

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 #1

This manuscript deals with aerosol chemical composition measurements based on observations made at two intensive field campaigns. The paper is scientifically sound, but has serious problems in the following respects: 1) it is improperly structured, 2) it lacks clear scientific goals and conclusions, 3) it fails in putting the obtained results into a broad atmospheric context. I cannot recommend acceptance of this paper for publications before these problems, explained in more detail below, will be addressed.

Major comments:

Paper structure: First, it is difficult to see how the AMS *CE* (section 3.2.1) fits into the section "Aerosol particle composition"

The collection efficiency of the AMS is known to be composition dependent. Moreover, we generate a new empirical function based on our findings. Other AMS research groups participating in the same campaigns across Europe found the same dependence when the overall aerosol composition was nitrate enriched. This further supports our new function. We believe that the issues, which were considered in the generation of the new CE function can be best explained when the overall particle composition and especially the fractional contribution of the different species was discussed beforehand (page 7, line 26).

Since the *CE* is composition dependent (Matthew et al., 2008; Crosier et al., 2007), its determination will be explained in detail in an upcoming section aerosol particle composition (3.2.1).

and why the instrument comparisons (section 3.2.3) have been left until the end of the paper. In my opinion, all instrumental issues should be discussed under the same subsection and preferably before further analyses of the measurement data.

We agree with the reviewer in this point. The instrument comparisons were now shifted to an earlier part of the paper to emphasize the results of the AMS data. The respective subsections are now:

3.2.1 Determination of CE and comparison of AMS with SMPS,

3.2.2 Comparison of inorganic composition from AMS and MARGA-Sizer, and

3.2.3 Comparison of nitrate and organics from AMS and TD-PTRMS.

Second, what is the point of discussing shortly on particle chemical composition in section 3.1 when there is a separate paragraph for this (section 3.2).

It was not our intention to discuss the particle composition in detail in section 3.1 Measurement Conditions. The particle composition was rather mentioned to give a full description of Figure 1. To draw the attention of the reader to the meteorological parameters displayed in Figure 1 and discussed in that section, the introductory sentence of the paragraph was rephrased (page 13, line 3).

Key meteorological parameters are shown in Figure 1.

Third, how is the last paragraph of section 3.2.1 connected with the CE?

We fully agree in the reviewers concerns and have consequently moved that paragraph to the end of section 3.2.1 Aerosol Particle Composition (page 15, line 7).

Scientific goals and conclusions: The authors should state scientific goals for this paper in the introduction. Comparing instruments and presenting diurnal patterns does not fulfill this issue. What are the respective scientific conclusions?

The main goal of the paper is to present an overview of the observations in two intensive observation periods. This is motivated by an increasing number of (modeling) studies using this (and other EUCAARI) dataset and our attempt is to inform the reader of the quality of this data set and general features of the aerosol chemical composition in this central European measurement site. Since this data set represents the first deployment of an AMS at Cabauw,

general observations of the online measurements of organics are presented. The observed nitrate and sulfate concentrations and diurnal behavior are reported and compared to MARGA, a measurement technique that has previously been applied at Cabauw. This was already emphasized in the original version of the manuscript. To make the goals of this paper clearer to the reader the respective part of the introduction was extended and now reads (page 3, line 28):

Here we present an overview of the aerosol composition as measured in two intensive observation periods at Cabauw, the Netherlands. The measurements were linked to the intensive observation periods of the European Integrated Project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI) (Kulmala et al., 2009) and activities of the European Monitoring and Evaluation Programme (EMEP, <http://www.emep.int/>). Previous work on this data set has focused on the aerosol direct effect (Roelofs et al., 2010; Morgan et al., 2010a) and showed that the high fraction of ammonium nitrate observed in May 2008 largely impacts the aerosol optical thickness (Roelofs et al., 2010). It was shown that due to its semi-volatile nature maximum concentrations of ammonium nitrate are observed at the top of the boundary layer (Morgan et al., 2010a). The height profile needs to be taken into account when modelling the aerosol direct effects. We focus on the comparison of different instruments that measured the inorganic aerosol components in May 2008. Aerosol particle mass spectrometric data is compared to the results obtained by Monitor for AeRosol and GAses (MARGA) and Thermal-Desorption Proton-Transfer-Reaction Mass-Spectrometry (TD-PTR-MS) measurements. We show that the inorganic particulate aerosol mass concentrations derived by the different approaches are in good agreement with each other. Diurnal patterns of particulate inorganic and organic aerosol are discussed and an overview of the concentrations observed in the two campaigns is presented. Beside analysis of the inorganic particulate matter, we extend the analysis by investigating the composition of the organic particulate phase by high resolution time of flight mass spectrometry. In particular the O:C ratio and individual tracer ions are used to track OOA and HOA in both observation periods. To our knowledge, this is the first time that online analysis of the organic particulate aerosol phase is reported for that measurement location.

Atmospheric context: The authors have done very little to compare their results those presented elsewhere in the scientific literature. This concerns specifically measured particle chemical size distribution and diurnal cycles. The authors should somehow be able to say whether their finding

bring something new into our understanding on aerosol chemistry in Europe or whether these measurements just confirm what has been observed by others.

To improve the discussion part, we added an extended section on organics (see also detailed answer to reviewer 2) and now give an increased number of references to literature data. Specifically we give references to observations at other European sites during the EUCAARI intensive measurement period and to previous observations made at Cabauw (page 20, line 17 and page 21, line 7).

Night time maxima of nitrate not only in the fractional abundance but even in absolute mass concentration were found also at other measurement sites during the EUCAARI campaign (Poulain et al., 2011).

The diurnal cycles of nitrate, sulfate and ammonium observed during the two campaigns agree well with observations reported by Schaap et al. (2011) for PM10 diurnal cycles measured with MARGA.

Minor/technical issues:

Section 2.3: The description of the SMPS is not sufficient. Has the used instrument participated in any inter-comparison measurements? How its performance has been tested and monitored? What are the expected uncertainties in measured size distributions and, most important for this paper, in particle mass concentrations derived from SMPS measurements?

The description of the SMPS was extended to give further information on its specific features (page 8, line 23).

The mobility size spectrometer (e.g. ten Brink et al. (1983)) consists of a sequential set-up of an impactor, neutralizer, differential mobility analyzer (DMA) and a condensation particle counter (CPC). In the DMA, aerosol particles are classified according to their electrical mobility. The analyzer consists of a cylinder with a negatively charged rod at the center. Only aerosols in a narrow range of mobility exit through the output slit, where they enter the CPC, which determines the particle concentration of that size. Before entering the DMA, aerosols are brought to a bipolar charge equilibrium using a ⁸⁵Kr bipolar charger (neutralizer). In charge equilibrium, the fraction of particles with a single elementary charge is known for all sizes (Wiedensohler, 1988). An impactor upstream of the DMA removes particles larger than the upper size limit of

the mobility spectrometer and allows for correction of multiple charged particles with same mobility as the singly charged particles that are to be counted.

The operated SMPS is a modified version of a commercially available instrument (TSI 3034). To ensure reliable measurement data that is comparable to other European measurement data, the technical standards for mobility size spectrometers developed within the EUSAAR project are followed (Wiedensohler et al., 2010). Moreover the SMPS participated to a series of three intercomparison workshops conducted between 2006 and 2009 at the World Calibration Centre for Aerosol Physics (WCCAP) facilities in Leipzig (Wiedensohler et al., 2010). At the workshops the particle counting efficiency of the CPC used here was experimentally determined and the inversion routine, necessary for converting measured mobility distributions into final particle number size distributions taking into account the bipolar charge distribution as well as the DMA transfer function, was compared to different commercial and custom-programmed inversion routines to insure optimal performance of the SMPS system.

Page 27675, lines 22–: It remains unclear where the authors have taken the *CE* curves (equations 1a and b)? Please explain explicitly. The assumed *CE* curve has a discontinuity (0.5 to 0.542) at the point when changing from 1a to 1b ($MF_{NO_3} = 0.3$). This is not physical.

The CE curve was empirically determined after thorough analysis of the aerosol composition and comparisons to other instruments. It makes use of two limiting cases observed in the campaigns: first when nitrate makes a minor fraction of the total aerosol mass, CE of 0.5 is observed. Second the CE increases (as seen in Figure 3) with increasing nitrate contribution starting at a nitrate mass fraction of 0.3. As a limiting case we set CE=1 for pure ammonium nitrate (which is the calibration situation in the AMS). This increasing trend in CE with increasing nitrate mass fraction was found to be valid for the majority of the measurements performed at the same time across Europe as part of the EUCAARI project (Nemitz et. al., in preparation). We agree that the CE as given in the manuscript had a discontinuity at CE=0.3 and eliminate the nonphysical discontinuity in the revised version (page 17, line 3).

To account for the known fact of a composition dependent *CE* of the AMS (Crosier et al., 2007), especially the dependence on MF_{NO_3} , an empirical function was generated. A constant *CE* of 0.5 was applied to all measurements with a MF_{NO_3} below 0.3 (equation 1a), which corresponds to the

value found in other field campaigns with dry, sulfate dominated aerosol particles (Allan et al., 2004). To reflect the increasing CE of particles with increasing nitrate fraction, the CE of particles with a MF_{NO_3} above 0.3 was calculated according to equation (1b):

$$CE = 0.5 \quad \text{for } MF_{NO_3} < 0.3 \quad (1a)$$

$$CE = 0.1875 + 1.0417 \times MF_{NO_3} \quad \text{for } MF_{NO_3} \geq 0.3 \quad (1b)$$

Page 27676, lines 22-24: A statement like this cannot be made without giving a reference.

References have been added.

Poulain, L., Spindler, G., Birmili, W., Plass-Dülmer, C., Wiedensohler, A., and Herrmann, H.: Seasonal and diurnal variations of particulate nitrate and organic matter at the IfT research station Melpitz, *Atmos. Chem. Phys.*, 11, 12579-12599, 10.5194/acp-11-12579-2011, 2011.

Section 3.3: All the comparisons have been made against the AMS instrument. This should somehow be brought up in the subsection titles.

The subsections titles have been rephrased and moved to an earlier part of the manuscript – see also answer above.

3.2.1 Determination of CE and comparison of AMS with SMPS

3.2.2 Comparison of inorganic composition from AMS and MARGA-Sizer

3.2.3 Comparison of nitrate and organics from AMS and TD-PTRMS.

Section 3.3.1: The SMPS and AMS show very similar mass concentrations although the SMPS misses particles between 470 nm and 1 μm . Does this mean that there is negligible mass in this size range?

A detailed explanation for the legitimacy of the AMPS/AMS comparison is now given in section 3.2.1 where the basis for the generation of the new CE function is laid. If the transmission efficiency of the aerodynamic lens of the AMS as well as the differences in geometric diameter

(d_{geo}) as given by the SMPS and the vacuum aerodynamic diameter (d_{va}) as measured by the AMS are considered, the two instruments cover very similar size ranges (page 16, line 13).

The particulate aerosol mass was determined from the measured SMPS number distributions. To compare the mass loading of the AMS to measurements of the SMPS two things need to be considered concerning the different size cut offs of AMS and SMPS (Kleinman et al., 2008). First, the AMS has an almost 100 % transmission efficiency of particles only between ~60 nm to ~600 nm. There is a steep decrease in transmission efficiency for particles smaller and larger than this size range. Already particles of 700 nm show significantly decreased transmission efficiency of only 67 % in laboratory experiments (Jayne et al., 2000). Second, the size range of the AMS is given as aerodynamic diameter (d_{va}). To compare to the geometric diameter (d_{geo}) reported by the SMPS, the particle density needs to be taken into account. In a rough calculation assuming spherical particles and an average particle density of 1.5 g/cm³, a d_{va} of 600 nm corresponds to a d_{geo} of only 400 nm. In the actual calculation, the following steps were performed.

Section 3.3.2: This comparison has 3 problems: 1) the two instruments were at different heights, 2) different cut off sizes were used, 3) AMS has its own CE and so probably also MARGA. Based on this, I think it is too optimistic to say that the two instruments were in good agreement. In absolute concentration levels, the agreement is qualitatively good as best. The two instruments appear to reproduce the temporal variability of the chemical ionic compounds quite well, but even in this respect one can identify periods (fig 7) when the 2 instruments disagree substantially.

As stated in the paper, the differences of the two instruments could be due to different sample positions (AMS 60 m/MARGA-Sizer 4 m), since the observed mass will depend on the vertical distribution of species as well as on the losses within the sampling line. The issue of a MARGA CE needs to be further investigated by the MARGA community. We do not expect absolute quantitative agreement in view of the instrumental accuracies and limitations due to different sampling locations AMS and MARGA-Sizer. We rephrased the last sentence of that paragraph to emphasize the agreement is rather qualitatively good (page 18, line 12).

Considering the instrumental accuracies and limitations due to different sampling locations AMS and MARGA-Sizer show a qualitatively good agreement.