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

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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.”

__Specific Comments:__

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 $\mu g\ m^{-3}$) 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 $\mu g\ m^{-3}$, 35% of total nitrate, 5.2% of total aerosol mass) and March 2009 (0.2 $\mu g\ m^{-3}$, 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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