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

Anonymous Referee #2

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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

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their observations. 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.

(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

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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 k_p versus k_{deliq} will be a significant simplification – the authors must re-think section 4.3 in this context.

(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.

(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 NO_x chemistry, and is created downwind of the emission sources of its precursor, NO_x. The phrase “local sources of nitrate” is therefore irrelevant – the question is whether there are sources of NO_x 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 HNO_3 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 HNO_3 to account for particle mass increases at night – this is insufficiently justified in the absence of HNO_3 observations that show that the total nitrate (gas + particle phase) is actually increasing at night. Instead, all that is needed is the same NO_x 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 HNO_3 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 HNO_3 source.

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 re-wording/explanation are needed; no arguments with the data collection or the data themselves.

Minor points:

Section 4.2: changes in organic particulate composition. This section was quite inter-

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esting, especially the m/z 44, 43 vs f_{44} , f_{43} 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, \rightarrow are oxidized \leftarrow , lowering their vapour pressure, hence result in the m/z 44 species fraction increase during the day. 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. Also section 4.2: Figure 3 appears in the paper, but is not mentioned in the text.

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.

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.

Page 11617: One concern on methodology here: you have the potential for off-gassing of volatiles (particularly HNO_3 and NH_3) 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?

Page 11620, line 7: "measurements period" should be "measurement period". Page 11620: "Due to the low solar radiation...". The term "background" gets used in an

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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.

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

Page 11626, line 19: I think the reference to “Fig 4” here should be “Fig 5”. Also, need a reference for the kdeliq equation on this page.

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

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