The authors thank the reviewers for their useful comments and provide detailed answers below. For clearer structure the *answers are given in italic* and changes made to the manuscript are repeated in red. Figures and sections will be cited according to the revised version of the manuscript.

Referee #2

This manuscript focuses on presenting AMS data obtained during two different time periods (May 2008,March 2009) in Cabauw Netherlands. Speciated mass concentration time trends are shown and comparisons with SMPS measurements are used to derive a dependence of the AMS CE on nitrate content. The AMS mass concentrations measured by the AMS are also compared to a MARGA instrument as well as a thermal desorption proton transfer reaction mass spectrometer (TD-PTR-MS). While the measurements are of interest, in principle, I do not think this manuscript can be published in its current state. The analysis presented in this manuscript is weak and does not provide enough new information to justify publication on its own. The information in this manuscript (the mass concentrations and chemical composition information) could be included as part of a larger overview paper, but to be published on its own it requires more detailed analysis. With additional major revisions, and new discussion and analysis, however, this work could be publishable.

Suggested Major Revisions include

1) Currently, a key weakness of this manuscript is that it does not go beyond the analysis of total organic AMS data to include organic PMF analysis or at least at a minimum, a mass spectral organic tracer analysis (*m*/z 57, *m*/z 44, etc..). This is now a routine procedure for AMS analysis, and it would provide key information and context to help understand the differences in the organic aerosol between the two campaigns.

We now include a section on analysis of the organic particulate fraction. This section is divided into two parts. In the first part we investigate the temporal evolution of specific ions determined by high resolution analysis of the mass spectra on the mass to charge ratios m/z 43, m/z 44, m/z 55, and m/z 57. We investigate the differences between oxidized and aliphatic ions and their different contribution in the two measurement campaigns. The second part deals with the diurnal *behavior of O:C and H:C ratios as an average as well as in specific periods of the two campaigns (page 21, line 11).*

3.5 Analysis of the organic phase

3.5.1 Organic tracer analysis

Figure 10a and b show the time traces of different organic ions at mass to charge ratio *m*/*z* 43, *m*/*z* 44, *m*/*z* 55, and *m*/*z* 57 from top to bottom. Please note, in 2008 the signals of $C_2H_3O^+$ on *m*/*z* 43 and CO_2^+ on *m*/*z* 44 are divided by a factor of 10 to allow for parallel display on the same axis as the other ions at the respective *m*/*z*. In 2009 this is only the case for CO_2^+. Furthermore, the CO2 signal reported here represents the particulate CO_2^+ after correction for gas phase CO_2^+ interference. While the ions at *m*/*z* 43 and *m*/*z* 44 can be considered as tracers for oxidized organic aerosol (OOA) the signals at *m*/*z* 55 and *m*/*z* 57 are considered as tracers of aliphatic/hydrocarbon-like organic aerosol (HOA) (Zhang et al., 2005a).

Due to the evaporation/ionization scheme of the AMS, almost all molecules are subject to substantial fragmentation. Therefore, the mass spectrum consists mainly of ions which are fragments of the mother ion. The high reproducibility of the fragmentation allows for assigning the ion fragments to specific molecular classes. That means for the ions presented here, that the non-oxidized ions most probably originate from aliphatic molecules or molecules which are dominated by an aliphatic structure. The ions containing a single oxygen atom most probably originate from molecules containing carbonyl groups such as aldehydes, ketones or ethers. Except for the CO_2^+ ion on *m*/*z* 44, which represents carboxyl compounds such as organic acids or esters, the concentration of ions containing two oxygen atom is highly dependent on the sample but generally and especially in these field campaigns negligible. Since the signals *m*/*z* 43 and *m*/*z* 44 are generally dominated by the oxidized ions, they are associated with secondary organic aerosol (SOA). Opposite to this, *m*/*z* 55 and *m*/*z* 57are dominated by aliphatic ions and are therefore associated with primary organic aerosol (POA, Zhang et al. (2005b).

High-resolution analysis of the organic mass spectra allows for exact attribution of signal intensity to different ions at the same nominal mass. While the CO_2^+ ion is shown in black, the other oxygenated ions are shown in green and the aliphatic ions in gray. At the nominal mass of *m*/*z* 43 the ions $C_3H_7^+$ and $C_2H_3O^+$ are detected. The latter is generally dominant and considered as a tracer of less oxidized/semi-volatile organic aerosol (SV-OOA, Ng et al. (2010)). $C_3H_8^+$ and

$C_2H_4O^+$ as well as CO_2^+ contribute to the signal at *m*/*z* 44. CO_2^+ is by far the dominating ion, originating from highly oxidized/low-volatile organic aerosol (LV OOA) such as organic acids Ng et al. (2010). Except for a few instances, the time traces of all ions are highly correlated. An interesting phenomenon can be seen on the 15th of May 2008. The aliphatic ions on *m*/*z* 43, *m*/*z* 55, and *m*/*z* 57 show a distinct peak in the early hours which is simultaneous with a very distinct peak in the chloride time trace. This supports the assumption of an organic origin of that chloride. This chloride peak was not only detected by the AMS but also by the collocated instruments MARGA Sizer (Figure 5) and TD-PRT-MS (Figure 7) The temporal correlation of the AMS chloride peak with the TD-PTR-MS *m*/*z*149 and the aliphatic ion time traces further supports the organic origin of AMS detected chloride.

As already seen in other field campaigns (Zhang et al., 2005a; Alfarra et al., 2004) and can be seen in the pie chart insets, *m*/*z* 43 and *m*/*z* 44 are dominated by the oxidized component and *m*/*z* 55, and *m*/*z* 57 are dominated by the aliphatic components. The pie charts give the contribution of the different ions a the respective *m*/*z*. The contribution of oxidized to aliphatic ions differs significantly for the two measurement periods. In general, the fraction of oxidized ions is higher in May 2008. We interpret this as a result of the increases oxidative potential of the atmosphere in spring/summer compared to winter. Higher intensity accompanied by longer duration of sunlight increases the production of •OH radicals, which are the major oxidants in the atmosphere (Finlayson-Pitts and Pitts, 2000) during day time. E.g. while $C_2H_3O^+$ contributes 85 % of the signal at *m*/*z* 43 in May 2008, the contribution is lowered to only 60 % in March 2009. Similar behavior can be observed on *m*/*z* 55 and *m*/*z* 57 where the signal is composed of contributions by $C_4H_7^+$ and $C_3H_3O^+$, and $C_4H_9^+$ and $C_3H_5O^+$, respectively. As already stated, these mass to charge ratios are generally dominated by the non-oxidized ions and associated with fresh, primary and/or anthropogenic emissions (Zhang et al., 2005a). The dominance of the aliphatic ion increases from summer to winter. The contribution of $C_4H_7^+$ on *m*/*z* 55 increases from slightly over half to more than two thirds and. This increase is even more pronounced for $C_4H_9^+$on *m*/*z* 57 , where the contribution increases from slightly over half to more than three quarters. The overall increase in the contribution of aliphatic ions is rather due to the significant decrease of the oxygenated ions than the moderate increase of the aliphatic ions from summer to winter.

3.5.2 Diurnal cycles of O:C and H:C ratios

Further insight to the composition of the organic particulate phase can be gained by investigating the oxygen to carbon (O:C) and hydrogen to carbon ratio (H:C), respectively. The O:C and H:C ratios can be determined from high resolution analysis of the organic mass spectra (Aiken et al., 2007). Figure 11a and b show the diurnal cycles of the O:C ratio (green dots, left axes) and H:C ratios (gray triangles, right axes) in May 2008 and March 2009, respectively. The top panel in each graph shows the diurnal average for the entire measurement period and the three panels below show the average diurnal cycles for three specific time intervals. The O:C and H:C ratios are highly anti-correlated in both measurement periods. The average O:C ratio in May 2008 is significantly higher than in March 2009. While the ratio reaches values of almost 0.7 in May 2008, which corresponds to highly oxidized LV OOA (Aiken et al., 2008), the O:C ratio did not exceed 0.4 in winter 2009. These low values are generally associated with less oxidized SV OOA (Jimenez et al., 2009).

On a daily basis, the O:C ratios show a minimum in the early morning hours and a maximum during the daytime. This maximum is pronounced and extended in May 2008 compared to March 2009 which correlates with more hours of sunshine in May and therefore longer time of photochemical aging. This indicates local aging of organic compounds by photochemical oxidation during the daytime. Interestingly, the period P2 during scavenged background conditions in May 2008 shows a reduced amplitude in O:C ratio accompanied by a high average value of 0.61. The combination of these two facts indicates the detected aerosol particles were aged and subject to long range transport in addition to the absence of local sources for OOA (Hildebrandt et al., 2010).

In both measurement periods, the H:C ratios show a maximum in the morning hours. In May 2008 a moderate increase between 0400 h and 0800 h can be seen. The ratio peaks between 0500 h and 0600 h UTC, which corresponds to 2 hours later in the day in local time. Therefore, the peak on H:C ratio appears at the time of morning traffic, which is generally accompanied by an increased emission of compounds high in H:C and low in O:C ratios from fossil fuel emissions (Aiken et al., 2008). In March 2009, morning peak values in H:C are found between 0600 h and 0700 h UTC which also corresponds to a local time of 0700 h to 0800 h due to reduced time shift of only one hour in winter. The decrease in H:C ratio during the daytime is not only due to the transformation from aliphatic to oxygenated compounds but also due to temperature increase.

Aliphatic compounds high in H:C tend to have higher vapor pressures than oxygenated species, causing the aliphatic compounds to evaporate from the particulate phase with increasing temperature. The temperature dependence of O:C and H:C ratios was shown by Huffman et al. (2009) by thermodenuder experiments on ambient aerosol particles. Reduced photochemical ageing due to reduced sunlight in addition to lower ambient temperatures can explain the significantly higher H:C ratios in March 2009. As expected, elevated H:C ratios were measured in winter compared to summer. While in March 2009, the H:C ratio fluctuates around 1.5, it fluctuates around 1.3 in May 2008. The increased H:C ratio corresponds to the finding of the tracer analysis showing reduced aging of the aerosol particles due to a lowered oxidative potential of the atmosphere in winter time

2) More context and comparison of why the aerosol composition between the two campaigns differ from each other (more details on differences in source influence, comparisons with tracers etc.). Context would also be provided by comparisons with any previous measurements in the area as well. Brief mention is made about the different meteorological periods observed during the two campaigns, but not enough information is available to really conclude anything about how/why composition really varies. The diurnal cycles which are reported do not contain enough useful information to really tease apart any useful details.

The authors extended the analysis by HR-analysis of the organics both with respect to tracer ions for HOA and OOA and with respect to overall O:C and H:C ratios. With this analysis we also provide insight into the reasons for different composition between the two campaigns. Overall the higher organic mass loading is dominated by photochemical processes as evidenced by the higher O:C ratio and larger concentration of OOA tracer ions in May 2008 compared to March 2009. See also detailed answer and changed text above.

3) A detailed report of the variation in CE with nitrate for different ambient measurements has been reported by Middlebrook et al. (A.M. Middlebrook, R. Bahreini, J.L. Jimenez, and M.R. Canagaratna. Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data. Aerosol Science and Technology, 46, 258–271, 2012). This work should be referenced and the CE formulation proposed here should be

compared with what is reported in that work. Is the NO3 fraction used in this formulation equal to NO_3/total AMS mass or NO_3/inorganic AMS Mass.

The authors would like to point out that the mentioned reference was only published after (end of September 2011) this paper was submitted (September 5th 2011). We did our best to cite the available literature and do cite papers concerned with the determination of CE (Matthew et al., 2008; Canagaratna et al., 2007; Quinn et al., 2006; Drewnick et al., 2004; Crosier et al., 2007; Allan et al., 2004).

The NO_3 fraction used in this formulation is equal to the NO_3/total AMS mass, which is now explicitly stated in the manuscript (page 16, line 6):

MF_{NO3} is defined as the particulate nitrate mass divided by the total particulate mass.

4) The smoothing of the size distributions reported in figure 5 seems too much and removes all the information necessary to understand the level of noise in this data. Why is the data smoothed so much? I recommend simply showing the average of the data without such extensive smoothing.

We have taken out the extensive smoothing and show the data now as campaign averages in Figure 8.

5) I think the comparisons between the AMS and TD-PTR-MS measurements are the most interesting portion of this paper and they could be discussed in more detail. Why, for example, does the relative agreement between the org from AMS and TD-PTRMS differ between the first and second part of figure 8? Does this change in relative agreement correlate with change of aerosol organic chemical composition?

The change in relative agreement of AMS and TDPTR-MS as visible in Figure 10 might be due to a change in aerosol particle composition. Organics were the most dominant contributors to the particle mass, partly exceeding 50 %, in the beginning of the measurement campaign. The particle composition was dominated by inorganic species between 15th of May and 24th of May 2008. The change to inorganic dominated particles was most probably accompanied in a change of particles hygroscopic growth factor. Since a key step in the particle collection of the TD-

PTR-MS humidification of the sampled particles, an increased growth factor might result in an increased collection efficiency. Unfortunately, no data of the TDPTR-MS is available for the time after the 24th of May, when the particle composition was again dominated by organics. Further parallel sampling of differently composed aerosol particles by AMS and TDPTR-MS are needed in the future to gain further insight to this issue (page 19, line 2).

The increase in detection sensitivity of the TD-PTR-MS might be due to changes in the composition of the aerosol particles. The fractional contribution of organics is significantly decreased at that time, which is most probably accompanied by an increase in the hygroscopicity of the aerosol particles. Since particle collection is achieved by humidification-aided impaction, an increased hygroscopicity of the particles could result in an increased collection efficiency. The organic contribution increases again after the 21th of May. Unfortunately, no TD-PTR-MS data is available after that time to investigate this hypothesis in greater detail.

Other comments

p. 27676, line 5-10: Is there a correlation between the excess ammonium that is observed and either chloride or oxidized organic species?

The authors investigated the behavior of excess ammonium thoroughly but did not find any clear correlation to any other species such as chloride. It was shown, that oxalic acid particles incorporate a substantial amount of ammonia from the gas phase under laboratory conditions. This contamination could be clearly detected by AMS measurements. In light of the high O:C ratios in May 2008, which point towards a significant contribution of organic acids to the particle composition, the excess ammonium might be a result of the presence of oxalic acid or other organic acids in the particles (page 15, line 7).

In 2008 the AMS measured ammonium concentration exceeded the mass needed for neutralization of nitrate and sulfate up to 20 %. Artifacts from data analysis are unlikely since special attention was paid in terms of possible interferences from gas phase ammonia and relative ionization efficiency of ammonium determined by repeated ionization efficiency calibrations. Unusually high ammonia concentrations measured at CESAR tower in previous campaigns were assigned to agricultural activities nearby (Schaap et al., 2011;Weijers et al., 2011). We speculate that our observed excess ammonium has agricultural sources, since high concentrations of nitrogen containing compounds such as ammonia and amines are known not only to be in the manure but also to evaporate in significantly amounts (Rotz, 2004). Particles containing oxalic acid can take up significant amounts of ammonia from the gas phase under laboratory conditions, which then can be detected as particulate ammonium by the AMS (Mensah et al., 2011). As discussed below there is evidence of substantial contribution of highly oxidized organic compounds, such as organic acids to the particulate aerosol mass in May 2008. Further characterization of the measurement location is needed for a final explanation of this observation, since a chicken farm is located only about 600 m north west of the CESAR tower..

Figure 2: It would be useful to report the average loading for the two time periods as well.

The average particulate mass loading is now included in the figure as well as in its figure caption.

The average mass loading was 10.21 μg/m^3 in May 2008 and 6.86 μg/m^3 in March 2009.

The authors should give a brief description of what is known about the quantification capabilities of the MARGA. What scaling factors are needed and what is the uncertainty in MARGA numbers?

As for the TD-PTR-MS we refer the reader to the literature for a full description of the MARGA principles of operation. Only aspects of data sampling and analysis specific to the operation during the two campaigns reported here are discussed in the manuscript. This is made explicitly clear in the respective text now (page 9, line 20):

Details of the calibrations, quality assurance and data analysis procedures routinely performed for MARGA are described in Trebs et al. (2004). Here we give only a summary of the specific sampling strategy for the Cabauw site**.**

Figure 5, it would be useful to see what the fractional contribution of the different species was as a function of size. It is interesting to note that there is considerable nitrate in the larger size distributions. Is all this nitrate ammonium nitrate? It could be useful also to see how the m/z 30 and m/z 46 that are used to obtain nitrate mass concentrations vary with respect to each other as a function of size.

To make the reader more aware of the change of the relative contributions of different compounds as function of size we added the following sentences (page 20, line 3 and page 20, line 6):

Maximum average mass fractions of nitrate were observed in the size range 500 nm – 1000 nm in May 2008 and between 300 nm – 800 nm in March 2009.

Note that the mass fraction of organics in particles smaller than 200nm was thus ≥ 60 % in May 2008 and ≥ 35 % in March 2009.

Based on comparisons with MARGA data we can exclude a large contribution of inorganic nitrate other than NH_4NO_3.