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Atmospheric Chemistry and Physics Discussions

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 #1

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

This is a solid paper that accumulates the evidence for an important role of nitrate aerosol in present and future conditions. I particularly appreciate the careful job that the authors did trying to understand similarities and differences with other studies. The emphasis on the key role of agricultural (NH3) emissions in future is justified, but per-

haps some more emphasis should be placed on the strong limitations resulting from the use of the RCP emissions dataset. For almost all pollutant emissions, except for SO2, they are to some extent assuming Kuznets assumptions, and it is very questionable what pollution levels in 2100 could be. Why not focus on 2050, a somewhat more foreseeable future?

In this paper we indeed focus on the RCP scenarios which have been the reference for the CMIP5 and ACCMIP simulations. Our choice for this first paper was to put the nitrate forcing in the context of these recent exercises on which the community concentrated over the past years. The RCP limitations for air quality are indeed clear and we mention them. For this paper we have simulated 2030, 2050 and 2100. The key figures of the article illustrate these three time horizons, again to put our results in the context of the CMIP5 and ACCMIP simulations. Several figures (now in the supplement) illustrate 2030 and 2100. 2030 (or 2050) are indeed more seeable futures. 2100 is also interesting despite the uncertainty on emissions in a context of a changing climate which will be more pronounced at the end of the century. We are now working on new simulations with new scenarios prepared by the IIASA institute in the framework of the ECLAIRE EU project. These scenarios are more 'realistic' in terms of air quality legislation than the RCPs and focus on 2030 and 2050. Results from this ongoing work will be presented in forthcoming publications.

On the more technical level, the authors have formulated a simplified thermodynamic aerosol formation scheme. While it has been demonstrated in the past (e.g. Metzger et al), that such parameterizations are relatively accurately mimicking more accurate schemes, such evaluation is missing in the present manuscript. I suggest that the authors present such evaluation in the supplement, especially because the whole paper is building on the accuracy of this scheme. Some simple plots scanning concentration/T/RH space would be indicative of the model's performance.

Based on this interesting suggestion, we have performed box model simulations and compared the results to the ISORROPIA model results. For these simulations we vary

the key parameters such as T, RH, total sulfate, total ammonia, total nitrate and compare the sensitivity of the two models. The comparison is quite encouraging and provides good confidence in the INCA model performance despite the simplified treatment. These results are mentioned in section 2.2 and are presented in the supplementary material under figure S1.

The amount of figures is quite excessive (26). On the hand there will be always somebody who will appreciate particular plots- but it may preclude others to start reading the paper. I would encourage the authors to place less essential plots in the supplementary material, and work on some good summary plots and tables. For instance I have seen a number of scatter plots, but it difficult to grasp if the overall picture is consistent among these figures.

Yes we agree. We have significantly reduced the number of plots in the main paper from 27 to 16. These former figures are now in the supplementary material. In addition, a table has also been introduced (Table 2) summarizing the correlations between model results and measurements. The correlation plots are now in the supplement as well.

With regard to the measurements evaluation, especially the ammonium-nitrate-sulfate system, the authors should be more explicit on the limitation of the measurements that they have used. For instance it is known that filter-pack measurements at temperatures above 20 C, are prone to large sample losses, and at most present a lower limit to the model. Can this explain the overestimates of nitrate/nh4 reported in the paper? Likewise an evaluation sub-regions- (perhaps in a table, regions from Chin et al??) could give more specific information on issues and model performance. We don't need more figures- but something that could summarize North-South differences in Europe/USA, for instance.

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 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 Northen 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 also added a remark in section 3.1 and in the conclusion:

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 in the supplement:

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. Bruggemann, 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.

The authors mention a potential issue with heterogeneous reactions of N2O5, which is much lower than in other studies, but even compared to the same model (Bauer et al. 2007). I appreciate the honesty, but it is something that has to be clarified, since it could influence the model performance especially in winter.

We do not really see it as an issue but more a difference we found comparing our budgets and HNO3 formation terms with those presented by Xu and Penner (2012). In our case the formation from heterogeneous reaction of N2O5 on sulfate aerosols is 4 TgN to be compared to 18 TgN in Xu and Penner. Bauer et al. (2004) used the LMDz-INCA model but in a very different version since the NMHC chemistry and the role played by gas phase NO3 or PANs for instance was not accounted for in this early version. With their version this term was 19 TgN. Interestingly, writing this reply, we realized that Xu and Penner also used a simplified nitrogen chemistry with fixed oxidants and without considering the role played organics. In addition, the reaction probability γ for the reaction of N2O5 hydrolysis has also been significantly updated from this very early version of the model. Therefore we have the feeling this discrepancy with Xu and Penner we mentioned is not an issue and the formation of HNO3 has been higher in previous work based on different and simplified treatments used for gas phase chemistry and reaction probability. We also realized that it was unclear which aerosols where actually considered for this hydrolysis of N2O5 in Xu and Penner. In our case, only sulfate aerosols are concerned. Moreover, as mentioned by Evans and Jacob (2005) who used an even smaller γ coefficient, there is still a large uncertainty on this reaction probably and on the role of this reaction. A few sentences have been added in order to mention briefly these elements in the paper.

Finally, I appreciate the attempts of the authors to compare to other studies. Nevertheless it remains difficult to do this comparison more systematically due to a lack of standard evaluation sets and methods. To my opinion AEROCOM could play a more a substantial role in defining such benchmark sets- that would allow easy comparison of model results (beyond the joint exercises that take place from time to time), and monitor progress. I would appreciate some paragraph on this as well.

Yes. We agree on the important role that AeroCom could play in this type of model intercomparison for nitrates and the role of AeroCom to reduce uncertainties in the nitrate particle budget is mentioned in our conclusion. The internet link to the model intercom-

parison protocol currently underway within AeroCom is now provided. The results from these simulations will be presented in the framework of the AeroCom conferences and in forthcoming papers.

Despite these criticisms, I recommend the paper to be published in ACP, as a welcome addition to the not very extensive literature on nitrate aerosol, after taking into account the remarks above, and the detail comments below.

Detailed comments: p. 6864 l. 8 same magnitude as ; represent=>compares to

The text has been clarified.

p. 6864 l. 18 All nitrates, or mainly NH4NO3?

Yes ammonium nitrates. This is now specified.

p. 6864 l. 20 RCP scenarios only?

Yes, only RCPs have been used in this paper. Other scenarios are currently being introduced in the model.

p. 6867 l. 7 The thermodynamic scheme is used in some regional/global models. Was it evaluated against more comprehensive scheme? How good was it?

We have now added such an evaluation of the thermodynamic model results against the ISORROPIA results by varying most of the input parameters. This evaluation is now summarized in the supplementary material by Figure S1. A reference to this evaluation is also provided in the model description section.

p. 6868l. 5-20 What is the thickness of the surface layer? How can the mixing of the model be characterized. These are essential parameters to understand NH3.

In this 19 level version the first level is located at 70 m. In several papers, the transport and mixing of tracers in the LMDz GCM have been investigated and evaluated against obervations for both inert tracers (e.g., Hourdin and Issartel, 2000; Hauglustaine et al.,

2004; Rivier et al., 2005) and in the framework of inverse modelling (e.g., Bousquet et al., 2005; Pison et al., 2009; Bousquet et al., 2010). These studies concluded that the model at this vertical resolution is well suited for the transport of tracers and chemical species. However it was also pointed out that the simulated inter-hemispheric exchange time is 1.1 years for fossil CO2 (Hauglustaine et al., 2004), in the lowest part of the range (1.1–2.1 years) provided by TRANSCOM1 model inter-comparison (Law et al., 1996; Rayner et al., 1995). This means that LMDZ has one of the fastest inter-hemispheric mixing among the models of TRANSCOM 1 and efficient mixing and transport. This limitation has been added in the model description.

p. 6870 l. 11 I am not sure, but to me equation 3 just looks like a rewrite of equation 2? Or is the point that the factor Beta is independent evaluated?

The text has been clarified to keep only the two key equations.

p. 6871 Given the equations in R1 to R9: what is the number of N2O production?

We added a short paragraph on N2O production and comparison with Dentener and Crutzen (1994) numbers when we discuss the actual Table 4. We find a production of 0.6 TgN/yr based on the budget presented in our actual table 4 providing the budget for NH3. This number is similar to the previous estimate.

p. 6872/6873 could probably move to supplement together with a more thorough evaluation.

The parameterization used for the equilibrium constant based on Mozurkewich (1993) has been moved to the Supplementary Material with the box model evaluation against ISORROPIA as suggested by the reviewer.

p. 6874 9- and further Only on dust and seasalt? Did the authors consider uptake on sulfate? And on Nh4NO3?

The reaction on sulfates and NH4NO3 formation is only considered for the formation of accumulation mode nitrate particles. In order to form coarse nitrates particles we

consider the reaction on dust and sea-salt. In this model only two very distinct classes are considered as described in 2.1 and references therein.

p. 6877 I assume one year was used as spin-up?

Yes. The year 2005 is used as a spin-up. This has now been specified in the paper.

p. 6878 I found the color scheme giving too little information in the regions below 1 ug/m3

Sorry. We have tried to keep a color scale suitable for most of the surface plots for the various gaseous and particulate species. We found this one as the best compromise among all others we have tried. In the original plots we have, the green between 0.2-0.5 and the green for 0.5-1 are more different than on the pdf version. We will provide the original postscript files for the final version.

p. 6878 It is important to tell how the data were used. E.g. can summer measurements on filters be used? Is there a threshold of # days to calculate a monthly average. Were there quality issues, and how were they used?

A monthly average is constructed from at least 2 days of measurements, but the filter measurements used cover almost at all stations more than 90% of the days in a given month. Temporal coverage is more a problem at some AERONET sites, when cloudy conditions prevail. Note that we have used matching daily data, which means that in a given month at a given site the same number of days form model and observation are used for the monthly averages. With respect to data quality: see added text in response to general remark above.

p. 6879 l. 29 and further. The authors seem to suggest that it is physics of global models that are causing the issue. What about resolution? What about measurements that may be biased? This aspect needs to be more expanded also for abstract and conclusions.

It is indeed quite a challenge to represent nitrates in a global model with coarse res-

olution, simplified chemistry and also simplified mixing and transport. The emission dataset is also crucial. We agree that the uncertainty on the measurements is not to be neglected but clearly regional models succeed better to represent the distribution of particles and nitrates in particular than global models. The uncertainty on the measurement is however now mentioned in the paper in reponse to the comment above. The uncertainty associated with the resolution, the simplified aerosol scheme, and physics has been added in this specific paragraph as well.

p. 6882 l. 27 I am confused about the sulfate remark, since previously the authors only talk about reactions with dust and seasalt.

The standard version of the LMDz-INCA model as described by Hauglustaine et al. (2004) and Folberth et al. (2006) includes the formation of HNO3 from the reaction of N2O5 on aerosols. We have emphasized the reference to these papers in Section 2.1.

p. 6883 l 4 ensured=>caused, or most nitrate is lost by wet deposition

Yes. Text corrected.

p. 6885 cloudiness formed?

No. We changed the text to specify that only the direct radiative forcings of aerosols are considered and hence the cloudiness is not affected by the presence of aerosols in this version of the model.

p. 6888 Future evolution of what?

Text modified : Future evolution of nitrate aerosols

p. 6893 It is good that the authors perform sensitivity studies, but we should realize that the RCP scenarios are not internally consistent. Possibly more useful is to increase/decrease within a scenario the emissions of specific components.

These sensitivity scenarios are only intended to illustrate the most important emissions explaining the differences seen in the two extreme RCP scenarios and the relative

importance of NOx, NH3 and SO2 emissions. We found these tests useful to, at least, better understand our results. Of course we agree that other scenarios could be used and tested in forthcoming studies.

p. I found the 'future' section relatively lengthy- and as I explained before, very dependent on relatively similar scenarios. Perhaps this is a section that could be reduced, while retaining the main points: the increasing importance of nitrate under future conditions.

This section has been significantly reduced and a lot of figures and related text moved to the Supplementary Material.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C4197/2014/acpd-14-C4197-2014-supplement.pdf

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