrecht University, Utrecht, The Netherlands

[2]Institute for Energy and Climate Research (IEK-8): Troposphere, Forschungszentrum Jülich, Jülich, D-52425, Germany

[3]Energy Research Centre of the Netherlands (ECN), Petten, The Netherlands

[4]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute (PSI), Villigen, Switzerland

[5]Netherlands Organisation for Applied Scientific Research (TNO), Utrecht, The Netherlands

Correspondence to: P. Schlag (p.schlag@fz-juelich.de).

Abstract

Intensive measurements of submicron aerosol particles and their chemical composition were performed with an Aerosol Chemical Speciation Monitor (ACSM) at the Cabauw Experimental Site for Atmospheric Research (CESAR) in Cabauw, NL, sampling at 5 m height above ground. The campaign lasted nearly one year from July 2012 to June 2013 as part of the EU-FP7-ACTRIS project (Q-ACSM Network). Including equivalent black carbon an average particulate mass concentration of 9.50 µg m^{-3} was obtained during the whole campaign with dominant contributions from ammonium nitrate (45%), organic aerosol (OA, 29%), and ammonium sulfate (19%). 12 exceedances of the World Health Organization (WHO) $PM_{2.5}$ daily mean limit (25 µg m^{-3}) were observed at this rural site using PM_1 instrumentation only. Ammonium nitrate and OA represented the largest contributors to total particulate matter during periods of exceedance.

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

1 Introduction

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

In addition, particles can impact adversely on human health by e.g. increasing the probability of cardiopulmonary and lung cancer mortality (Pope et al., 2002). The World Health Organization (WHO) recently estimated that globally, 3.7 million deaths were attributable to ambient air pollution in both cities and rural areas in 2012 (EU, 2008). This mortality is reported to be due to exposure to small particulate matter (PM_{10}), which can cause cardiovascular and respiratory disease, and cancers. Particles with lower diameters such as $PM_{2.5}$ or PM_1 are reported to have enhanced toxicological effects since they can deposit more deeply in the respiratory system and remain suspended for longer periods of time (Pope and Dockery, 2006). Therefore, a number of institutions established several air quality standards for different particle sizes to limit aerosol mass. The WHO air quality guideline (global update 2005, WHO (2006)) defines a $PM_{2.5}$ daily mean limit of 25 $\mu g\ m^{-3}$ and a $PM_{2.5}$ annual mean limit of 10 $\mu g\ m^{-3}$. The European Union Air Quality Directive 2008/50/EC provides only a target value of the annual mean limit of $PM_{2.5}$ of 25 $\mu g\ m^{-3}$ (EU, 2008).

Air quality and climate effects are not only depending on the particle number concentration and size, but also on their chemical composition. This information is not only relevant to investigate the nature and magnitude of each effect, but also for the identification and quantification of aerosol sources and mitigation strategies for a potential reduction of aerosol mass concentrations. Major inorganic components of PM_1 consist mainly of ammonium nitrate (NH_4NO_3) and ammonium sulfate ($(NH_4)_2SO_4$), formed in the presence of ammonia (NH_3), nitrogen oxides ($NO_x = NO + NO_2$) and sulfur dioxide (SO_2), respectively (Seinfeld and Pandis, 2006). Therefore NH_4NO_3 and $(NH_4)_2SO_4$ are strongly attributed to anthropogenic sources (Finlayson-Pitts and Pitts, 2000). Since the reactions leading to inorganic aerosol happen from gaseous precursors in the atmosphere, the condensed products are considered as secondary aerosols, while primary aerosols like black carbon (BC) are emitted directly.

In contrast, organic aerosols (OA), which can also be of primary (POA) or secondary (SOA) origin, consist of up to hundreds of thousands of different molecules (Goldstein and Galbally, 2007), where SOA contributes on average 70% to organic aerosol mass (Hallquist et al., 2009). SOA is formed by gas to particle conversion of atmospherically oxidized semi- and low-volatile organic compounds (VOC's). Guenther et al. (1995) estimated a global VOC budget in the order of 1150 Tg carbon per year. Biogenic VOC's (BVOC's) contribute approximately 90% of total VOC, including isoprene (50% of total BVOC's), monoterpenes (15%), and sesquiterpenes (3%) (Guenther et al., 2012). In turn, 10% of emitted VOC's are of anthropogenic origin, including e.g. alkanes, alkenes, benzene and toluene.

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

The development of online aerosol mass spectrometric techniques during the last decades enhanced the possibilities to investigate aerosol chemical composition in real-time (DeCarlo et al., 2006; Jayne et al., 2000; Jimenez et al., 2003). The Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc., Billerica, MA, USA) is a powerful instrument to quantitatively measure the chemical composition of the non-refractory fraction of PM_1 ($NR-PM_1$) with high time and mass resolution. Due to the high amount of maintenance from skilled and trained personnel needed for continuous operating measurement campaigns using an AMS are usually not exceeding one or two months (Sun et al., 2012). Since the variation of aerosol composition is very high depending on measurement site and season (Jimenez et al., 2009), long term measurements (≥ 1 year) are clearly needed. At a European level, this effort is supported by the Aerosols, Clouds and Traces gases Research InfraStructure network (ACTRIS) program that aims at pooling high-quality data from state-of-the-art instrumentation such as the Aerodyne Aerosol Chemical Speciation Monitor (ACSM). The Quadrupol-ACSM (Q-ACSM) is specially designed for long-term continuous and real-time measurements of mass concentrations and composition of $NR-PM_1$ species (Ng et al., 2011b).

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

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

2 Methodology

2.1 Site description: CESAR

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

The tower is equipped with external platforms and booms at 2 m, 10 m, 20 m, 40 m, 80 m, 140 m, and 200 m. At all these levels, meteorological observations of standard parameters like wind speed, wind direction, dew point temperature, and ambient temperature are routinely performed (Ulden and Wieringa, 1996). These data sets are available at the CESAR data base (KNMI, 2013). In addition, other meteorological data like precipitation, radiation and remote sensing, including lidar, radar and radiometer techniques, are acquired at the tower and submitted to the CESAR data base. Also concentrations of gaseous compounds, including greenhouse gases, are monitored at CESAR (Russchenberg et al., 2005; Vermeulen et al., 2011). The National Institute for Public Health and the Environment (RIVM, the Netherlands) provides hourly data from gaseous CO, NO, NO_2, SO, SO_2, and O_3, but also daily PM_{10} measurements. Data of ambient CO_2, CH_4 (both measured at 20 m, 60 m, 120 m, and 200 m height), and Radon 222 (^{222}Rn, measured at 20 m and 200 m height) is determined by ECN on a time scale of 30 minutes. A map indicating the land use of the Netherlands is given in the supplement (Fig. S1).

2.2 ACSM sampling and data analysis

The ACSM measures the NR-PM$_1$ fraction, including the organic fraction (Org), ammonium (NH$_4$), nitrate (NO$_3$), sulfate (SO$_4$), and chloride (Chl), using mass spectrometric information on a time base of approximately 30 minutes. The ACSM used in this work is equipped with a commercial grade Quadrupole Residual Gas Analyzer (RGA), thus it is also called a Q-ACSM. This instrument is described in detail by Ng et al. (2011b). The RGA provides unit mass resolution (UMR) mass spectra. Fractions of measured UMR signals were assigned to individual aerosol species using the fragmentation table introduced by Allan et al. (2004). Due to the automated zeroing system used for the ACSM, adjustments of the fragmentation table entries concerning interferences from air beam molecules are not needed. All ACSM data processing and analysis within this work was performed using software provided by Aerodyne Research (ACSM Local, version 1.531, ARI (2012)) within IGOR Pro version 6.2.3.

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

Mass calibrations were performed approximately every month and were based on determining the instrument response factor (RF) (Ng et al., 2011b) using monodisperse NH$_4$NO$_3$ (320 nm) as calibration substance and a Condensation Particle Counter (CPC, TSI 3022a) as reference instrument (Jayne et al., 2000; Jimenez et al., 2003). An average RF_{NO3} of $2.74 \pm 0.45 \cdot 10^{-11}$ was obtained and used for the calculation of aerosol mass concentrations. Instead of performing a mass calibration for every aerosol species, relative ionization efficiencies (RIE's), compared to that of nitrate, were used. The RIE's of NH$_4$ and SO$_4$ were determined directly during the mass calibrations by measuring dry NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ particles after another. Averaged over all calibrations, a RIE_{NH4} of 7.53 ± 0.21 and a RIE_{SO4} of 0.81 ± 0.10 were found and used for the whole data set. Calibration results gained from this particular instrument during an intercomparison in Paris as described by Crenn et al. (2015) were within the uncertainty or only slightly different ($RF_{NO3}=2.34\cdot10^{-11}$, $RIE_{NH4}=6.54$, $RIE_{SO4}=0.62$) considering the large differences between individual instruments at the intercomparison. RIE values of 1.4 and 1.3 for organics and chloride, respectively, were taken from the literature (Alfarra et al., 2004; Canagaratna et al., 2007).

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

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

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

2.3 Collocated aerosol measurements

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

The MAAP instrument has been introduced by Petzold and Schönlinner (2004) and Petzold et al. (2005). It is designed for the determination of the black carbon (BC), which is a product of incomplete combustion. There is in the scientific community a general consensus over what black carbon is in terms of properties (Bond et al., 2013) The MAAP measures the strong visible light absorption property of BC by simultaneous measurements of the radiation penetrating through and scattered back from a particle-loaded fiber filter. According to Petzold et al. (2013), optical BC determined by MAAP is to be referred to as equivalent black carbon (eBC). One property of BC is that it is highly refractory with a vaporization temperature near 4000K (Schwarz et al., 2006), thus BC is not vaporized at 600°C and cannot be measured by the ACSM. The MAAP achieves a time resolution of 5 minutes with an uncertainty of 12% (Petzold and Schönlinner, 2004). A mass absorption cross section (MAC) of 6.6 m^2 g^{-1} for a wavelength of 637 nm (Müller et al., 2011) was chosen to convert the measured particle absorption coefficient to eBC mass concentrations. Although the MAAP has no size selective inlet beside the PM_{10} heads described below, it can be assumed that eBC-containing aerosol generally fall into the submicron size range (Bond et al., 2013). Thus eBC mass concentrations are considered as part of the PM_1 fraction from hereon. As seen later the eBC fraction is rather low throughout the campaign, meaning that the overall error of this assumption is not significant.

The SMPS (TSI, Model 3034) is a sequential combination of several integrated components: an impactor, a neutralizer, a differential mobility analyser and a condensation particle counter. It determines the size distribution of particles in a range of 10 nm to 487 nm (electromobility diameter). The SMPS aerosol mass concentration was calculated from the measured volume distributions using the particle density determined by the aerosol composition information derived from the ACSM and the MAAP. Assuming spherical particles, the total density is computed by using the densities of the aerosol species, weighted by their mass fractions. Bulk densities of NH_4NO_3 (1.72 g cm^{-3}) and $(NH_4)_2SO_4$ (1.77 g cm^{-3}), and densities of 1.8 g cm^{-3} for BC (Bond and Bergstrom, 2006; Park et al., 2004) of organics (1.4 g cm^{-3}, Hallquist et al. (2009)) were taken into account. Considering its low influence on the total particle density at this site, it is acceptable to set the density for chloride to 1 g cm^{-3} (Mensah et al., 2012).

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

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

The MARGA measures water soluble components of both the gas and aerosol phase simultaneously, including the aerosol species nitrate, ammonium, sulfate, and chloride. It uses a Wet Annular Denuder (WAD) followed by a Steam Jet Aerosol Collector (SJAC). The operational and calibration procedures, as well as details of the data analysis are given by Trebs et al. (2004). During the campaign the MARGA collected alternately the PM_1 and $PM_{2.5}$ fraction of ambient particles at ambient RH and temperature, each fraction sampled hourly with a measurement error smaller than 10% (Schaap et al., 2011). The detection limits for the most abundant aerosol species were 0.05, 0.10, 0.08, 0.01 µg m^{-3} (4σ, Rumsey et al. (2014)) for ammonium, nitrate, sulfate, and chloride, respectively.

The MARGA inlet was equipped with a PM_{10} size selective head (Rupprecht and Pataschnick, R&P), placed on the roof of the tower building next to the ACSM inlet aperture at 5 m height. The sample air was transferred into the instrument within a polyethylene („Polyflo“) tube with an inner diameter of 0.5” (= 1.27 cm) and a sample flow of 16.7 L min^{-1}, which is either directed through a PM_1 or a $PM_{2.5}$ size selective cyclone. A detailed description of the MARGA inlet system at the Cabauw tower was previously described by Schaap et al. (2011). There, wall losses were investigated and found to be less than 2% for several gaseous and particulate compounds. To compare with the ACSM, only MARGA data containing PM_1 composition is considered within this work.

An Aerodyne HR-ToF-AMS was connected to the MARGA inlet during the first 6 days of the campaign. As the ACSM is built upon AMS, the latter measures likewise the chemical composition of the PM_1 non-refractory (NR) fraction. Instrumental details are available in Jayne et al. (2000), Jimenez et al. (2003), and DeCarlo et al. (2006).

2.4 Statistical methods of organic aerosol data analysis

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

The extraction of OA data and error matrices as mass concentrations in µg m^{-3} over time, as well as their preparation for PMF/ME-2 according to Ulbrich et al. (2009), was done within the ACSM software. Only m/z’s ≤ 100 were considered here since they represented nearly the whole OA mass (around 98%) and did not interfere with ion fragments originating from naphthalene (e.g., m/z 127, 128, and 129, see also Sec. 2.2). From these matrices, the m/z 12 was discarded because it showed negative signals, probably due to too short delay time of the quadrupole scan (125 ms) after a valve switch (Fröhlich et al., 2015). In addition, the m/z’s 37 and 38 were also removed from the organic matrices of the whole campaign except for winter 2013. This was done because the signal at these masses showed high interferences with the chloride related ions ^{37}Cl and $H^{37}Cl$. Including these ions lead to unreasonable PMF factors which mainly contained only these two masses and represented the chloride time series, whereas during Winter 2013 no such interferences were observed.

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

- The quality parameter Q/Q_{exp} was minimized.
- Factor profiles have reasonable mass spectra, as expected for the measurement site.
- Factor time series have high correlations with respective external data sets such as gaseous CO, CO_2, NO_x, and particulate nitrate, sulfate and black carbon.
- When a proper solution is found, 50 seed runs were used to find the global minimum for Q/Q_{exp}.
- Investigation of the rotational ambiguity of the solution space is carried out using the a-value approach for the constrained factor profiles

3 Results and discussion

3.1 Cross-validation of particulate total mass and chemical species concentrations

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

Since the MARGA measures routinely the water soluble inorganic aerosol compounds, data from ACSM inorganic species were synchronized and compared to corresponding MARGA PM_1 data for the whole measurement period. The temporal overlap with the collocated high resolution AMS was between 11 and 17 July 2012. The correlation parameters of individual aerosol species and respective total masses between the ACSM data and the data sets from the MARGA and AMS are given in Table 1, using 1943 and 294 common data points, respectively. The corresponding correlation graphs are shown in the supplement (Fig. S5 and S6). Except for chloride, high correlation coefficients were achieved. Furthermore, the comparison to both total mass time evolutions shows very high qualitative and quantitative agreement. The quantitative difference between ACSM- and AMS-organics is also very low, and the discrepancies in case of ammonium and nitrate are within the stated ± 30% accuracy of the AMS and ACSM (Ng et al., 2011b) and the ± 10% for the MARGA–NO_3, respectively (Makkonen et al., 2012). Similar variations were also found by Crenn et al. (2015) as well as Budisulistiorini et al. (2014). The latter reported of a comparison between two collocated ACSM's (± 27%, $R^2 = 0.21$ for Chl, $R^2 > 0.8$ for the other species) and between these ACSM's and a continuous Tapered Element Oscillating Microbalance (TEOM, $PM_{2.5}$) instrument. Note that the major ions used for nitrate detection in AMS and ACSM (NO^+ and NO_2^+) are produced from both inorganic and organic nitrate (e.g. Farmer et al. (2010)). The higher ACSM nitrate compared to MARGA nitrate can therefore also be explained by the presence of organic nitrates. In case of nitrate the ASCM and MARGA comparison cannot be seen as independent. The underestimation of the ACSM in case of sulfate exceeding the uncertainties may arise from calibration issues. The mass calibration procedure used in this work was mainly adopted from AMS procedures which may not be directly suitable for the ACSM. The RIE of sulfate might be overestimated due to high observed background signals during the calibration using $(NH_4)_2SO_4$ particles. An overestimated RIE_{SO4} results in underestimated mass concentrations. This would in turn explain the low SO_4 mass concentrations comparing to the MARGA and AMS. Additionally, the ACSM fragmentation table could not be adjusted for interferences of ions from different aerosol species on the same m/z properly because ACSM software used in this study did not allow plotting time series for specific fragments apportioned by the fragmentation table. Thus, the standard table had to be used. Furthermore, the MARGA measured only low concentrations of Mg, Na, K and Ca (average sum: 0.08 µg m^{-3}). Thus, contributions of their corresponding sulfate salts, for which the ACSM is less sensitive, are negligible in this context. It should also be noted, that chloride concentrations can originate from particulate organic and inorganic chloride components originating from e.g. sea salt. For the latter, the ACSM is much less sensitive than the MARGA. As described above, influences from sea salt can be considered rather low. In turn, the MARGA might be less sensitive to organic chlorides, as they are likely less water soluble than inorganic chlorides. These explanations would explain the low agreement between the two instruments in case of chloride.

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

May 2013 (see below) can be explained by the correction of losses through the 60 m inlet line which was done size dependently and did not account for losses of individual species as mentioned in chapter 2.3. As the quantitative agreements of individual inorganic species as well as of total inorganics between the ACSM and the MARGA during these periods are much higher, the mass loadings determined from these instruments are more reliable than the SMPS data.

3.2 Aerosol chemical composition

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

Data coverage of 75% for one day and 90% for one calendar year, respectively, is defined mandatory for a proper risk assessment according to the WHO air quality guideline. The last requirement could not be achieved either with the ACSM or with the MARGA between July 2012 and June 2013 (70% and 71% coverage, respectively). Nevertheless, the average total mass derived from the combination of the MARGA $PM_{2.5}$ data (including all water soluble inorganic components NO_3, NH_4, SO_4, Cl, Na, K, Mg, and Ca), MAAP eBC and ACSM PM_1 organics resulted in 12.5 µg m^{-3} during this time, clearly exceeding the WHO $PM_{2.5}$ annual mean limit (10 µg m^{-3}) by 25%. Even the PM_1 concentration inferred from ACSM + MAAP data (campaign average 9.5 µg m^{-3}) approached the WHO $PM_{2.5}$ limit.

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

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

Overall, particulate nitrate and organics were the dominant species, representing 39% and 29% of the total aerosol, respectively. Both compounds show similar contributions in summer (period 1) and autumn 2012 (period 2), whereas in winter (January-February-March, period 3 and beginning of 4) and spring (April-May-June, periods 4 and 5) the NO_3 fraction increased up to an average of 46% of the total particulate mass, and the organic and eBC fractions decreased. The contributions of the other components showed only small variations between the seasons (see Table S2).

The most significant pollution events (17 to 21 August 2012, 21 to 25 October 2012, 16 to 27 January 2013, and 5 to 8 May 2013) are highlighted with shaded backgrounds in Fig. 2. During these events, MARGA $PM_{2.5}$ data showed up to 33% higher (e.g. on 17 to 21 August 2012) total inorganic masses than ACSM PM_1 inorganics as implicated in Fig. 1. As mentioned above the number and proportions of exceedances of the WHO $PM_{2.5}$ daily mean limit is therefore even higher than when only PM_1 data is considered. During the last three events, northerly and north-easterly winds dominated. The period 16 to 27 January 2013 showed also the lowest temperatures (average: -4°C) with respect to the whole campaign and a temperature inversion between 2 m and 40 m height in the in the morning 25 January 2013, where both instruments showed total mass concentrations of ca. 20 µg m^{-3}. On the other hand, no temperature inversion was seen during times when very high (> 40 µg m^{-3}) aerosol mass loadings were observed, even in winter times. Many sudden drops of the particulate mass can be either explained by changes in wind direction and/or precipitation events, like in case of the two latter pollution events (16 to 27 January 2013, and 5 to 8 May 2013).

Figure 3 shows the diurnal patterns of each individual species and the total particulate mass for the whole campaign. Corresponding plots with data averaged separately for the five chosen periods can be found in the supplement (Fig. S8). Overall, NO_3 showed the largest diurnal variation, with a maximum during the night/morning hours, reflecting its nighttime production and a minimum during the day due to the volatility of NH_4NO_3. This pattern is more pronounced in the warmer periods 1 and 5. Since the majority of ammonium is originated from NH_4NO_3, NH_4 has a similar pattern to that of NO_3. SO_4, which is mainly formed photochemically during the day from gaseous SO_2, showed peaks during daytime, although its overall variation is rather low. The maxima of BC can be attributed to direct emissions from traffic (morning and evening rush hours) and biomass burning events (domestic heating in the evenings/nights). Finally, OA showed peaks at the evening hours during the colder periods and a daytime minimum during the summer. More detailed discussion of the diurnal patterns of individual OA factors is given below.

An ion balance of all inorganic compounds indicates that too less NH_4 was measured to neutralize all NO_3 and SO_4 to their corresponding ammonium salts. The measured NH_4 mass concentration against the predicted NH_4 from the ion balance is plotted in the supplement (Fig. S9) and resulted in a slope of 0.83 ± 0.00. One uncertainty of the ion balance is introduced by the use of RIE's for the inorganic species. As shown below we consider uncertainties of RIE to be of minor importance in explaining the observed low particulate NH_4 concentration. It should be noted that for the calculation of the ion balance all measured NO_3 is considered. In addition to NH_4NO_3 organic nitrates give rise to nitrate signal in the AMS, albeit with distinct difference in relative ion abundance (Alfarra et al., 2004; Fry et al., 2011; Fry et al., 2009). It was not possible to distinguish the organic and inorganic nitrate fraction based on their mass spectra with the ACSM. Since a relatively high amount of particulate organic nitrates was found in previous campaigns at CESAR using an AMS (Mensah, 2011), and the region is characterized by high NH_3 emissions (Derksen et al., 2011), the potential contribution of organic nitrates to the gap in the ion balance was explored as follows.

In contrast to the ion balance from the ACSM data, MARGA PM_1 measurements during the whole campaign showed a nearly 1:1 correlation of measured against predicted NH_4 (slope of the linear regression line: 1.03 ± 0.00, Pearson-$R^2 = 0.97$), but with a negative offset of ca. $0.30 \pm 0.01\ \mu g\ m^{-3}$. This offset, which is at least 3 times higher than the detection limits of the MARGA, cannot be explained by including positive metal ions to the ion balance, since the sum of Mg, Na, K and Ca mass concentrations had low contribution to particulate mass as mentioned in section 3.1. Thus, significant influence of their nitrate salts to total nitrate can be excluded. In addition, as the MARGA is measuring the water-soluble nitrate fraction, the MARGA-NO_3 can be considered to be exclusively NH_4NO_3. This assumption is acceptable, as shown by using the MARGA-NO_3 instead of the ACSM-total-NO_3 for the ion balance of ACSM data (including ACSM-SO_4, -Chl and -NH_4), following a procedure given by Xu et al.

(2015) who calculated the organic nitrate fraction by subtracting the inorganic nitrate concentrations measured by a particle-into-liquid sampler (PILS, see Orsini et al. (2003)) from ToF-AMS total nitrate concentrations. In the Cabauw data set, the correlation of measured against predicted NH_4 resulted in a nearly 1:1 regression line without a significant offset (Fig. S10). This is in agreement with the MARGA internal ion balance which also indicates neutralized inorganic aerosols. Therefore, the mass concentration of nitrate groups associated with organic molecules (hereafter called organic nitrate or $OrgNO_3$), can be estimated by subtracting the MARGA-nitrate from the ACSM-nitrate concentration. The $OrgNO_3$ time series using this approach is plotted in Fig. S11, the respective diurnal variation averaged over the whole campaign in Fig. S12. An average mass fraction of 9% was calculated for $OrgNO_3$ (average concentration: 0.43 µg m^{-3}) in respect to total ACSM-NO_3. The organic nitrate fraction shows a maximum concentration in the night, followed by a decrease during the day. These findings are in agreement with previously reported relatively high AMS organic nitrate fractions by Mensah (2011) in May 2008 (0.5 µg m^{-3}, 35% of total nitrate, 5.2% of total aerosol mass) and March 2009 (0.2 µg m^{-3}, 10% of total nitrate, 3.6% of total aerosol mass) in Cabauw.

3.3 Factor analysis of organic aerosols

Prior to PMF analysis, the ACSM data set was subdivided into four data sets, which were explored by PMF separately, mainly due to the operational time of the ACSM that are in the following referred as: (i) July-August-September 2012: Summer 2012; (ii) October-November-December 2012: Autumn 2012; (iii) January-February-March 2013: Winter 2013; (iv) April-May-beginning of June 2013: Spring 2013. A more detailed overview of the selected seasons is given in Table S3.

Figure 4 summarizes the time series of PMF factor classes (two POA factors: HOA and BBOA; and two SOA factors: OOA and a humic-like substances (HULIS) related factor, see below for descriptions) found for all seasons, except for BBOA in Summer 2012. A corresponding graph dividing these PMF results into the five periods according to Fig. 2 is shown in Fig. S13. The POA profiles were constrained within ME-2 using the HOA and BBOA mass spectra found by ME-2 operated PMF analyses by Crippa et al. (2014) at the CESAR tower in Cabauw in March 2009. For the HOA profile, a constant a-value of 0.1 was found to be most suitable for every season. If observed, the BBOA a-value was set to either

0.2 (Autumn 2012) or 0.3 (Winter and Spring 2013). The a-values based on different sensitivity tests for each season as described by Canonaco et al. (2013). Factor profiles including fractional contributions of marker ions (*f44*, *f43*, and *f60)* and diurnal variations for Winter 2013 are displayed in Fig. 5 as a representative example. Corresponding graphs for every season are shown in Fig. S14 and S15, respectively. Table S4 gives an overview of the temporal correlations of each factor with external data sets, while scatter plots from Winter 2013 profiles against profiles found in May 2008 at CESAR by Crippa et al. (2014) are given in Fig. S16.

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

The seasonal average HOA contribution to total organic mass was highest in Summer 2012 and lowest in Spring 2013 (16% and 8%, respectively). All HOA diurnal patterns (Fig. 5b) showed a maximum at 7 and 11 am (LT) and a slight increase in the evening, emphasizing that its main source is related to traffic likewise to BC (see Sec. 3.1). In Winter 2013, these maxima were less distinctive comparing to the other seasons. HOA Highest temporal agreements with HOA were seen by the POA tracers BC, NO_x and CO ($R^2 = 0.38$, 0.47, and 0.47, respectively) over the entire campaign.

The BBOA profile showed a very high contribution of m/z 60, which is dominated by the $C_2H_4O_2^+$ ion. This fragment is characteristic for anhydrosugars such as levoglucosan (Alfarra et al., 2007) which are established markers of wood combustion processes (Simoneit and Elias, 2001; Simoneit et al., 1999). The fractions of m/z 60 to the BBOA profile in Autumn 2012 (3.7%) and Winter 2013 (3.2%) are higher than in Spring 2013 (2.4%). As mentioned, BBOA was not found in Summer 2012. This was verified by the fact that the contribution of m/z 60 to the BBOA profile decreases for higher a-values in that season, which is an indication for the non-existence of BBOA. The highest contributions of BBOA to total organics were seen in the colder Autumn (23%) and Winter seasons (15%). This and the diurnal maximum during the evenings and nights match the expectations for a factor linked with domestic heating activities, together with the fact, that this factor was not seen during the warmer summer season. Averaged over the whole campaign, the contribution to total organics was 13%, including Summer 2012, where its fraction was set to zero. In Winter, the correlations with eBC and CO were higher (R^2 = 0.64 and 0.57, respectively) than over the whole campaign ($R^2 = 0.39$ and 0.49, respectively), meaning that these compounds are reasonably more attributed to domestic heating during the colder periods comparing to the contribution of heating to BC and CO during the other seasons in this region.

The OOA profile is similar to a MS pattern as expected for a low volatile OOA (LVOOA) factor. The correlation coefficients (Pearson-R^2) with the OOA and LVOOA spectra given by Ng et al. (2011a) are 0.94 and 0.97, respectively. Similar agreement was found compared to the LVOOA factor observed by Mensah (2011) and Crippa et al. (2014) (R^2 = 0.97 and 0.94, respectively) at the CESAR tower in May 2008. The OOA factor showed a night-time maximum and a day-time minimum. This is rather characteristic for a semi volatile OOA (SVOOA) behavior, as well as the high agreement with NO_3 over the whole year (R^2 = 0.63), as described by Lanz et al. (2007). The correlation to the LVOOA associated compound SO_4 is less significant (R^2 = 0.48). OOA dominated the organic fraction in Winter and Spring 2013 (47% and 48% contribution, respectively; 33% over the whole year). During the defined pollution events the increase of the OOA mass concentration (up to 11.8 $\mu g\ m^{-3}$), relative to the campaign average (1.05 $\mu g\ m^{-3}$), is much stronger compared to the other PMF factors, demonstrating that this factor is mainly responsible the high total OA mass during these periods.

The so called HULIS factor showed the highest *f44* values of all factors, increasing from Summer 2012 to Spring 2013 from 0.23 to 0.35. The HULIS factor class was first observed by Mensah (2011) in previous AMS campaigns at the CESAR tower in May 2008 and March 2009. The identification and characterization of this factor class was done in the 2008 campaign by the comparison with data from an ion-exchange chromatographic method for direct quantification of humic-like substances (HULIS) and from water-soluble organic carbon (WSOC) analyzed offline on a set of filters collected in parallel (Paglione et al., 2014). The HULIS factor provided the highest contribution to the total organic mass over the entire campaign (41%) and was the dominant factor in Summer and Autumn 2012. Since it had no distinct diurnal variation and preferential wind direction, it can be considered as regional background aerosol at this rural site. Additionally, the variation between the seasonal average concentrations of HULIS within the ACSM data set is less than ± 10%. Also the comparison to the most important tracers (Table S4 in the supplement) showed no preferential attribution, either to a low-volatile (R^2 = 0.41 with SO_4), semi-volatile (R^2 = 0.39 with NO_3) or to primary organic aerosol (R^2 = 0.47 with eBC). These characteristics were also reported for the HULIS factor found at CESAR in May 2008 (Crippa et al., 2014; Mensah, 2011). The correlation of the sum of the secondary inorganic species NO_3 and SO_4 with the sum of the OOA and HULIS time series gives a coefficient of R^2 = 0.70, which is slightly higher than with OOA only (R^2 = 0.67). This might confirm the SOA character of the HULIS factor. The reason why HULIS was the dominant factor in Summer and Autumn 2012, is due to the lower mass concentrations of the other factors compared to the remaining periods. In turn, OA mass increased during pollution events mainly due to the increase of the other SOA factor, namely OOA. A number of studies are published with different theories on the formation and sources of atmospheric HULIS. It shows similarities to terrestrial humic acids (HA) and fulvic acids (FA) due to their (poly-) acidic nature, but with lower molecular weight (< 1000 amu) than HA or FA (Graber and Rudich, 2006; Kiss et al., 2003). On the other hand, solid-phase extraction protocols for HULIS associate them with the more hydrophobic fraction of water-soluble aerosols (e.g. Varga et al. (2001)). Graber and Rudich (2006) suggested that the formation of HULIS happens by oligomerization of lighter organic acids in liquid droplets in the atmosphere within time scales of hours to days. This emphasizes, that HULIS is an ubiquitous background factor at Cabauw, characterized as regionally well mixed aerosol of long atmospheric lifetime.

Note that the correlation (Pearson-R^2) of the POA factors with eBC data is relatively low (R^2 = 0.38 and 0.39 with HOA and BBOA, respectively), while in turn HULIS shows a higher correlation with eBC, R^2 = 0.47. This can be understood in the light of a study by Andreae and Gelencser (2006) who pointed out that the fiber filters, as used by the MAAP, loaded with macroscopic amounts of humic like substances samples look very dark brown or nearly black. This implies an interference of HULIS with BC measurements and in consequence explains why the HULIS factor, in contrast to the POA factors, has a relatively high correlation coefficient with BC data.

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

3.4 Composition and sources of aerosols during pollution events

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

Since the major inorganic components NH_4NO_3 and $(NH_4)_2SO_4$ are produced by atmospheric processes, they are considered as secondary aerosols. Together with the high abundance of SOA (OOA, HULIS), chemically aged aerosol components have the largest impact on total particulate mass (up to 90%) at Cabauw. The largest effect on a potential reduction of particulate mass can therefore be achieved by reducing NO_x and/or NH_3 emissions, the anthropogenic precursors of particulate NH_4 and NO_3. Indeed, on 16 January 2013 highest NO_x values were observed compared to the whole campaign (daily mean: 96 $\mu g\ m^{-3}$; seasonal average: 29 $\mu g\ m^{-3}$). Also the highest NH_3 values were obtained between 17 and 19 August 2012 (daily means: 26-28 $\mu g\ m^{-3}$; seasonal average: 10 $\mu g\ m^{-3}$). These ammonia values are higher than previously reported for Cabauw, e.g. by Derksen et al. (2011) in May 2008 (approximately 20 $\mu g\ m^{-3}$). Lolkema et al. (2015) gave an annual average of 5.3 $\mu g\ m^{-3}$ for 2013 in this region.

4 Conclusions

This work provides chemical composition data of atmospheric aerosols acquired during one year at the CESAR tower in Cabauw, the Netherlands, which is a representative rural site for North Western Europe. The concentration of submicron particles from combined ACSM and MAAP data showed 12 exceedances from the WHO $PM_{2.5}$ daily mean limit. The respective campaign average of 9.5 µg m^{-3} approached the WHO $PM_{2.5}$ annual mean limit. Taking MARGA $PM_{2.5}$ into account the number and proportions of these exceedances are even higher, emphasizing the importance of these high ACSM PM_1 results shown here which represent lower limits. As carbonaceous compounds are estimated to be five times more toxic than inorganic particles (Lelieveld et al., 2015) MARGA data alone would not give sufficiently possible implications regarding adverse health effects. While few people live in the direct vicinity of the measurement site, the high aerosol concentration measured at the site can be considered to represent the regional background. This regional background is adding to local aerosol contributions in high populated urban sites (Pandis et al., 2013), namely the 4 largest cities of the Netherlands which have a distance of 40 km or less from the CESAR tower.

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

As indicated by model results for the South Western United States from Zhang and Wu (2013), the reduction of NH_3 emissions, in conjunction with already implemented SO_2 and NO_x emission reductions, can further reduce $PM_{2.5}$ than reducing SO_2 and NO_x emissions alone, particularly for regions with high emissions of NH_3 from agricultural sources. The latter is clearly the case for Cabauw with its high number of animal husbandry and the use of nitrogen containing fertilizers around the CESAR tower. Banzhaf et al. (2013) derived similar conclusions for PM_{10} using different emission scenarios within domains covering Germany and Europe. Applying a 3d chemical transport model over Europe Megaritis et al. (2014) found that a reduction of NH_3 emissions by 50% would have a much higher effect on reducing $PM_{2.5}$ than decreasing NO_x emissions by 50%. The latter scenario would even result in negative side effects such as higher tropospheric ozone concentrations (especially in summertime 4% over Western Europe and up to 40% in major urban areas) and higher amounts of particulate sulfate and OA by 8% and 12%, respectively, in winter.

The local mitigation of organic aerosol mass (29% contribution on average) is more challenging, as secondary organic aerosols are highly abundant at the Cabauw site (74% and 22% of OA and total PM_1 on average, respectively). The presented data set shows a large and ubiquitous HULIS fraction (37%) which based on diurnal patterns and a lack of correlation with wind direction can be considered as long-range background aerosol formed from atmospheric aging processes. In turn, primary organic aerosols emitted mainly from traffic and biomass burning (12% and 13% of OA on average) have only minor importance. For a more detailed identification of the SOA sources compound specific measurements of OA as well as routine VOC monitoring are needed.

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

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

		Slope	intercept [µg m^{-3}]	R^2
Chl	MARGA	0.49 ± 0.02	0.11 ± 0.01	0.24
	AMS	0.67 ± 0.01	-0.01 ± 0.01	0.31
NH_4	MARGA	0.88 ± 0.01	0.07 ± 0.01	0.93
	AMS	0.82 ± 0.03	0.01 ± 0.02	0.71
SO_4	MARGA	0.63 ± 0.01	-0.08 ± 0.01	0.86
	AMS	0.49 ± 0.02	-0.18 ± 0.02	0.76
NO_3	MARGA	1.23 ± 0.01	-0.37 ± 0.03	0.96
	AMS	1.17 ± 0.02	-0.04 ± 0.02	0.89
Organics	AMS	1.03 ± 0.04	0.07 ± 0.04	0.73
Total	MARGA	1.05 ± 0.01	-0.70 ± 0.06	0.93
	AMS	0.90 ± 0.02	-0.02 ± 0.07	0.84

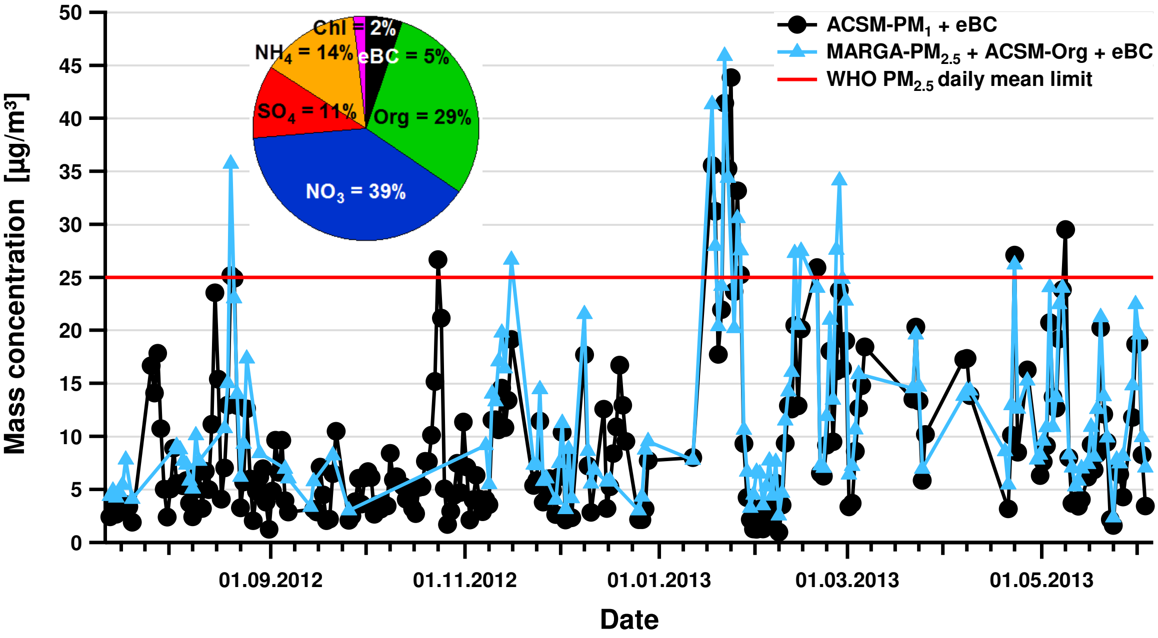

Figure 1: Time series of the daily mean. The black line represents the sum of eBC and all ACSM species, the blue line the sum of eBC, ACSM organics and all MARGA-PM$_{2.5}$ species. The pie chart shows the fractional abundances of individual eBC and ACSM species averaged over the whole campaign. For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

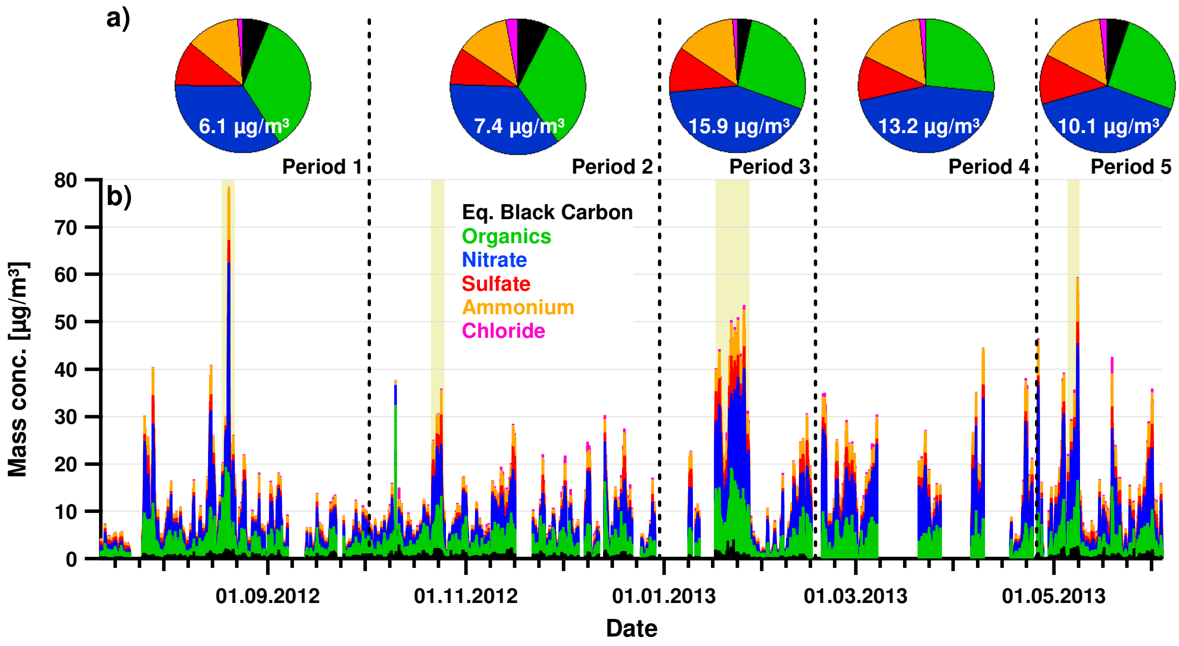

Figure 2: Overview of the ACSM campaign: a) Pie charts of average fractional abundances of aerosol species, separated in five periods. The respective average total mass concentration is written inside the pie chart. b) Stacked time series of mass concentrations of aerosol species. Pollution events are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

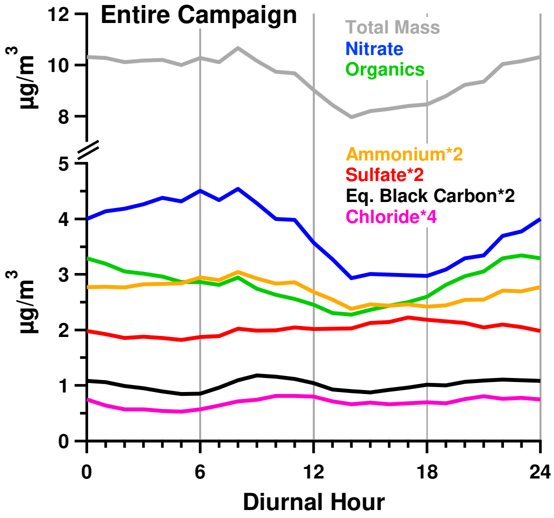

Figure 3: Diurnal variation (local time, LT) of individual species and the total mass, averaged over the whole ACSM campaign

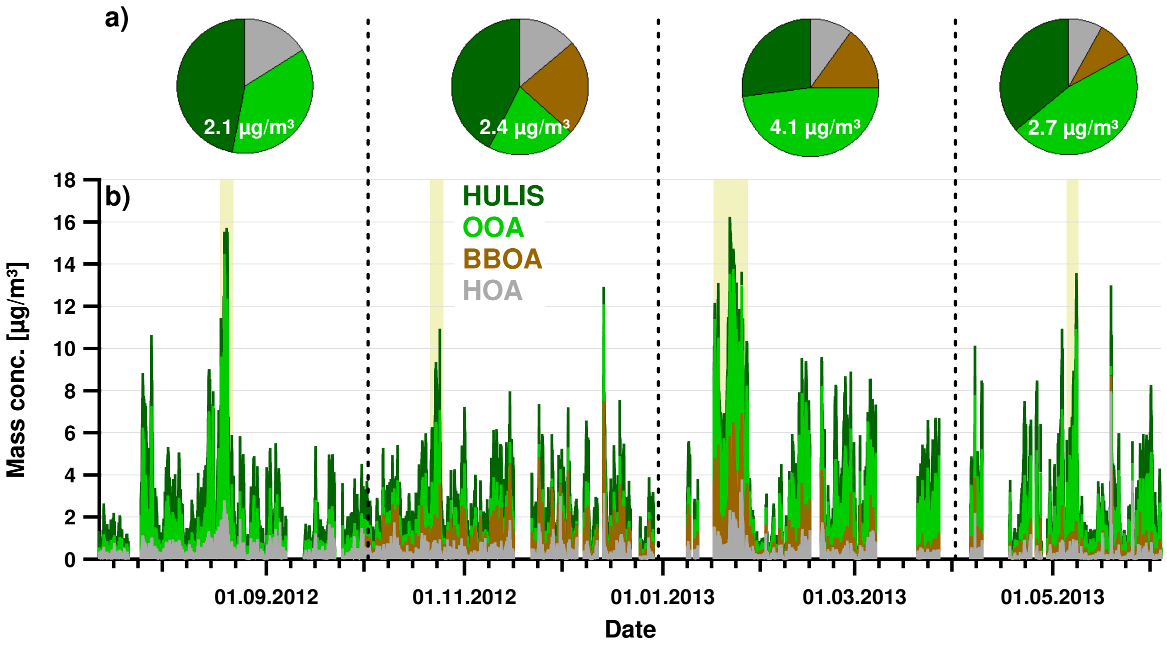

Figure 4: Overview of ACSM PMF factors: a) Seasonal pie charts of the factor contributions. The respective average total organic concentration is written inside the pie chart. b) Stacked time series of mass concentrations. Shaded areas represent highly polluted events.

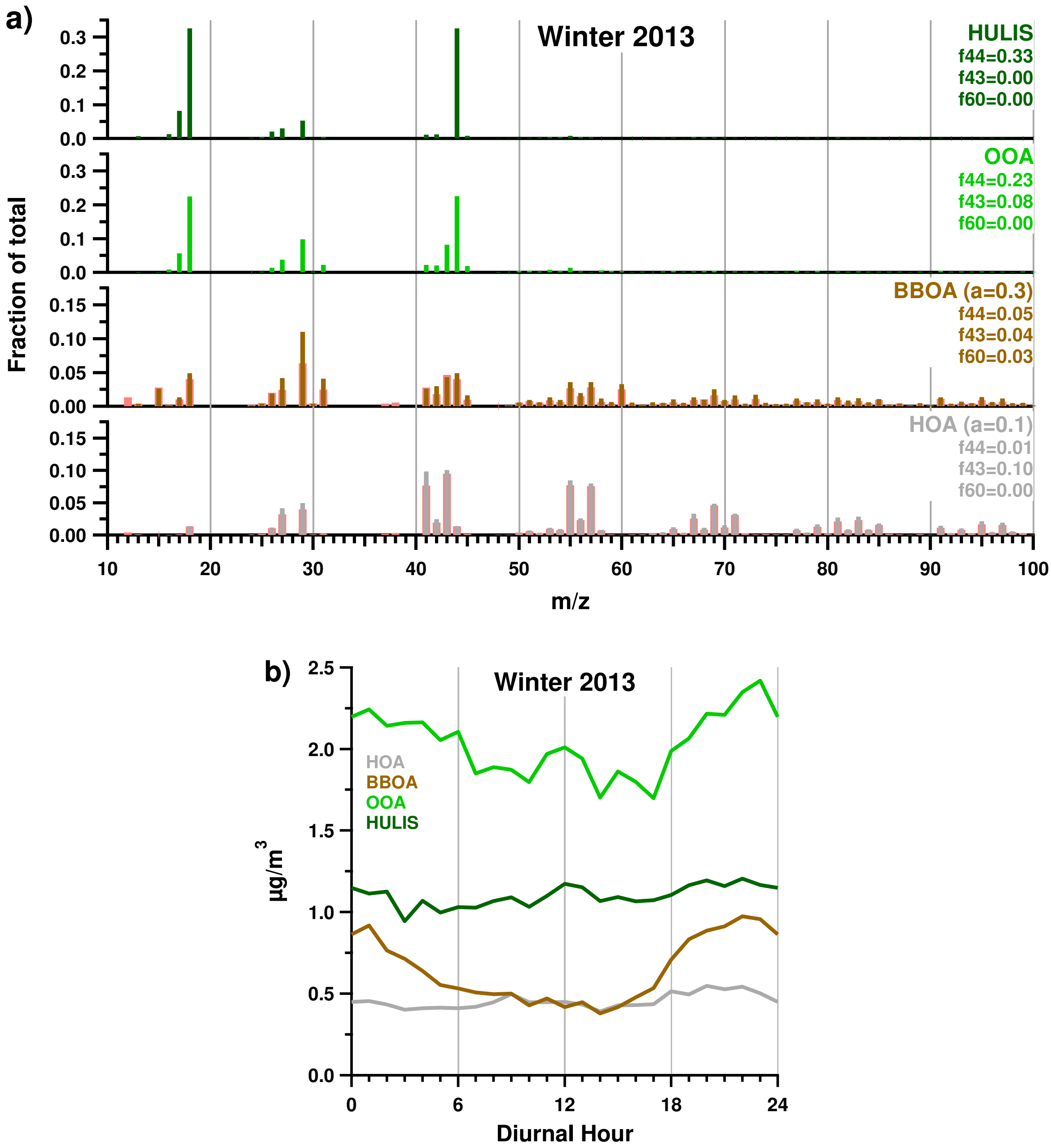

Figure 5: a) Mass spectra of ACSM PMF factors and b) average diurnal variations (LT) of ACSM factors found in Winter 2013. For the constrained profiles HOA and BBOA, the applied a-value is written in brackets. Corresponding reference spectra are shown by red bars. Note that the y-axis scales of the POA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

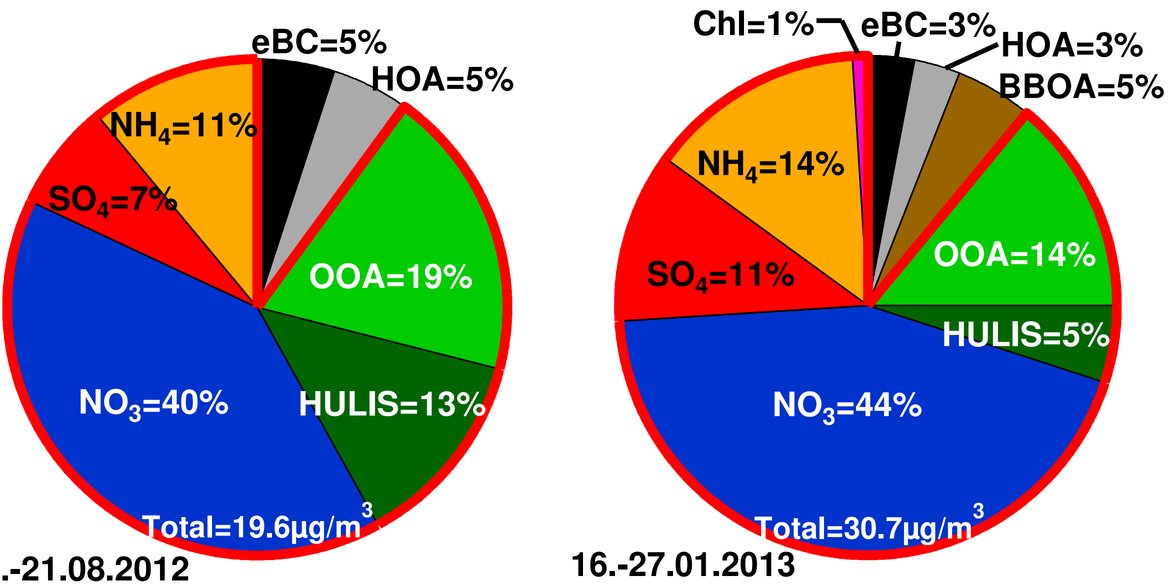

Figure 6: Average contributions of individual aerosol species and PMF factors during selected pollution events. Surrounded red regions represent the secondary aerosol fraction.