

Interactive comment on “Seasonal and diurnal variations of particulate nitrate and organic matter in the Central European atmospheric aerosol” by L. Poulain et al.

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We would like to thank the referee for the constructive comments and suggestions made to improve the manuscript. Our responses to each comment are given below.

The paper presents observations of the aerosol composition as measured at Melpitz, Germany in three intensive observation periods in 2008 and 2009. Aerosol composition was measured with a high resolution AMS for the non refractory PM1 and MAAP for soot in PM1. Meteorological parameters and O₃, NO_x, and SO₂ were measured in all three campaigns. Additionally photolysis rates and OH, and H₂SO₄ were measured during the summer campaign. The observed aerosol composition is discussed

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with respect to different seasonal influences. In particular the observations of organics and nitrate are discussed in more detail and determining factors for aerosol composition are presented. While the overall topic of the paper is within the scope of ACP, the manuscript has several weaknesses and needs major revision before it can be considered for publication.

Major points: 1. The authors focus their discussion on organics and nitrate when it seems from the data coverage that they should be best able to derive determining factors of aerosol sulphate. In the summer campaign in addition to NO_x, ozone and SO₂ also H₂SO₄ and OH were measured, providing an ideal data set to compare measured ammonium sulphate concentrations with predictions based on gas phase observations.

Response: We understand the present comment and appropriate comparisons are under investigation. Our manuscript only focused on the seasonality of the aerosol chemical composition while H₂SO₄ and OH were measured, as mentioned in the text, during summer time only. For this reason, we decided to not include a specific description of the sulfate formation during summer, but only compared all three campaigns together.

2. It is not clear why the authors consider low volatile OA (or rather high f₄₄) to be of regional origin and how they differentiate between regional photochemical effects on OA and long range transport aging effects. The data analysis is based on two major fragments (m/z 44 and m/z 43) only, without exploiting the high resolution possibilities of the AMS. Also from figures 2 and S2 it is shown that f₄₄ is correlated with ozone in all seasons. The possible effects of ozone chemistry on f₄₄ would have to be pointed out more clearly than is currently the case. Different individual ions present at nominal m/z 43 and 44 should be considered for this data analysis. The authors present OM/OC ratios, so the high resolution analysis must have been performed.

Response: Details on the organic mass spectra over the campaigns were added in a

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new subsection 4.2.1. We now present a description of the organic mass spectra based on the presence of different ion categories ($Cx+$, $CxHy+$, $CxHyO+$ and $CxHyOz+$) as well as on the elemental composition of C, H, O atoms. A discussion focusing on the compositions and diurnal profiles of m/z 43, 55 and 57 was added, too. We also explained that regarding the large contribution of the oxygenated fragments to the m/z 55 and 57 and the low contribution of m/z 60 to the total organic signal, the organic aerosols can be considered as principally made of oxygenated organic aerosol, with a minor contribution of primary organics aerosol (POA), especially during autumn. The correlation between f_{44} and ozone suggests that a regional aging should affect the organics aerosol independently of their origins (long range transport or local formation), especially during summer. While a higher influence of regionally formed OA should be expected in summer (larger biogenic emissions), this influence should be lower during winter. Therefore, winter OA might basically be influenced by long range transports. However, as no VOCs gas phase measurements were performed, it is difficult to quantify the influence of regionally formed OA on aging of long range transport OA only. The following text was added: "The averaged high resolution organic mass spectrum (HRMS) of each campaign is presented in Fig. 2. According to their composition, the organic fragments were divided in different ion categories ($Cx+$, $CxHy+$, $CxHyO+$ and $CxHyOz+$). The contribution of each category to the total organic signal as well as the corresponding elemental composition of C, H and O atoms is also presented in Fig. 2. The contribution of $CxHy+$ was rather constant during the three campaigns and represented almost 50% of organic aerosol (OA). The oxygenated categories, $CxHyO+$ and $CxHyOz+$, represented the second half of OA and a small change of the respective contribution of $CxHyO+$ and $CxHyOz+$ has been observed between summer and the two other seasons. However, the average elemental composition did not show a pronounced seasonal variation. The structure of the HRMS for each season was very similar. The most important peak was m/z 44 which is characteristic of the highly oxidized OA (e.g. Alfarra et al., 2004; Zhang et al., 2005a). The CO_2+ fragment was the most important contributor to m/z 44 and represented more than 95% of the total

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m/z 44 signal. The presence of CO_2+ can be attributed to multifunctional organic acids (Takegawa et al., 2007). The second most important peak was m/z 43. However, the contribution of m/z 43 to total HRMS decreased from summer to winter. The fragment m/z 43 was basically made of two fragments, C_2H_3O+ and C_3H_7+ (Fig SI 2). The fragment C_2H_3O+ was the most important fragment of m/z 43 during the three campaigns. However, the contribution of C_2H_3O+ was slightly higher in summer (92%), than in autumn (84%) and winter (80%) due to a slightly higher contribution of C_3H_7+ in these seasons. The fragment m/z 57 which is commonly considered as tracer for primary organic emissions of fossil fuel combustion (Zhang et al., 2005b; Canagaratna et al., 2004; Aiken et al., 2008) had a low contribution to total HRMS. The m/z 57 was made of two fragments, C_3H_5O+ and C_4H_9+ . The contribution of each fragment to the total m/z 57 signal changed during the three campaigns (Fig. SI 2). While in summer, m/z 57 was principally made of C_3H_5O+ (68% of total m/z 57 signal), the contribution of C_4H_9+ increased in autumn (53%) and winter (57%). Comparing the diurnal profiles of these two fragments during the different campaigns, a small increase of C_4H_9+ early in the morning during summer and autumn can be observed (Fig. SI 2). This might indicate a possible increase of primary organic aerosol at this time. It has been shown for a rural station in Canada that the ratios of C_3H_5O+ to C_4H_9+ increased with the photochemical aging (Liggio et al., 2010). Therefore, these authors suggest that the C_3H_5O+ might be associated with SOA and/or oxidized POA. Following this, the largest contribution of the C_3H_5O+ during summer might be attributed to a larger photochemistry aging OA, while the high correlation between C_3H_5O+ and C_4H_9+ , observed during each campaign ($r^2 = 0.60, 0.65$ and 0.65 in summer, autumn and winter, respectively), might suggest a similar source for these two ions. Another important organic fragment is the m/z 55 which like m/z 57 is often associated to primary organic emission (Alfarra et al., 2004; Canagaratna et al., 2004). The fragment m/z 55 was made of C_3H_3O+ and C_4H_7+ . Similarly to m/z 57, m/z 55 was basically made of the oxygenated fragment, C_3H_3O+ . However, a slight increase of the non oxygenated fragment could again be observed in autumn and winter (Fig. SI 2). In

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addition, the diurnal variation of the different seasons was very similar to m/z 57. The composition of the main organic fragments (m/z 43, 55 and 57) indicated that in Melpitz, organic aerosol was dominated by oxygenated organic aerosol, with a low contribution of primary organic aerosol during the different measurement campaigns. Because of a larger concentration of C₄H₉⁺ and a clear peak of C₄H₇⁺ and C₄H₉⁺ early in the morning during the autumn campaign, a small contribution of POA might be expected during this period. Finally, the presence of biomass burning organic aerosol is generally linked to the m/z 60 (Alfarra et al., 2007; Schneider et al., 2006). During the different seasons, m/z 60 had a small contribution to total OA (around 0.3%). Such low contribution of m/z 60 to total OA was considered as representative for a background level value of SOA dominated ambient organic aerosol (Cubison et al., 2011). Based on the m/z 60 contribution, it is concluded that there is only a minor influence of biomass burning aerosol on total OA, even during winter. However, like for POA, a limited contribution of biomass burning may be expected during the autumn campaign due to the small increase of m/z 60 contribution to OA”.

3. The presented framework for calculating determining factors of ammonium nitrate (AN) formation is an oversimplification of the real situation. While this may be justified by the typical lack of consideration of AN in regional models, the limitations of the approach should be clearly pointed out. If hygroscopicity data for the aerosol are available, the authors should consider testing their assumption on deliquescence RH with observations. The part on N₂O₅ and HONO impacts on particulate AN do not go beyond speculation and should be substantiated or left out.

Response: We agree that the method used to estimate the ammonium nitrate concentration was a simple and theoretical approach. It is now clearly mentioned that considering R1 and R2 only displays an extreme simplification. Regarding the comments of the other referees, a discussion on the influence of the different factors on the ammonium nitrate concentration was also added. We thank the referee for his/her suggestion to compare the estimated DRH with that one derived from hygroscopic-

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ity measurements. However, we have to admit that our estimated DRH was corresponded to pure ammonium nitrate and was only applicable for the evenings, when RH increased. In the morning, when RH decreased, it is the Efflorescence Relative Humidity (ERH) that should be considered. For these reasons, the section on the estimation of DRH was deleted and the following discussion on the influence of DRH and ERH on the total amount of particulate water concentration and on the influence of RH history was added: “Moreover, when RH increases, the transition from solid phase equilibrium (R1) to aqueous phase (R2) directly depends on the ambient RH value compared to the Deliquescence Relative Humidity (DRH) of the particle. When RH decreases, the transition from R2 to R1 depends on the ambient RH value compared to the Efflorescence Relative Humidity (ERH). For example, at 298K, pure ammonium sulfate particles have a DRH of 80% and an ERH of 35% while pure ammonium nitrate particles have a DRH of 62% and no ERH is observed (Seinfeld and Pandis, 2006; Martin et al., 2003). For RH values lying between the values of DRH and ERH, particles are in a so-called metastable state; and in this condition, the prediction whether particles are in solid or liquid phase does not depend on the chemical composition of the particle only, but also on the RH history of the particles (Martin et al., 2003). Particles containing a significant fraction of ammonium nitrate have the tendency to remain liquid, even for quite low ambient RH (Shaw and Rood, 1990). Similarly, Martin et al. (2003) draw the conclusion that in Europe, due to their RH history, particles with chemical composition far from pure ammonium sulfate should remain liquid at 293 K. Consequently, regarding the RH values and the diurnal variations of RH during the different seasons, most of the aerosol is considered to be in the aqueous phase. Therefore, R2 and equation Eq. 4 can be considered to describe the dissociation equilibrium of ammonium nitrate.”

Finally, in agreement with the referee comment, the discussion on the HONO impacts on particulate ammonium nitrate was deleted. However, to better estimate the contribution of N₂O₅, a simple model, based on reactions R3 and R4 and considering a complete heterogeneous dissociation of N₂O₅ in particulate nitrate, was run. This model was used to estimate the maximum of nitrate that could be expected by the night-

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time chemistry. The results were then compared to the measured nitrate concentration. Therefore, the following text was added: "In order to evaluate the role of the nighttime chemistry on the nitrate formation, we ran a simple model, based on reactions R3 and R4 only and assuming a fully conversion of N₂O₅ via its heterogeneous reactivity (R5). This model estimates the maximum of particulate nitrate that could be expected from N₂O₅ decomposition (R5) in one hour. To do this, we used the averaged diurnal concentrations of ozone and NO₂ for each season and for each hour of the night and initialized our model to calculate the maximal nitrate concentration out of these ozone and NO₂ concentrations. We concede that this model simplifies the nighttime chemistry mechanisms. For example, the reactivity of the nitrate radical with organic compounds and the wet deposition of N₂O₅ were not considered at this stage. The model simply assumed an instantaneous and complete transfer of N₂O₅ on particle. Therefore, this approach provides the maximum of particulate nitrate expected from nighttime chemistry rather than the real nitrate formation. The hourly production flux of particulate nitrate estimated during the night time of each season is presented in Fig. 9. The maximum of nitrate concentration produced during night via this pathway as well as the comparison of measured and calculated ozone and NO₂ concentrations are also presented in Fig. 9. First of all, it can be seen that the reactions R3 and R4 successfully reproduced the variations of ozone and NO₂ night concentrations for each season. As expected, our simulated nitrate concentrations are higher than the measured concentrations for each season. However, a linear relationship between measured and estimated nitrate concentrations can be observed for each season (Fig. 10). This suggests that nighttime chemistry may be a significant source of ammonium nitrate, especially during winter. The importance of the nitrate radical and N₂O₅ nighttime chemistry was previously reported by several authors (e.g. Brown et al., 2006; Brown et al., 2003; Chang et al., 2011; Geyer et al., 2001; McLaren et al., 2004). For example, Li et al. (1993) demonstrated that nitrate radical and N₂O₅ nighttime chemistry can contribute as much as 80% and 10% to the night time nitrate production respectively, in a Canadian rural place. Therefore, the authors concluded that in their conditions, reaction R2

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represented a minor source. Finally, the slope of the relationship between measured and simulated nitrate concentration increased from summer (0.11) to winter (0.47). At the same time, the increase of nitrate concentration measured during the night was lower in summer (DNO₃ = 0.7 μg m⁻³), increased in autumn (DNO₃ = 1.6 μg m⁻³) and reached a maximum in winter (DNO₃ = 3.6 μg m⁻³). The lower value of the thermodynamic properties of ammonium nitrate in winter (Fig. 7) and the higher value of the regression slope between the measured and the simulated nitrate concentration suggest that nitrate radical nighttime chemistry might be the dominant source of nitrate in winter, which is in agreement with Chang et al. (2011). Regarding the different parameters influencing the particulate ammonium nitrate concentration, two of them seemed to have a special importance during our measurements at the research station Melpitz: the thermodynamic properties of ammonium nitrate and the nitrate formation by nighttime chemistry. Due to the higher temperature and the lower regression slope between measured and simulated nitrate concentrations during summer, our results suggest a larger influence of the thermodynamic equilibrium during warmer periods (summer). Contrary to this, the thermodynamic factors have only a small impact during colder and darker periods (winter). Therefore, the nighttime particle nitrate formation can be explained very well by nitrate radical nighttime chemistry. Our results highlight the strong influence of the factor "season" on the particulate nitrate formation during the night for the conditions of this study at Melpitz which are representative for the central European aerosol".

Specific: The title of the manuscript announces to deal with the Central European atmospheric aerosol which would imply a more general data coverage. The title should be changed to state it is measurements from one location in Central Europe.

Response: We decided on the title "Central European atmospheric aerosol" because the research station Melpitz is considered to be representative for the central European background conditions. Following the comment of the referee, we modified this title to "Seasonal and diurnal variations of particulate nitrate and organic matter at the IfT

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research station Melpitz”

P11614 L19 and elsewhere in the MS: the impression is given that measurements were performed throughout the year, instead three intensive periods were covered, this should be clarified.

Response: We do not completely agree with this comment. Although the formulation “over the year” was mentioned in the introduction of our manuscript, it was emphasized a few lines below that our results were based on 3 different periods, summer, autumn and winter. In the rest of the manuscript, we principally referred to these 3 seasons. However, according to the present comment, we replaced “during the year” by “during the three campaigns” in the body of the article/manuscript.

P11617 L10: check grammar

Response: The sentence was corrected to “This evaluation yielded to a CE of 0.38 and 0.5 for the autumn and winter campaigns, respectively.”

P11618 L20: Isn't isotopically labelled SO₂ used in this approach?

Response: Absolutely, OH was measured by added an excess of ³⁴SO₂ to form H₂SO₄ from OH oxidation as described in the cited papers. Therefore, we corrected SO₂ by ³⁴SO₂.

P11620 L16 and elsewhere: data are given to two digits after comma, is this justified by measurement accuracy?

Response: According to DeCarlo et al. (2006), the AMS detection limit in V-mode is ranging from 39 ng.m⁻³ for ammonium to 2.9 ng m⁻³ for nitrate. Usually, the AMS results are displayed with 2 digits after comma.

P11621 L 21: the numbers in the figure caption of figure 1 would imply that the aerosol is not fully neutralized in Summer and Autumn and excess ammonium is measured in Winter.

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Response: It is right that it was only in winter that the measured ammonium perfectly corresponded to the expected one. During summer and autumn, slopes appeared to be slightly below 1 (0.86 and 0.9, respectively). Although once in a while, especially in summer during new particle formation events, the presence of a small amount of ammonium bisulfate can be expected, we assume the particles to be fully neutralized. This assumption is based on the following aspects: Uncertainties of measurements as well as limited contributions of organic nitrate and sulfate, enlarging the nitrate and sulfate counting, cannot be excluded (Farmer et al., 2010). The text was modified as follows: “The results presented in Figure 1 show that the particles can be considered to be fully neutralized during the different seasons according to the instrumental uncertainties and a minor contribution of the organic nitrate and organic sulfate to the nitrate and sulfate signals (Farmer et al., 2010). The lower slope value of the summer cannot completely exclude the presence of a limited amount of ammonium bisulfate once in a while, especially not during events of intensive new particle formation (see discussion in section 4.3.2). This also indicates that there is enough ammonia in the gas phase to fully neutralize particle nitrate and sulfate.”

Moreover, a discussion on the excess of ammonia in the gas phase and the expected sulfate salt was added. This discussion was based on both the total ammonium to total sulfate ratio and on the ammonium to sulfate ratio and was included in a new subsection that describes the factors influencing the ammonium nitrate concentration in the particle phase (see answer to Referee #2).

P11623 discussion of figure3: it might be interesting to focus on the 25th and 27th of May for which the f₄₄ and OM/OC are high during low OH. Could the impact of OH versus O₃ chemistry on OA composition be explored in these situations or was the high f₄₄ caused by other factors?

Response: It was not possible to link the presence of these two peaks early in the morning on 25 and 27 May with local chemistry. Although no OH measurements were performed at this time on 27 May, the ozone and OH profiles on 25 May did not strongly

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different to the rest of the campaign. Additionally, the OM/OC appears to be not correlated to the ozone concentration. A possible explanation is the presence at these two periods of a different air mass.

P11623 L 24: r^2 is presented for summer values only here, this should be mentioned.

Response: The section containing the mentioned r^2 values only focused on the description of the summer campaign. Therefore, similar to the two following sections describing autumn and winter, the season was not mentioned.

P11624 L 25: Why is f43 not considered anticorrelated for winter?

Response: We added the following text "As described in section 2, ozone had only a small diurnal variation in winter and only f44 seemed to be slightly correlated to the ozone variation (Fig. SI 3, f44 vs. O3: $r^2 = 0.94$) while f43 still anticorrelated to ozone (Fig. SI 3, f43 vs. O3: $r^2 = 0.75$)."

P11625 L 3: it has not been shown that the season strongly influences the nitrate concentration, rather it is shown that nitrate varies strongly with different seasons.

Response: The sentence was rewritten as follow: "As discussed previously, the nitrate concentrations vary strongly with different seasons"

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C7383/2011/acpd-11-C7383-2011-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 11611, 2011.

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