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Atmospheric Chemistry and Physics Discussions

# *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.

My overall evaluation of this paper is that it may be publishable after major revisions: this is due to some conceptual issues that I think need better explanation. These may change the paper's conclusions once addressed, hence the rating. My main concerns are as follows, and deal mostly with section 4.3:

Section 4.3: particle nitrate concentrations. The authors present reactions R1 and R2 as if they are the only reactions relevant to the system, and the subsequent analysis

seems to have the inherent assumption that only these two reactions will affect the equilibrium between ammonium and nitrate, and this has led to what I believe may be erroneous speculation regarding the role of surface formation of HONO and HNO3 in their observations.

Response: We agree that it was not clearly explained that reactions R1 and R2 are not the only reactions affecting the ammonium nitrate equilibrium and that they were considered as a simplified and theoretical approach only. This is now clearly mentioned: "The philosophy of our approach was based on a comparison between measured nitrate concentration and theoretical equilibrium constants for pure ammonium nitrate (Kp* and Kdeliq). This is a simple and theoretical approach, considering only that ammonium nitrate is externally mixed, which is generally not the case, and that the gas-to-particle equilibrium is reached instantaneously". Additionally, a discussion on the factors influencing the ammonium nitrate equilibrium was added on a specific subsection.

Several other processes should be considered for completeness, specifically:

(1) The presence or absence of particulate sulphate. Sulphate will be created by OH oxidation of SO2 during the day, and sulphuric acid is the dominant acid compared to nitric acid for ammonia uptake. HNO3 will be off-gassed from ammonium nitrate (aqueous or solid phase) sulphuric acid condenses to existing ammonium nitrate particles, and both HNO3 and NH3 will be off-gassed from ammonium nitrate particles if sulphuric acid particles are nucleating in the same vicinity. The authors show the presence of significant levels of sulphate in Table 2, yet Figure 4 does not (and should!) show the sulphate time signal. What I would expect to see is particle sulphate peaking in early afternoon, and that the daytime particle nitrate concentration of figure 4 should be anticorrelated with the sulphate concentration. The sulphate may be lower at night, hence less important – but the authors need to show this, before focusing solely on the nitrate chemistry. The analysis on pages 11625 through 11627 only makes sense in the context of particle ammonium and nitrate being the only possible components of

the particulate matter at the site. E.g. if sulphate is present, then the statement "kdeliq was the only factor controlling the AN equilibrium during the nighttime" is not correct.

Response: We admit that the neutralization of sulfuric acid competes with ammonium nitrate and that this should be considered. However, it was mentioned in section 4.1 that "particles can be considered as neutralized during the different season. This also indicated that there is enough ammonium in the gas phase to fully neutralized nitrate and sulfate". Nevertheless, to describe the role of sulfate in the nitrate concentration regarding our measurements even clearer, we added the following discussion on the subsection describing the factors influencing the ammonium nitrate equilibrium: "The formation of ammonium nitrate also depends on the aerosol chemical composition as well as on the available ammonia in the gas phase. Indeed, ammonia is preferentially scavenged by sulfuric acid. Only when sulfate is neutralized, the excess of ammonia leads to the formation of ammonium nitrate (Seinfeld and Pandis, 2006). For all sampling periods, the ratio of total ammonium (TA = NH3 + NH4+) to total sulfate (TS = SO2 + SO42-) was calculated. Most of the time, the ratio was larger than 2 corresponding to an excess of ammonia. At this level, the formation of ammonium nitrate is therefore possible. Moreover, the particulate ammonium to sulfate ratio was also estimated and the resulting averaged ratio of each campaign was larger than 2 which is interpreted as corresponding to ammonium sulfate formation (inserts in Fig. 8). The ammonium to sulfate ratio is in agreement with the neutralization state of the particles previously discussed (see section 4.1). However, during a few afternoons in summer, the ammonium to sulfate ratio was slightly below 2 (down to 1.6). This may indicate a possible small amount of ammonium bisulfate. These periods also coincided with important new particle formation events. Figure 8 shows the relationship between Kp* and the ammonium to sulfate ratio. The highest Kp* values happened during a low ammonium to sulfate ratio and a lower nitrate concentration. The relationship between nitrate formation and the ammonium to sulfate ratio was very well pronounced during the summer campaign, a period of strong photochemistry and sulfuric acid formation. This suggests a possible enhancement of nitrate depletion during day by larger ammonia consumption to

sulfuric acid neutralization during summer."

(2) The role of metastable states and activity coefficients on the partitioning: The authors describe the system correctly from the standpoint of ammonium, nitrate, and the corresponding particulate phase, for low concentration equilibrium chemistry. However, two other confounding factors on their analysis will be: (a) Metastable states: when the system is not purely a single salt, e.g. through the addition of other compounds, and, importantly, the addition of organics, the system may be metastable. In a visual sense, when the system is metastable, the deliquescence curves will become blurred without sharp transitions at the individual salt deliquescence values. In a more practical sense, this will mean that there will always be some water in the particle. Most methods for solving the system of high concentration equilibrium reactions have an option for including metastable states: these essentially force the solver to solve the R2 system even for RH < DRH. (b) Activity coefficients: the authors describe the system as if particulate formation was low concentration (aka "ideal") solution chemistry. In high molality solutions such as are found in particulate matter, activity coefficients must be considered; highly nonlinear corrections to the equilibrium constants that take into account the other species present in the particles and gas phase. Both of these factors will tend to mean that an "either/or" analysis of kp versus kdeliq will be a significant simplification – the authors must re-think section 4.3 in this context.

Response: It is true that this was not properly described in the manuscript. The following discussion on the influence of the aerosol chemical composition to the deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH) was added. We also outlined the reasons why during our measurements, particles might still have contained water and why only reaction R2 should be considered. "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."

(3) Coarse mode versus fine mode chemistry: The authors have focused on PM1, and mention that there are relatively small amounts of other cations in PM1 (pg 11621), but the role of the other cations in the coarse mode can be very significant where particle nitrate formation is concerned. Calcium, magnesium and sodium nitrate form much more readily than ammonium nitrate (the equilibria for calcium carbonate, magnesium carbonate, and sodium chloride + HNO3 will favour the formation of calcium nitrate, magnesium nitrate and sodium nitrate over ammonium nitrate, even when excess ammonia is available). This in turn will mean that in the presence of coarse mode cations, the formation of ammonium nitrate in the fine mode will be inhibited. In this respect (and given that an Anderson impactor was available), its important that the authors show particulate matter for total PM10, especially the coarse mode – hopefully their analysis has been limited to times when the coarse mode is small and unlikely to affect the fine mode results, but they should try to establish this.

Response: According to the comment and the suggestions made here, a discussion

on the influence of the coarse mode on the ammonium nitrate concentration in the fine mode was added. This discussion also compares the daily PM1 and PM2.5 filters. The following text was added: "In Europe, the formation of ammonium nitrate is considered to be limited by the formation of HNO3 (Sartelet et al., 2007). Unfortunately, no measurements of HNO3 were performed here. However, we can note that HNO3 does not react with NH3 only; it can also directly interact with the inorganic fraction of the aerosol, e.g. calcium carbonate, magnesium carbonate, and sodium chloride, leading to the formation of calcium nitrate, magnesium nitrate, and sodium nitrate, respectively. As previously mentioned in section 4.1, contribution of Na+, Ca2+, K+ and Mg2+ was negligible due to their low concentrations compare to NH4+, SO42- and NO3-. Moreover, the presence of these cations on the coarse mode will limit the formation of ammonium nitrate in the fine mode. The comparison of the daily PM1 and PM2.5 inorganic composition during autumn and winter is presented in Table 3. Larger differences between fine and coarse modes are observed for sodium, chloride and nitrate. This is in agreement with the western air masses influence, reported during the autumn and winter campaigns, which included a certain maritime influence. Nevertheless, as Melpitz is located far away from the sea coast (minimum distance of approximately 400 km); the sampling place is influenced by aged marine air masses rather than fresh ones. However, aging degree and for example conversion rate of NaCl to NaNO3 depends on the history of the air mass over the continent (crossing or not polluted area, RH . . .). Hence, in some specific situations (e.g. marine air mass with little processing), coarse mode may contribute to trap HNO3 and therefore limit the ammonium nitrate formation. With only a daily time resolution, however, it is difficult to estimate the real contribution of the coarse mode on the nitrate equilibrium.

(4) Interpretation of local effects: "First, the increase of nitrate mass concentration might be linked to changes in local air quality, corresponding to local emissions. However, due to the location of the sampling place, local sources of nitrate are relatively low". Nitric acid is a termination product of NOx chemistry, and is created downwind of the emission sources of its precursor, NOx. The phrase "local sources of nitrate"

is therefore irrelevant – the question is whether there are sources of NOx sufficiently far upwind that nitric acid has had time to form. Similarly, upwind emissions of SO2 will be oxidized to sulphuric acid, hence creating particulate sulphate, by the time they reach the measurement site. Whether or not it HNO3 partitions to the particle phase will depend on the presence of total ammonium (ammonia gas + particle phase ammonia), and the ratio of total ammonium to total sulphate, on a mole basis, at the site. The authors' preamble mentions that the site is near agricultural areas: these will emit ammonia, locally, which will have a large impact on the potential for particle nitrate formation. The authors invoke an additional source of HNO3 to account for particle mass increases at night – this is insufficiently justified in the absence of HNO3 observations that show that the total nitrate (gas + particle phase) is actually increasing at night. Instead, all that is needed is the same NOx sources as before + a lower boundary layer mixing depth than during the day + some local sources of ammonia gas, to account for the observations. Surface HONO and HNO3 formation is certainly possible (even likely, in my view, and the NO peak of Fig 6 suggest that this is possible), but the authors measurements are insufficient to make the case for it, and they need to acknowledge and eliminate the simpler explanations for their observations (basically, show that sulphate interference is unlikely, and ammonia is available in abundance), before invoking surface conversion as a HONO and HNO3 source.

Response: As we mentioned at the beginning of the manuscript that particles can be considered to be fully neutralized, a discussion on the influence of sulfate salts was not included. Nevertheless, we now added a discussion on the influence of the total ammonium to total sulfate ratio as well as on the influence of the particulate ammonium to sulfate ratio on the expected form of sulfate salts in the particles. The results show that most of the time, an excess of ammonia could be observed in the gas phase and that sulfate was principally present in the ammonium sulfate form. Therefore, it is only during a few afternoons in summer that a small amount of ammonium bisulfate can be expected (see added discussion in our answer to comment 1). Due to the absence of HONO measurements, Fig 6 and the corresponding discussion were removed. However, to provide a better estimation of the influence of the nighttime chemistry on the total ammonium nitrate concentration during the night, a simple model approach was performed. Two reactions were considered: the nitrate radical formation according to NO2+O3 -> NO3 + O3 and NO3 + NO2 -> N2O5 (the N2O5 formation), and an instantaneous and fully conversion of N2O5 into nitrate by heterogeneous reactivity. The model successfully reproduced ozone and NO2 concentrations during the night for all measurement periods. The model was used to estimate the maximum of particulate nitrate that could be expected from N2O5 decomposition in one hour. A linear relationship between the expected maximum nitrate concentration and the measured nitrate was observed in all cases. This confirms the strong influence of the nighttime chemistry on the nitrate concentration during the night.

Details description of the model output was added as follows: "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 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 (ïĄĎNO3 = 0.7 $\mu$g m-3), increased in autumn (ïĄĎNO3 = 1.6 $\mu$g m-3) and reached a maximum in winter (ïĄĎNO3 = 3.6 $\mu$g 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.”

Figure 5: I think a more convincing case would be made through the use of a correlation scatterplot rather than a comparison of time series. i.e. to what extent is the nitrate correlated with the two equilibrium constants as a function of time? A correlation plot wherein the points are colour-coded according to the molar ammonium to sulphate ratio might also be interesting, in that the scatter might be expected to be larger when significant sulphate is present. In the above, I want to stress that reanalysis and rewording/explanation are needed; no arguments with the data collection or the data themselves.

Response: The figure was corrected according to the requests of the referee. A scatter plot of Kp* vs. ammonium to sulfate ratio colored by the nitrate concentration was inserted.

Minor points: Section 4.2: changes in organic particulate composition. This section was quite interesting, especially the m/z 44, 43 vs f44, f43 plots, and the OM/OC discussion (figure 2). The authors’ interpretation of the data miss a couple of possibilities. E.g. they mention the evaporation of semi-volatiles during the day and their condensation at night as a possible reason for the variation, but they should also consider that the 44 species may result from the oxidation of the 43 species during the daytime; that is, the m/z 43 species evaporate during the day, -> are oxidized<- , lowering their vapour pressure, hence result in the m/z 44 species fraction increase during the day.

Response: It is correct that the oxidation of organic compound will lead to a decrease of f43 and an increase of f44. It should also lead to a decrease of the volatility of the organics. The discussion on how the OH oxidation of the organics leads to an increase of f44 and OM/OC ratio did not explicitly refer to the oxidation of m/z43 species in m/z44 species. Therefore, the following sentence was added: “When f44 increased, f43 decreased which might be explained by the presence of more low-volatile compounds in the OA as well as by the oxidation of the OA, leading to conversion of m/z 43 to m/z 44."

The relative abundance of 44 vs 43 help explain the summer and autumn OM/OC ratio plots of figure 2. What about the winter? The winter plot shows a peak at night, and a dip during the day. A likely explanation for this is low PBL heights in the winter (especially at night), coupled with the absence of photochemical oxidation to create the nighttime peak – didn't see that in the paper, though I might have missed it.

Response: The following sentence was added: "A small peak was observed at night and a limited dip during day time. This might be explained by the limited impact of the dynamics of the atmosphere as well as by the thermodynamic properties of the OA, because of the lowest temperature at this period."

Also section 4.2: Figure 3 appears in the paper, but is not mentioned in the text.

Response: A reference to Fig. 3 can be found on the text page 11623, line 18

Page 11614, line 8: ammonium sulphate is not the only compound; at lower total ammonia to sulphate ratios, letovicite and ammonium bisulphate are also possible. There's also some evidence for the presence of binary salts, though these don't tend to affect the actual amounts of ammonium, sulphate and nitrate in the particle phase, that much. As noted above, the coarse mode composition may impact partitioning of the available nitric acid between the fine and coarse mode.

Response: A discussion on the different forms of sulfate expected during these measurements and on the influence of the coarse mode was added. Please see our responses to the main points 3 and 4 (above).

Page 11616: I'm not sure if the details of the HRTOF-AMS operation are necessary; could simplify this and reference DeCarlo et al, 2006.

Response: As suggested by the referee, we simplified the AMS description and only referred to DeCarlo et al. (2006).

Page 11617: One concern on methodology here: you have the potential for off-gassing of volatiles (particularly HNO3 and NH3) from filters for time averaged measurements. Was there any thought to adding denuders to prevent this off-gassing (and get a better estimate of what is really in the particle phase?

Response: We agree that adding a denuder could prevent off-gassing effects in the filter samples. Installing such system would require significant modifications of the setup. Additionally, an important validation step and high quality controls would have to be preformed afterwards. However, as our measurements were standardized such equipment was not installed.

Page 11620, line 7: "measurements period" should be "measurement period".

Response: corrected

Page 11620: "Due to the low solar radiation. . .". The term "background" gets used in an imprecise fashion frequently – what do you mean by it here? No local ozone production? If so, it would be better to just say that the lack of diurnal variation shows that no local ozone production is occurring. "Background" could just as easily mean that this is the ozone that you might expect to be present in the absence of local chemistry in the summer, or something like that.

Response: term "background" was replaced by "limited local production"

Page 11624, line 21: "of the dynamic" should be "of the dynamics"

Response: corrected

Page 11626, line 19: I think the reference to "Fig 4" here should be "Fig 5".

Answer: corrected

Also, need a reference for the kdeliq equation on this page.

Response: the reference to Seinfeld and Pandis (2006) was added

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