

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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Anonymous Referee #1:

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.

This review supplements an earlier review which it was not possible to complete because some of the figures were extremely difficult to read in their original size.

The first section of this paper concerning the organic content of the aerosol appears generally sound and presents some interesting results. However, the section con-

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cerning particulate nitrate is both extremely difficult to read and highly speculative and requires considerable revision if it is to be published at all.

1- The authors have provided some clarification of the dissociation constant and deliquescence constant, and as they concede, both should be indicated with a capital letter K rather than the lower case letter currently used. It is nonetheless confusing that the dissociation constant (K_p) is a product of two gas phase concentrations, whereas judging from the units, K_{deliq} , appears to be the concentration product of two ions in solution. Consequently, these two constants are very different, one focussing on the gas phase, the other on the aerosol phase. It would have been far more helpful if both expressed the gas phase concentration product with K_{deliq} taking account of humidity as well as temperature.

Response: The equilibrium constants K_p and K_{deliq} are now both expressed in ppb^2 . Moreover, the equilibrium constant of dissociation was recalculated as follows (based on Mozurkewich (1993)): - for dry particles:

$$\ln(K_p) = 118.87 + (24080/T) - 6.025 \ln(T)$$

- for deliquescent particles:

$$K_p^* = (P_1 - P_2(1-a_w) + P_3(1-a_w)^2 \times (1-a_w)^{1.75} \times K_p$$

with

$$\ln(P_1) = -135.94 + (8763/T) + 19.12 \ln(T)$$

$$\ln(P_2) = -122.65 + (9962/T) + 16.22 \ln(T)$$

$$\ln(P_3) = -182.61 + (13875/T) + 24.46 \ln(T)$$

and a_w water activity in the range 0 to 1. The dissociation constant K_{deliq} was calculated as follows (Seinfeld and Pandis, 2006):

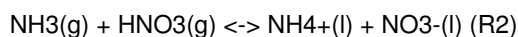
$$K_{deliq}(T) = K(298) \exp[a((298/T)-1) + b(1+\ln(298/T)) - (298/T)] \times 10^{-18}$$

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With $K(298) = 3.35 \cdot 10^{16} \text{ atm}^{-2}$, $a = 75.11$, $b = -13.5$ and, 10-18 a conversion factor that provides the same unit as K_p^* .

2- The lack of definition and poor explanation of these terms makes it very difficult to follow the arguments. Studies of the ammonium nitrate/ ammonia/nitric acid system are numerous in the literature and generally contain measurements of the gas phase species as well as the aerosol. It is a considerable weakness of this study that the gas phase concentrations are not available and this is one of the reasons that the discussion of the data appears highly speculative.

Response: We completely agree with the fact that there is only a small number of gas phase measurements, limiting the range of investigation. However, this was clearly mentioned in the manuscript. Unfortunately, only ammonia was measured during these campaigns using a photo-acoustic device (TGA 310, OMNISENS, Switzerland). These measures are now available, so we included them in the manuscript. The section describing the changes in particulate nitrate concentration was completely rewritten, providing a better description of the equilibrium constants and their comparison with nitrate concentration. The following text was added: "The particulate ammonium nitrate is a semi-volatile compound in equilibrium with its gas phase precursors (HNO_3 and NH_3). The gas-to-particle phase partitioning of ammonium nitrate is well described in the literature and strongly depends on the gas phase precursors concentrations, temperature, relative humidity (RH) and aerosol chemical composition (e.g. Seinfeld and Pandis, 2006; Mozurkewich, 1993; Ansari and Pandis, 2000; Nenes et al., 1998). In Figure 7, the relationship between nitrate concentration, temperature and RH can clearly be observed. The nitrate concentrations were basically anticorrelated with temperature and correlated with RH. This is in agreement with results reported by Rupakheti et al. (2005) who also related the nitrate diurnal profile to temperature and RH variations. The gas-to-particle equilibrium of ammonium nitrate can be described by the following reactions: $\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \leftrightarrow \text{NH}_4\text{NO}_3(\text{s})$ (R1)



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Reaction R1 corresponds to the gas-to-particle partitioning of dry ammonium nitrate particle. The dissociation equilibrium constant of ammonium nitrate into HNO_3 and NH_3 (K_p) was described by the following equation (Mozurkewich, 1993): $\ln(K_p) = 118.87 + (24080/T) - 6.025 \ln(T)$

For deliquescent particles, the influence of RH should be considered. Therefore, for $\text{RH} < 99.7\%$, reaction R2 can be described by the following equation (Mozurkewich, 1993):

$$K_p^* = (P_1 - P_2(1-aw) + P_3(1-aw)^2 \times (1-aw)^{1.75} \times K_p$$

with

$$\ln(P_1) = -135.94 + (8763/T) + 19.12 \ln(T)$$

$$\ln(P_2) = -122.65 + (9962/T) + 16.22 \ln(T)$$

$$\ln(P_3) = -182.61 + (13875/T) + 24.46 \ln(T)$$

and aw water activity in the range 0 to 1.

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

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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. K_p^* was calculated for each season (with $RH < 99.7\%$) and its time series and diurnal variations are presented in Fig.7 and 8. Even if the absolute values of K_p^* correspond to equilibrium of pure ammonium nitrate, it is noticeable that the nitrate concentrations anti-correlate to K_p^* for all seasons. The decrease of nitrate concentration when K_p^* increases agrees with an increased conversion of particle phase ammonium into gas phase HNO_3 and NH_3 during daytime. The equilibrium constant of reaction R2 could also be expressed as describing the formation of ammonium nitrate on deliquescent particles (K_{deliq}) instead of describing its dissociation (K_p^*). K_{deliq} can be calculated as follows (Seinfeld and Pandis, 2006):

$$K_{deliq}(T) = K(298) \exp[a((298/T)-1) + b(1+\ln(298/T)) - (298/T)] \times 10^{-18}$$

With $K(298) = 3.35 \cdot 10^{16} \text{ atm}^{-2}$, $a = 75.11$, $b = -13.5$ and, 10^{-18} a conversion factor that provides the same unit as K_p^* . A similar approach is used to describe nitrate concentration in the ISORROPIA model by Fountoukis and Nenes (2007) and Nenes et al. (1998). As for K_p^* , the time series and the diurnal variations of K_{deliq} are presented in Fig 7 and 8. Because K_{deliq} describes the reverse mechanism of K_p^* , the diurnal variation of K_{deliq} correlates with diurnal changes on nitrate concentrations during day. The same observations were made by Zhang et al. (2005a) and Sun et al. (2011) who also considered the presence of deliquescent particles only. The fact that diurnal profiles of nitrate follow very well their thermodynamic properties (K_p^* and/or K_{deliq}) suggests an important evaporation of ammonium nitrate during the day and a condensation process on pre-existing particles during the night. As previously shown for the organic fragment m/z 43, the nitrate size distribution between the summer's day and night is presented in Fig. 5. As m/z 43, a typical nitrate size distribution peaks around

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300 nm during day and shows a double mode with a first maximum at 120 nm and a second one around 300 nm during night. The similarity of the m/z 43 and the nitrate size distribution is consistent with a nighttime condensation of nitrate on pre-existing particles.”

A subsection was also added, discussing the limits of our approach, the influence of the gas phase precursor concentrations, the aerosol chemical composition and the size effect. Introducing a small model, this section also provides a better consideration of the nighttime chemistry. The following text was added: “The philosophy of our approach was based on a comparison between measured nitrate concentration and theoretical equilibrium constants for pure ammonium nitrate (K_p^* and K_{deliq}). This is a simple 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. While Pio et al. (1992) observed a kinetic effect on the ammonium nitrate formation, other studies about fine particles have shown that the instantaneous equilibrium assumption is applicable (Takahama et al., 2004; Yu et al., 2005b) in agreement with our estimation. However, this does not seem to be the case for larger particles (Meng and Seinfeld, 1996).

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 ($TA = NH_3 + NH_4^+$) to total sulfate ($TS = SO_2 + SO_4^{2-}$) 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

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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 K_p^* and the ammonium to sulfate ratio. The highest K_p^* 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.

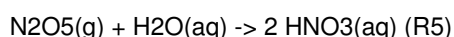
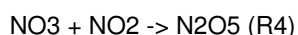
In Europe, the formation of ammonium nitrate is considered to be limited by the formation of HNO_3 (Sartelet et al., 2007). Unfortunately, no measurements of HNO_3 were performed here. However, we can note that HNO_3 does not react with NH_3 only; it can also directly interact with the inorganic fraction 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^+ , Ca^{2+} , K^+ and Mg^{2+} was negligible due to their low concentrations compare to NH_4^+ , SO_4^{2-} and NO_3^- . 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 PM_{10} and $\text{PM}_{2.5}$ 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 NaNO_3 depends on the history of the air mass over the continent (crossing or not polluted area, $\text{RH} \dots$). Hence, in some specific situations (e.g. marine air mass with little processing), coarse mode may

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contribute to trap HNO_3 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.

The importance of the dynamics of the atmosphere on the particulate nitrate concentration was demonstrated by Morino et al. (2006). However, no direct measurements of the mixed layer height were performed during these campaigns, except for 3 days at the end of the summer campaign, which is not enough to draw global conclusions. Considering only these 3 days, the decrease of nitrate concentration early in the morning goes together with the increase of the mixed layer height. Therefore, the mixed layer development should contribute to the observed decrease of nitrate concentration, while the stratification during night should support the increased concentration. Because of the low value of the dissociation equilibrium, the influence of the mixed layer height should be an important factor during winter.

Up to now, particulate ammonium nitrate formation has only been considered as resulting from the gas-to-particle partitioning. The reactivity of NO_2 and O_3 as well as N_2O_5 hydrolysis are more important during night and will be favored by the high RH (R_3 to R_5). $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ (R_3)



In order to evaluate the role of the nighttime chemistry on the nitrate formation, we ran a simple model, based on reactions R_3 and R_4 only and assuming a fully conversion of N_2O_5 via its heterogeneous reactivity (R_5). This model estimates the maximum of particulate nitrate that could be expected from N_2O_5 decomposition (R_5) in one hour. To do this, we used the averaged diurnal concentrations of ozone and NO_2 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 NO_2 concentrations. We concede that this model simplifies the nighttime chemistry mechanisms. For example, the re-

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activity of the nitrate radical with organic compounds and the wet deposition of N_2O_5 were not considered at this stage. The model simply assumed an instantaneous and complete transfer of N_2O_5 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 NO_2 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 NO_2 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 N_2O_5 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 N_2O_5 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 ($\Delta\text{NO}_3 = 0.7 \mu\text{g m}^{-3}$), increased in autumn ($\Delta\text{NO}_3 = 1.6 \mu\text{g m}^{-3}$) and reached a maximum in winter ($\Delta\text{NO}_3 = 3.6 \mu\text{g m}^{-3}$). 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

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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."

3- The implicit assumption made by the authors that equilibrium is obtained instantaneously is incorrect. There are published studies demonstrating marked kinetic constraints. These would be greatest in relation to equilibration of solution droplets (i.e. above the deliquescence humidity) and may well explain some of the apparent lags seen in the data. The authors should also recognise that thermodynamic studies of the ammonium nitrate system nowadays generally take account of internally mixed aerosol whereas their calculations are based purely on an externally-mixed ammonium nitrate particles. Addition of temperature and RH to Figure 4 would be helpful.

Response: We now mentioned that "The philosophy of our approach was based on a comparison between measured nitrate concentration and theoretical equilibrium constants for pure ammonium nitrate (K_p^* and K_{deliq}). This is a simple 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." However, we cannot completely agree with the comment on the influence of the kinetic effect to the gas-to-particle equilibrium for fine particles. Several articles reported that an instantaneous equilibrium assumption is applicable for fine particles (compared to larger ones). This discussion was included in the text: "While Pio et al. (1992) observed

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a kinetic effect on the ammonium nitrate formation, other studies about fine particles have shown that the instantaneous equilibrium assumption is applicable (Takahama et al., 2004; Yu et al., 2005) in agreement with our estimation. However, this does not seem to be the case for larger particles (Meng and Seinfeld, 1996).”

RH and Temperature were added in Figure 7.

4- There is also an explicit assumption made by the authors that diurnal changes in advected pollutant load are not significant. This is not justified through data and this is again a reason why measurements of ammonia and nitric acid vapour would have been especially useful.

Response: A discussion on the influence of the mixed layer height on the ammonium nitrate concentration was added: “The importance of the dynamics of the atmosphere on the particulate nitrate concentration was demonstrated by Morino et al. (2006). However, no direct measurements of the mixed layer height were performed during these campaigns, except for 3 days at the end of the summer campaign, which is not enough to draw global conclusions. Considering only these 3 days, the decrease of nitrate concentration early in the morning goes together with the increase of the mixed layer height. Therefore, the mixed layer development should contribute to the observed decrease of nitrate concentration, while the stratification during night should support the increased concentration. Because of the low value of the dissociation equilibrium, the influence of the mixed layer height should be an important factor during winter.” Additionally, based on the high resolution analysis of the organic fragments m/z 55 and 57, we reported a possible increase of primary organic aerosol early in the morning during summer and autumn. However, it is difficult to distinguish between the influence of local emissions and the advection from aloft. Therefore, we only mentioned a possible increase of primary organic aerosol at this time.

5- The authors hypothesise that their data demonstrate the formation of nitrous acid vapour and aqueous nitric acid (neither of which was measured) and that photolysis of

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nitrous acid vapour is occurring leading to an early morning peak in nitric oxide. They presumably also have data for NO_2 or NO_y which they do not include in Figure 6, and taken together with the lack of HONO and HNO_3 data, the picture is highly incomplete. Figure 6 includes a plot of both $\text{J}(\text{NO}_2)$ and $\text{J}(\text{O}1\text{D})$. They do not provide data for $\text{J}(\text{HONO})$ but the diurnal profile of $\text{J}(\text{HONO})$ is not very different from that of $\text{J}(\text{NO}_2)$. There is a large rise in nitric oxide occurring almost immediately that $\text{J}(\text{NO}_2)$ begins to rise which persists for about 5 hours. According to Seinfeld and Pandis (p252) the photodissociation lifetime of HONO is about one hour for early morning sun. This rise in NO seems more probably associated with photolysis of NO_2 , or possibly advection. The reader is unable to assess whether photolysis of NO_2 may be a contributor to the peak in NO as the data are not shown. Perhaps most importantly, the diurnal profile of hydroxyl radical parallels that of $\text{J}(\text{O}1\text{D})$ suggesting that photolysis of HONO is a very small source compared to photolysis of ozone.

Response: We admit that the suggested HONO photodissociation early in the morning was rather speculative, especially due to the lack of any gas measurements. Based on the referee's comments, we decided to remove Fig. 6 and the corresponding discussion.

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C7426/2011/acpd-11-C7426-2011-supplement.pdf>

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