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Comment

Interactive comment on “A global model simulation of present and future nitrate aerosols and their direct radiative forcing of climate” by D. A. Hauglustaine et al.

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Referee #3

We thank the two reviewers for their helpful comments and suggestions which significantly improved our paper.

In this study, the authors document the addition of a nitrate aerosol scheme in the LMDz-INCA model, and use that model to highlight the dramatic change in aerosol composition that would happen over the 21st century if RCP are followed. The paper is well written and presents interesting results, notably that ammonium burden remains

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fairly constant in the future as ammonium nitrate formation replaces ammonium sulphate formation; that ammonia is the limiting factor explaining differences between different RCPs; and that the change in aerosol composition has important consequences on direct radiative forcing (Figures 24, 26, and 27). The authors also do a good job at placing their study within the existing scientific literature, although they could be bolder in highlighting the strengths of their study.

For those reasons, I recommend publication of the manuscript, with minor changes to address the comments below.

1 Main comments

“ The authors state several times that their results replicate those by previously published papers. Replication is important, but the authors should evaluate previous results more critically. For example, some of the previous studies did not include coarse-mode nitrate, or did not model ammonium explicitly. Do those limitations matter? The scheme implemented by the authors is fairly complete – at least from a global modelling point of view – and I believe the results in this paper can be seen with more confidence than some of the previous, more simple, analyses.

Thank you for this encouraging comment. The recent nitrate models by Xu and Penner (2012), Bellouin et al. (2011), and Pringle et al. (2010) were actually already fairly detailed and in the case of Xu and Penner (2012) quite detailed in their nitrate chemistry. We do not pretend to have a more complex model. However, Xu and Penner used a very simplified nitrogen chemistry excluding NMHC chemistry and with imposed monthly mean OH and O₃ fields and didn't investigate the RCP future evolution of nitrates and the associated future forcing. Bellouin et al. look into this but didn't focus too much on the chemistry evolution and did not include the coarse particle formation. This can be quite important since HNO₃ is used to form coarse nitrate particles instead of fine particles and hence this reduces the nitrate forcing for present-day conditions. This is an interesting aspect of our work in addition of applying the model for future

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evolution and looking into the relative contribution of nitrates to the forcing. This added value of our study has been added at several places in the manuscript and in particular in the abstract, conclusion, and when the present-day forcing of nitrate is mentioned. The fact that Xu and Penner used a simple chemistry is also mentioned now since we overlooked this limitation in their work.

One defining characteristics of nitrate aerosols is their ability to easily dissociate back into the gas phase. This means that nitrate aerosols have a very pronounced diurnal cycle, spending most of daytime hours in the gas phase (Dall'Osto et al., 2009). This is crucial for their direct radiative effects, which is exerted by the aerosol phase only. Previous studies have overlooked that aspect, so it would be very interesting to add a short discussion of the diurnal cycle in LMDz and demonstrate that it follows the observed behaviour.

This is an interesting suggestion. Even if it is quite out of the scope of this paper to evaluate a global model on such a fine temporal scale, we have output the surface concentrations with a 30 min time step. Interestingly, a diurnal cycle with minimum concentrations of NO₃ during daytime is obtained at several stations and coincides with peak HNO₃ concentrations. Even if we don't pretend to perform a detailed comparison with Dall'Osto et al. (2009), the model results at a similar location and time of year than the performed measurements show very similar features, variability and concentration range. A few words on this are now given in Section 3.1 and a figure provided in the supplementary material (Fig. S2).

There is a large number of figures in the paper, some of which being only discussed briefly in the text. I would suggest merging some of the figures together, especially Figures 1, 2, and 6; Figures 4 and 5; Figures 11 and 12; and possibly Figures 22 and 23.

Yes we agree. We have now significantly reduced the number of figures in the main paper from 27 to 16. The figures which were not key to the discussion are now in

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the supplementary material together with new figures requested by the reviewers. A table has been introduced (Table 2) which summarizes the model-measurement comparisons and the correlation plots sent to the supplement.

Furthermore, the same kind of information (change in surface concentrations) is presented in different ways across Figures 16 to 18. The reason for that choice is unclear: Why doesn't Figure 17 show RCP4.5? Why does Figure 18 show timeseries rather than distributions? With regard to the subject matter, a Figure similar to Figure 21, but showing in addition regional changes, would be very helpful. By showing the evolution of all the species involved in nitrate formation (NH₃, HNO₃, SO₄) it would provide an efficient way of identifying the causes for the change in nitrate concentrations.

Most of these figures showing future changes in atmospheric composition are now in the supplement. The change in surface sulfate concentration for scenario RCP4.5 has been added to the former Figure 17 (now Fig. S9). We also added a new figure (Fig. S10) showing the map of changes in nitrate surface concentration in 2030 and 2100 for both RCP8.5 and RCP4.5. All these figures showing the regional changes help to have a better insight into the future changes of nitrate particles under the RCP scenarios.

2 Other comments

Page 6866, line 1: Are the radiative forcings reported in this sentence for the direct effect only, or is it a mixture of direct-only and direct+indirect studies?

The text has been clarified. Since we focus only on direct forcings in this paper, those are for the direct forcing only.

Page 6868, line 8: Out of curiosity, what does the z in LMDz stand for?

'z' stands for 'zoom'. But this capability of the model to zoom over a specific area is not used in the present version.

Page 6869, lines 6–7: The distinction between anthropogenic and natural aerosols

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made here is a bit arbitrary, since sulphate aerosols can be both, for example. I suggest rephrasing that statement.

Absolutely. The text has been clarified.

Page 6872, line 1: It is worth stating here that the fact that sulphate formation takes precedence over that of nitrate is justified by the low vapour pressure of sulphuric acid.

Text modified accordingly.

Page 6874, line 13: In the introduction, limitations to the first-order removal method have been mentioned, with Feng and Penner (2007) as a reference. In section 2.2, it would be useful to shortly summarise what those limitations are.

We have modified to text to mention two major limitations of the formulation: the relative humidity and aerosol chemical composition dependences. The method used to partly overcome these limitations are then described.

Page 6878, lines 4 and 23: Does “agreement” refer to patterns, magnitudes, or both?

It is more the patterns which agree since the magnitude can vary significantly among the various studies mentioned. The text has been clarified.

Page 6878, line 19: What do the authors mean by “anthropogenic nitrates” in that context?

Fine mode nitrates. The text has been corrected.

Page 6879, line 24: Another difficulty when comparing with measurements of nitrate aerosol concentrations is that they are difficult to measure, because nitrate aerosols dissociate easily. See for example Schaap et al. (2002). It is likely that those difficulties translate into underestimated concentrations in the observations.

The reviewers are correct in pointing to the measurement limitations. We have added the following text in the supplementary material where the model-measurement plots

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have been moved:

To obtain a large spatial coverage with respect to evaluation of nitrate and ammonium model values we have included measurements from different methods. These use different combinations of filterpacks and denuders. Little harmonization of the methods has been achieved globally and there is virtually no choice to pick just one method. Depending on filter type, sampling set-up, temperature and changing ambient conditions during a sampling interval considerable sampling artefacts may occur. At higher temperatures, evaporation of ammonium nitrate from filters has been shown to lead to losses of up to 50% in summer conditions (Vecchi et al., 2009; Sickles and Shadwick, 2002; Allegrini et al., 1994; Yu et al., 2005, Hering and Cass, 1999; Chow et al., 2005, Ashbaugh and Elfred, 2004, Schaap et al., 2004, Schaap et al., 2002). Such sampling artefacts may explain in total a positive model bias, while negative model bias clearly points to model errors. We do not find a clear north-south gradient in bias, neither in Europe nor in Northern America, higher temperatures in the south are not associated with higher positive model bias. However, in central Europe there are several sites, where the positive bias of the model is high in summer and almost absent in winter. In depth inspection of nitrate bias on a map and per measurement site may be accessed via the AeroCom web interface (http://aerocom.met.no/cgi-bin/aerocom/surfobs_annualrs.pl?PROJECT=INCA&Run0=LOI_DH10n&Parameter0=SCONC_NO3).

We have also added a remark in section 3.1 and in the conclusions:

A positive bias in simulated nitrate aerosol is suspected to be partly linked to negative sampling artefacts in measurements, because evaporation of ammonium nitrate has been frequently reported to create occasionally losses of up to 50%, in particular in warm weather. Further work is needed to better characterize the individual nitrate measurement error, to see where modeled nitrate is consistent with measurements.

The following citations have been added:

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Allegrini, I., A. Febo, C. Perrino and P. Masia. "Measurement of Atmospheric Nitric Acid in Gas-Phase and Nitrate in Particulate Matter by Means of Annular Denuders." *International Journal of Environmental Analytical Chemistry* 54, no. 3 (1994): 183-201.

Ashbaugh, L. L. and R. A. Eldred. "Loss of Particle Nitrate from Teflon Sampling Filters: Effects on Measured Gravimetric Mass in California and in the Improve Network." *Journal of the Air & Waste Management Association* 54, no. 1 (2004): 93-104.

Chow, J. C., J. G. Watson, D. H. Lowenthal and K. L. Magliano. "Loss of Pm2.5 Nitrate from Filter Samples in Central California." *Journal of the Air & Waste Management Association* 55, no. 8 (2005): 1158-1168.

Hering, S. and G. Cass. "The Magnitude of Bias in the Measurement of Pm2.5 Arising from Volatilization of Particulate Nitrate from Teflon Filters." *Journal of the Air & Waste Management Association* 49, no. 6 (1999): 725-733.

Schaap, M., K. Muller and H. M. ten Brink. "Constructing the European Aerosol Nitrate Concentration Field from Quality Analysed Data." *Atmospheric Environment* 36, no. 8 (2002): 1323-1335.

Schaap, M., G. Spindler, M. Schulz, K. Acker, W. Maenhaut, A. Berner, W. Wieprecht, N. Streit, K. Muller, E. Brüggemann, X. Chi, J. P. Putaud, R. Hitzenberger, H. Puxbaum, U. Baltensperger and H. ten Brink. "Artefacts in the Sampling of Nitrate Studied in the "Intercomp" Campaigns of Eurotrac-Aerosol." *Atmospheric Environment* 38, no. 38 (2004): 6487-6496.

Sickles, J. E. and D. S. Shadwick. "Biases in Clean Air Status and Trends Network Filter Pack Results Associated with Sampling Protocol." *Atmospheric Environment* 36, no. 29 (2002): 4687-4698.

Vecchi, R., G. Valli, P. Fermo, A. D'Alessandro, A. Piazzalunga and V. Bernardoni. "Organic and Inorganic Sampling Artefacts Assessment." *Atmospheric Environment* 43, no. 10 (2009): 1713-1720.

Yu, X. Y., L. Taehyoung, B. Ayres, S. M. Kreidenweis, J. L. Collett and W. Maim. "Particulate Nitrate Measurement Using Nylon Filters." *Journal of the Air & Waste Management Association* 55, no. 8 (2005): 1100-1110.

Section 3.1, and Figures 2,4,5,6: It is worth clarifying early in the text and figure captions the units used for concentrations and burdens, i.e. whether they are given as [S] or [N], or as [SO₄], [NO₃], etc.

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We have now specified at the beginning of Section 3.1 that all concentrations and burdens are expressed in mass of the species (e.g. $\mu\text{g}/\text{m}^3$ for $\mu\text{g}\text{-NO}_3/\text{m}^3$) unless otherwise stated (e.g., $\mu\text{g}\text{-N}/\text{m}^3$ or $\mu\text{g}\text{-S}/\text{m}^3$).

Page 6881, line 12: I'm not sure I understand the statement "nitrate on pure sulfates" here. By redoing the calculation, it seems that it means "fine mode nitrates".

Yes. The text has been modified accordingly.

Page 6886, line 13: A global-, annual-averaged total AOD of 0.059 is a surprisingly small number. Is that really correct? Looking at Table 5, it seems it is in fact not the total AOD, but excludes mineral dust and sea-salt aerosols.

The value of 0.059 is indeed for accumulation mode. The total AOD is 0.1355. The text has been corrected.

Figure 13a: looking at Figures 5, I would have expected a more equal contribution of fine and coarse mode nitrate to total column around 50N, but it is difficult to judge by eye.

We double checked the figure and the results are correct. Please note the coarse mode shown on Figure 13a is the sum of dust particles (Fig. 5b) and sea-salt particles (Fig 5c).

Figure 13b: Has the y-axis really been multiplied by 100? The magnitudes and the lines 18–20 on page 6887 suggest that is not the case.

The figure is correct but the text didn't account for the x100 factor! The text has been corrected.

Page 6891, lines 17–25: The discussion of Figure 20 is confusing, since it mixed hemispheric averages (which decrease) with regional changes that are of varying signs. It would be clearer to say that although Figure 20 seems to show an increase in nitrate column in most regions of the north hemisphere, that increase is in fact more

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than compensated by strong decreases over Europe and China, where present-day nitrate concentrations are large. Having said that, I am surprised by how localised the European and Chinese changes are: Why don't they extend downwind?

This figure has been moved to the supplementary material (Fig. S10) and we have added another figure showing maps of the change in nitrate surface concentration (Fig. S11). The text has been clarified according to the reviewer's comment. This change in surface nitrates shows are localized the decreases are over Europe and Asia due to a strong reduction in HNO₃ concentrations and hence nitrate formation. Since nitrates are short-lived, these changes remain localized to these regions and are not transported aloft or only to a small extent.

Page 6895, lines 5–8: I would rephrase this statement slightly as “because deposition of nitric acid, which dissociates readily in water, causes a significant drop in pH, but deposition of NH_x increases the water alkalinity.”

The statement has been rephrased accordingly.

Page 6901, line 16: At this stage, I would think that understanding the sources of uncertainty is a more likely outcome of an intercomparison project than reducing those uncertainties.

Yes, the sentence has been modified accordingly.

3 Technical comments The level of English language is very good, but there are recurring mistakes when plurals are used as adjectives, and a few other grammatical mistakes. To list but the first instances:

• Page 6864, line 2: fine nitrate particle formation

• Page 6865, line 2: nitrate exerts; line 9: nitrogen oxide emissions; line 10: soil emissions.

• Page 6870, line 14: organic carbon

I encourage the authors to pay particular attention to these matters when proof-reading the paper.

Thank you. We paid attention to those and other additional mistakes.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C4208/2014/acpd-14-C4208-2014-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 6863, 2014.

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