

We thank both reviewers for their constructive comments and suggestions. Replies and corrections (in italics) are listed thereafter

Reviewer 1

Like most other nitrate modelling papers in the literature, the authors do not discuss and evaluate the diurnal cycle of nitrate aerosols in their model. It is unfortunate because the ability of nitrate aerosols to dissociate back to the gas phase means that their diurnal cycle is quite pronounced (Dall'Osto et al. , 2009). It is important to reproduce that diurnal cycle well in a model because when nitrate is in the gas phase (which includes most daylight hours), it will not exert radiative effects and forcing by interacting with radiation. The authors may not have the diagnostics required to evaluate the diurnal cycle, but may have looked at it in another context and could discuss it briefly in the paper

We have included a comparison between observed and simulated diurnal cycle of NO_3^- at the YRK site from the SEARCH network. The following text has been added to the manuscript.

Note that the diurnal cycle of NH_3 emissions has a small impact on the simulated mean surface $[\text{NO}_3^-]$ concentration, but reduces surface $[\text{NH}_3]$ and increases its export to the free troposphere. Fig. S20 shows the observed and simulated diurnal cycle of $[\text{NO}_3^-]$ at the YRK SEARCH site. NO_3^- exhibits a pronounced diurnal cycle with a maximum in the early morning and a minimum in the late afternoon (as a result of both thermodynamics and boundary layer height). AM3N and AM3N_diu capture the timing of the diurnal cycle well. As NH_3 emissions peak in the afternoon, the magnitude of the NH_4NO_3 diurnal cycle in AM3N_diu is lower than in AM3N. Higher daytime concentrations of NH_4NO_3 in AM3N_diu suggest that accounting for the diurnal cycle of NH_3 emissions may increase the magnitude of the radiative forcing associated with NH_4NO_3 .

In an otherwise rigorous modelling of nitrate aerosols, the authors are surprisingly lax about nitrate aerosol optical properties. They are simply taken as identical to sulphate aerosols (page 25743, lines 20–23). Why not do things properly? Refractive index datasets are available, as are hygroscopic growth curves. The authors state that using sulphate optical properties yields errors of 20% in extinction (page 25743, line 22). How was that estimated? The paper should clearly state that that 20% is a big number compared to the sensitivities in emissions and chemistry explored later. As such, the paper would have benefited from including nitrate optical properties in the sensitivity analysis

As shown in Fig. S1, below (added to supplementary materials), the mass extinction of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ at 550nm calculating using standard Mie calculations differs by less than 20% below 95% relative humidity (we do not consider hygroscopic growth beyond that point) and by less than 10% between 90% and 95%. Consistent with a small impact of this simplification on the simulation NO_3^- optical depth, the simulated burden and optical depth for NO_3^- over the 2008–2010 period are very similar to those reported by Hauglustaine et al. (2014), who treated the optical properties of NH_4NO_3 explicitly. Other uncertainties such as the degree of internal mixing between NH_4^+ , SO_4^{2-} , NO_3^- , and BC, the cap on aerosol hygroscopic growth or even as highlighted in our work the simulation of RH are likely to be much more important in determining NO_3^- optical depth at 550nm.

However, we agree with the reviewer and we recognize that this simplification has important limitations. As a result we chose to only present the simulated AOD at 550 nm rather than the radiative forcing associated with nitrate. This simplification was motivated by current limitations in the treatment of aerosol optical properties in the GFDL-AM3 model associated with the mixing of NH_4^+ , SO_4^{2-} , NO_3^- , and BC. Revisions to the radiative code in the next GFDL atmospheric model (AM4), will allow us to use observed refractive index and hygroscopic growth for ammonium nitrate. The main findings of this study, such as the importance of the convective transport of NH_3 to the free troposphere for future projections of NO_3^- burden and optical depth are not expected to change.

Page 25751, line 11: The quality of the simulation of precipitation rates will also matter.

We agree with the reviewer. However, the change in the convective scheme between AM3 and AM3N has little impact on the precipitation rates while it increases the efficiency of both convective removal and convective transport. Further analysis suggests that the finer discretization of the convective plumes in AM3N improves the stability of the tracer convective transport scheme. We have modified the text as follow:

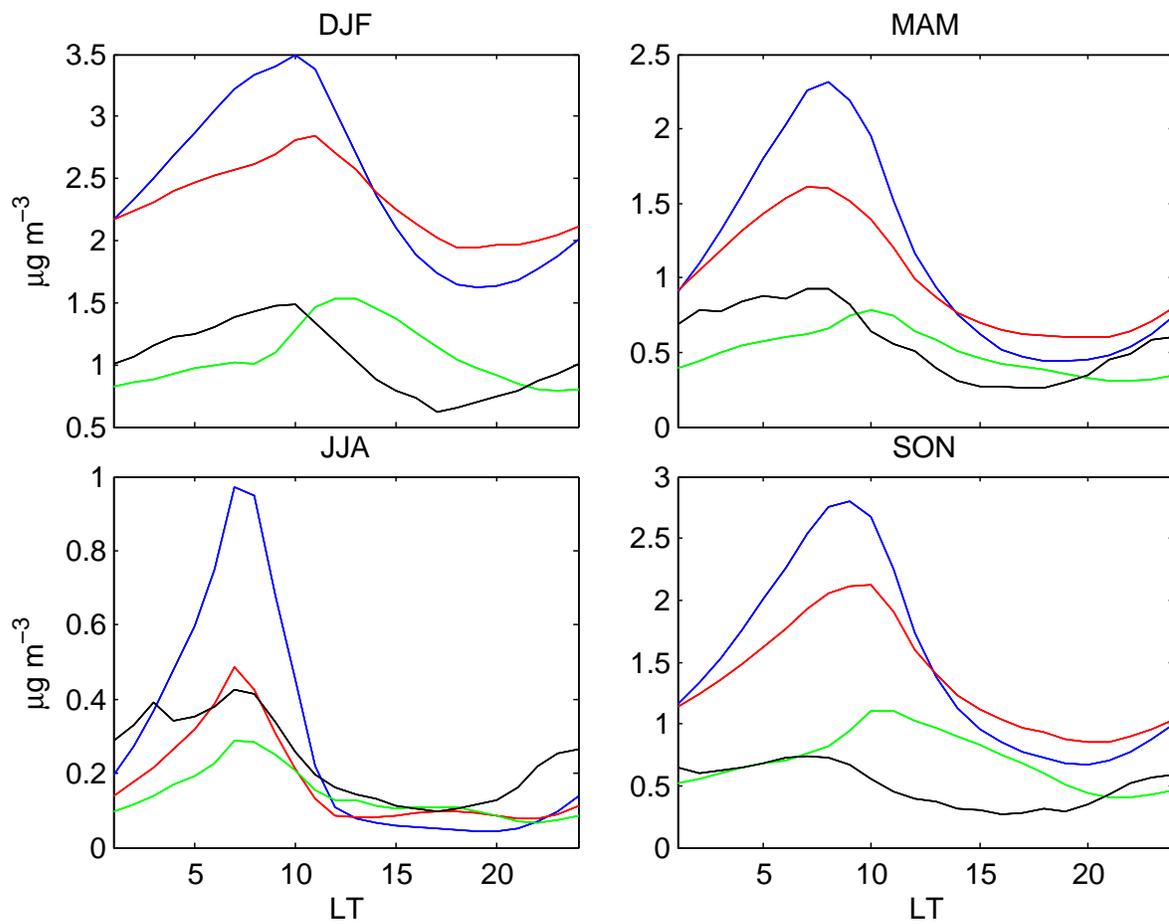


Figure S20: Average diurnal profile of NO_3^- at the YRK SEARCH site (33.93N, 274.95E, 395m asl) in 2008. Simulated nitrate diurnal profiles from AM3N, AM3N_diu, and AM3N_fdep_diu are shown in blue, red, and green respectively. Observations are shown in black

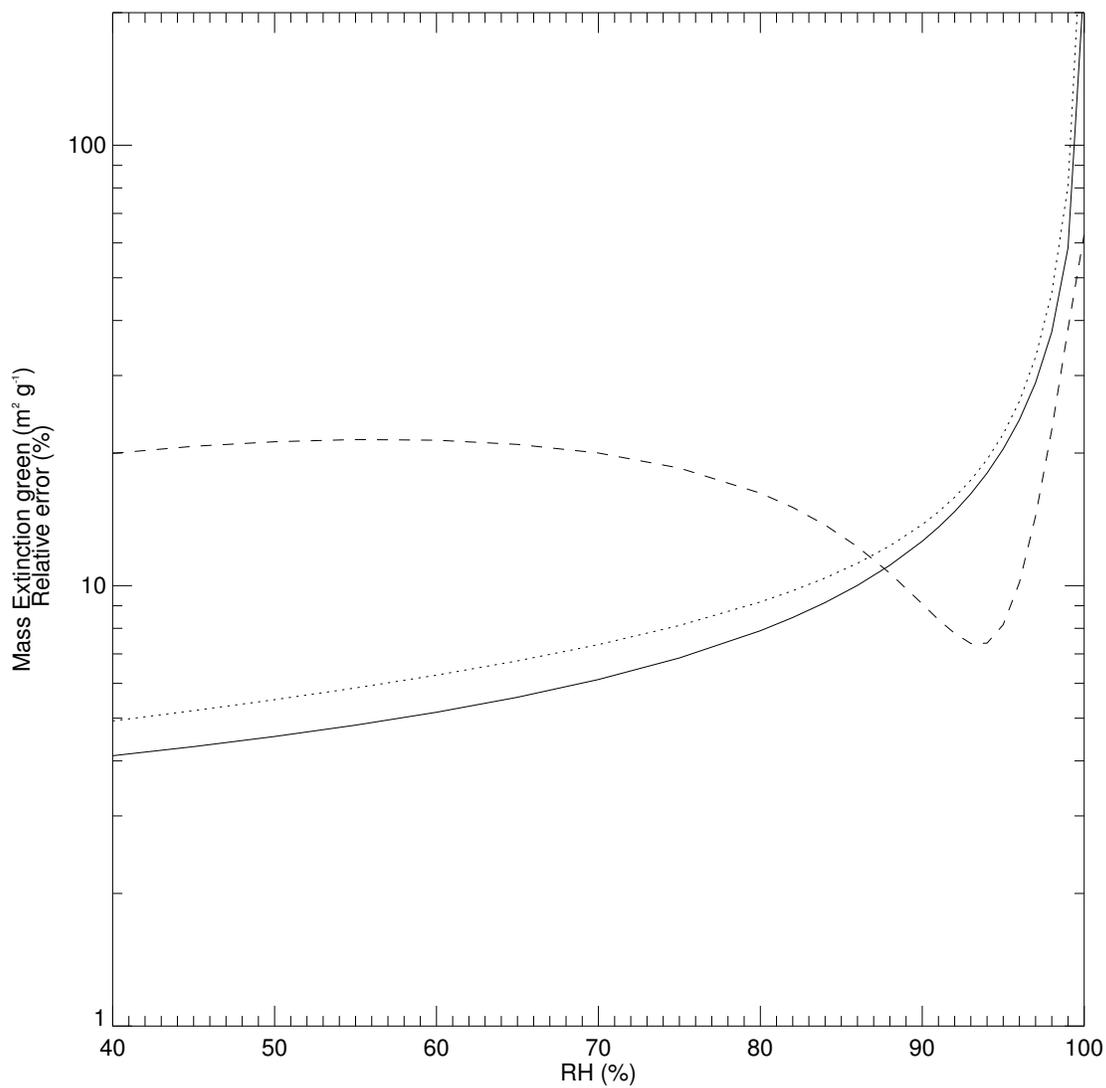


Figure S1: Mass extinction of $(\text{NH}_4)_2\text{SO}_4$ (dotted line) and NH_4NO_3 (solid line) at 550nm. The dash line shows the relative error between $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 mass extinctions. Refractive index and hygroscopic growth for NH_4NO_3 are taken from Gosse et al. (1997) and Tang (1996) respectively.

The improved discretization of the convective plume has little impact on precipitation at the surface but increases the convective wet removal of tracers as we will show [...]

Page 25753, line 16: Using sulphate aerosol hygroscopic growth curves may also be a problem.

The use of sulfate optical properties for nitrate introduces a small error at high RH (<10% for RH>90%), much less than the discrepancy between observed and simulated AOD at Bondville. The error is likely to be larger (<20%) under the low RH conditions (RH<40%) used to measure aerosol dry extinction. Thus the model high RH bias in winter is likely to cause the high bias in simulated AOD in all AM3N configurations. Excessive hygroscopic growth also helps explain that AM3 captures winter AOD remarkably well in spite of neglecting nitrate aerosol and underestimating sulfate surface concentrations. In summer, nitrate aerosol is very low and cannot explain the large underestimate of the aerosol optical depth (see Fig. S2).

Page 25758, line 20 to Page 25759, line 9: Those changes are due to changes in the strength and location of emissions alone. It would be useful to speculate on the effect of climate change as well. Climate change would presumably increase transport to the free troposphere, thus making NH3 limitation bite even more than suggested by those simulation.

We have performed a new simulation with reduced convective removal of NH₃. In this configuration, the simulated nitrate burden is found to be similar to that reported by Hauglustaine et al. (2014) in the tropics and exhibits more sensitivity to changes in anthropogenic emissions. Fig. 12 and its description in the last section have been revised (see reply to the last comment of reviewer 2) to emphasize a) that the response of convection to climate change has important implications for future projections of nitrate burden and b) that differences in the representation of convective transport and removal across models contribute to the large variability in the modeled response of nitrate to projected changes in anthropogenic emissions.

Reviewer 2

Considering the comparison of the response of NO3 AOD to future emissions (compared to that of Hauglustaine), for this simulation you start with a model in which NO3 is already biased high, and compare to a set of scenarios in which NH3 levels are already much higher, muting the response of the system to the emissions changes. It thus seems that some of the differences in the projected changes in AOD between the two studies may be owing to different starting conditions.

We have clarified that there is a large absolute difference between the projections for the NO₃⁻ burden in 2050 obtained from most AM3N configurations and that reported by Hauglustaine et al. (2014) for 2050. In particular, when using AM3N with RCP8.5 emissions for 2050, NO₃⁻ optical depth is 0.0076, 36% less than reported by Hauglustaine et al. (2014). One notable exception is AM3N_ndust, which produces a similar NO₃⁻ optical depth in 2050 (0.01) to the one reported by Hauglustaine et al. (2014).

We have added the following text in the 2050 emission section:

The response of NO₃⁻ to changes in anthropogenic emissions is weaker than reported in recent studies. For instance, Hauglustaine et al. (2014) reported a NO₃⁻ optical depth of 0.01 for 2050 and an increase of the conversion rate from NH₃ to NO₃⁻ from 0.36 day⁻¹ to 0.57 day⁻¹ from 2000 to 2050. Using the same anthropogenic emissions, the simulated NO₃⁻ optical depth in AM3N in 2050 (the configuration closest to that used by Hauglustaine et al. (2014)) is 0.077 and the conversion rate from NH₃ to NO₃⁻ is 0.33 day⁻¹.

It seems a bit odd to show the model evaluation for one of the sensitivity simulations (AM3N_fdep_diu) but then report results for the AM3N simulation for subsequent analysis. It seems like whichever simulation is justifiably ‘best’, both in terms of the details of the mechanisms included as well as the model evaluation, would be most suitable for reference in the rest of the work. I think this may actually be the case, but there is some ambiguity in the text and certainly some ambiguity in the figures and Tables 1 somebody who looks at Table 2 and then Fig 9 would never suspect that here “AM3N” actually means (I think) “AM3N_fdep_diu”.

Fig. 9 shows AM3N_fdep_diu not AM3N and we have corrected the caption. In the manuscript, we chose to focus on the comparison between observations and AM3N_fdep_diu as it better captures surface NO₃⁻ concentration than AM3N. However, in the analysis we use AM3N as our reference for two reasons: a) this facilitates the analysis of the impact of different processes as the sensitivity tests performed in this study (Table 2) are all based on AM3N,

b) the magnitude of the perturbations are large and often represent upper bounds. This is especially the case for the simulations with increased deposition of NO_3^- and no heterogeneous production of HNO_3 .

We have added AM3N_fdep_diu to Fig. 12. It can be seen that the difference between AM3N and AM3N_fdep_diu cannot explain the differences with the simulation performed by Hauglustaine et al. (2014). Further revisions are detailed in the response to the reviewer's last comments

Abstract: “only find a modest” I was confused about how this was presented. 30% changes in nitrate AOD in response to 30-40% changes in SO2 and NH3 seems significant. I guess after reading the paper I understand that this may seem like a small change, relative to some other studies, but by itself it doesn't seem modest. It might be best to just remove such qualifiers and just present the quantitative results, or alternatively explain the context a bit more.

We agree with the reviewer and we have removed references to previous studies from the abstract. In the main text, we now emphasize absolute differences more. The abstract was revised as follow:

Simulated nitrate optical depth increases by less than 30 % (0.0061–0.010) in response to projected changes in anthropogenic emissions from 2010 to 2050 (e.g., –40 % for SO_2 and +38 % for ammonia). This increase is primarily driven by greater concentrations of nitrate in the free troposphere, while surface nitrate concentrations decrease in the midlatitudes following lower concentrations of nitric acid. With the projected increase of ammonia emissions, we show that better constraints on its vertical distribution (e.g., convective transport and biomass burning injection) and on the sources and sinks of nitric acid (e.g., heterogeneous reaction on dust) are needed to improve estimates of future nitrate optical depth.

Abstract: The focus here is on changes in global budgets. Given that secondary inorganic aerosol though is rather regional, is that the best way to summarize the impacts? Later in the manuscript evaluation is considered for the top percentiles of locations. would that be more suitable here as well, or in addition?

We have added the following sentence in the abstract

In wintertime, nitrate aerosols are simulated to account for over 30% of the aerosol optical depth over western Europe and North America.

Introduction: It seems like the set of references cited need to either be more comprehensive or “i.e.” inserted when citing only representative studies.

corrected

25741.15: Also see West et al., AE, 1998, Marginal direct climate forcing by atmospheric aerosols, and Henze et al., ES&T, 2012, Spatially refined aerosol direct radiative forcing efficiencies.

Both references have been added

Section 2.1: I was expecting a description of heterogeneous chemistry here. Granted, it comes later. Maybe that can be indicated?

We have clarified that the parametrization of the heterogeneous chemistry is based on Mao et al. (2013). We have also expanded the description of changes to the heterogeneous chemistry to include changes in the γ for N_2O_5 , NO_2 , and NO_3 between AM3 and AM3N (see revised Table S1).

We also reduce the reaction probabilities (γ) of N_2O_5 , NO_2 , and NO_3 on aerosols relative to AM3 (Mao et al., 2013) (see Table S1 and Sect. 2.3.2). The implications of these changes for the budget of HNO_3 and aerosol NO_3^- are described in Sect. 2.4.

Section 2.2: Similarly, I was expecting a description of NH3 emissions, but that came later

We have added the contribution of the different sectors to the emissions of NH_3 in Table 1.

25743.23: Why is this neglected?

Coarse-mode nitrate is expected to make a small contribution to present-day nitrate optical depth and contributes little to the response of NO_3^- optical depth to future anthropogenic emissions (e.g., Hauglustaine et al. (2014)). We have modified the text as follows:

The optical depth of NO_3^- associated with dust is expected to be small relative to fine-mode NO_3^- (e.g., Hauglustaine et al. (2014)) and it is not considered here.

25747.1: That production of HNO₃ from N₂O₅ is the dominant pathway in the northern mid latitudes in the winter has been known much earlier than 2010.

We have added references to Dentener and Crutzen (1993) and Tie et al. (2003)

25747.10, 25747.14: why are these neglected?

We have revised the text to clarify that the AM3N_nhet and AM3N_ndust configurations are designed to quantify the impact of different treatments of heterogeneous chemistry on the simulated NO_3^- optical depth.

Wintertime production of HNO_3 in the northern midlatitudes boundary layer is dominated by the uptake of N_2O_5 on aerosols (e.g., Dentener and Crutzen (1993); Tie et al. (2003); Lamsal et al. (2010)). The probability for the heterogeneous conversion of N_2O_5 to HNO_3 (γ) remains uncertain (Chang et al., 2011) with field and laboratory observations showing that it is inhibited by aerosol nitrate and organics (Brown et al., 2009; Brown and Stutz, 2012; Wagner et al., 2013; Gaston et al., 2014), but enhanced by cold temperatures (Griffiths and Anthony Cox, 2009; Wagner et al., 2013). To quantify the impact of the heterogeneous production of HNO_3 on aerosol NO_3^- , we neglect the heterogeneous production of HNO_3 via N_2O_5 aerosol uptake in AM3N_nhet. We also neglect the productions of HNO_3 by NO_3 and NO_2 reactive uptake, as they may modulate the wintertime budget of NO_y in polluted region (Paulot et al., 2013). Note that previous characterizations of NO_3^- optical depth also neglected the heterogeneous chemistry of oxidized nitrogen (e.g., Bellouin et al. (2011)). We also evaluate the impact of the heterogeneous chemistry on dust as it is not included in all model (e.g., Pye et al. (2009); Bellouin et al. (2011)). In AM3N_ndust, we neglect the uptake of HNO_3 , N_2O_5 , NO_3 , H_2SO_4 , and SO_2 on dust.

25748.20: Also agrees well with observed values (e.g., Lee et al., JGR, 2011, SO₂ emissions and lifetimes: Estimates from inverse modeling using in situ and global, space-based SCIAMACHY and OMI observations

Thank you. We have added this reference to the manuscript.

Section: Description of biases are largely qualitative. Without changing this to be an extensive numerical catalog, it would be good in places to be more specific about what is a low or high bias, small or large, more quantitatively

We have incorporated some key numbers from Table 3 and S3 in the text.

25754.15: Does increased convective precip also increase loss of HNO₃?

Yes it does. We have modified the text as follows:

Increased convective removal of HNO_3 and NH_3 also reduce the low bias in simulated summer wet deposition NO_3^- (-50% to -23%, Fig. S9) and NH_4^+ (-46% to -16%, Fig. S10).

25755.3: The same was shown in Zhu et al., ACP, 2015, Global evaluation of ammonia bi-directional exchange, which also found bigger impacts on surface NO₃ than indicated in the present work. Also, on the following page the impact of NH₃ diurnal variability is said to impact NH₄NO₃ (25757.2), so it seems odd to say here that the effect on NO₃ is small.

We have clarified here that we only refer to surface concentrations. The impact on the NO_3^- burden (mentioned in line 25757.2) is more significant but it is primarily driven by an increase in the export of NH_3 to the free troposphere, consistent with the large sensitivity of NO_3^- to the convective removal of NH_3 . We have added a reference to the study of Zhu et al. in the section devoted to NH_3 emissions. See also the replay to reviewer 1 first comment regarding the diurnal cycle of NH_4NO_3 .

Abstract, Conclusions, etc: The authors purportedly evaluated the sensitivity of nitrate with respect to “uncertainties in NH₃ emissions”, but it seems that they only investigated but it seems that they only investigated the sensitivity with respect to the diurnal or seasonal variability in NH₃ emissions. The net emissions themselves are probably uncertain by x2 globally, and maybe much more than that regionally. So it seems that either the authors can’t really claim to have investigated the impacts of NH₃ emissions uncertainties in the most general sense. Either more numerical experiments are required, or more precise language is called for.

Throughout: Bidirectional exchange of NH₃ is never mentioned. Should it be included in discussion of uncertainties, since it isn’t considered here?

We agree with the reviewer that there are considerable uncertainties in NH₃ emissions. We believe that differences between RCP8.5 NH₃ emissions and HTAP emissions capture some of this uncertainty. These inventories differ significantly both spatially (see Fig. 1) but also temporally (RCP8.5 NH₃ emissions have no seasonality). For instance, India anthropogenic emissions of NH₃ in HTAPv2 are more than twice as large as in RCP8.5. These large differences have a small impact (<10%) on the NO₃⁻ burden simulated for 2050, consistent with the diminishing sensitivity of NO₃⁻ to NH₃. In AM3N, ammonia remains confined to the surface. As NH₄NO₃ becomes more and more limited by HNO₃ following projected changes in anthropogenic emissions, the representation of 2050 ammonia anthropogenic emissions has little impact on the simulated nitrate burden in our model. Models with more efficient transport of NH₃ to the free troposphere may exhibit a greater sensitivity to NH₃ emissions including to the bidirectional exchange of NH₃. This has been clarified in the conclusion.

The text was modified as follow:

2050 emissions:

Figure 12 shows that the NO₃⁻ burden is projected to shift equatorward in the Northern Hemisphere in response to changes in anthropogenic emission from present-day to 2050. NH₄NO₃ increases in the free troposphere but decreases near the surface, a vertical redistribution also noted by Hauglustaine et al. (2014). The decrease of surface NO₃⁻ in the midlatitudes is primarily driven by lower NO emission. Large differences in the seasonality, spatial distribution, and magnitude of anthropogenic NH₃ emissions in RCP8.5 (dotted line) and scaled HTAPv2 for 2050 have little impact on the simulated NO₃⁻ burden (<10%), which reflects the diminishing sensitivity of surface NH₄NO₃ to NH₃. However, NO₃⁻ remains sensitive to NH₃ in the free troposphere, where it can persist longer than in the boundary layer thanks to lower temperature. The solid line in Figure 12 shows the impact of lower convective removal of NH₃ (achieved by neglecting the impact of pH on NH₃ solubility) on the NO₃⁻ burden. Over the 2008–2010 period, this results in a 40% increase of the NO₃⁻ burden with a near quadrupling in the tropics, qualitatively matching the results of Hauglustaine et al. (2014) in this region. In 2050, the impact is much more pronounced and the simulated burden is more than twice as large as in 2010, a similar response to that found by Hauglustaine et al. (2014). Note that increasing NH₃ emissions from biomass burning and distributing these emissions vertically (Naik et al., 2013) also increases tropical NO₃⁻ (not shown) but to a much lower degree (<50%). These results suggest that differences in the transport of NH₃ to the free troposphere across models contribute to the variability in the projected NO₃⁻ burden and optical depth. Such differences may arise from differences in the parameterizations of convection (Folkins et al., 2006) as suggested by the much lower tropical NO₃⁻ burden in AM3N than in LMDz-INCA model (Hauglustaine et al., 2014) but also from changes in the tropical circulation in response to climate change (e.g., Ma et al. (2012)).

Conclusion:

We have examined the response of simulated NO₃⁻ optical depth to projected changes in anthropogenic emissions from 2010 to 2050 in RCP8.5. Depending on the configuration of AM3N (Table 2), NO₃⁻ optical depth varies from 0.0061 to 0.01 in 2050. The increase of NO₃⁻ (< 30 % relative to 2008–2010) is partly inhibited by greater limitation of NH₄NO₃ production by HNO₃ at the surface due to lower NO emissions, more efficient removal of HNO₃ by dust, and a large decrease in the heterogeneous production of HNO₃ by N₂O₅ (associated with lower aerosol surface area). In the Northern Hemisphere, the NO₃⁻ burden is projected to shift southward, following the increase of tropical NH₃ emissions and the decrease of NO emissions in the midlatitudes. This shift is associated with an increase of the NO₃⁻ burden in the free troposphere, where NH₄NO₃ formation is limited by NH₃. We suggest that the convective transport of NH₃ and its response to climate change (not considered here) play an important role in modulating the response of NO₃⁻ optical depth to changes in anthropogenic emissions. The complexity of the response of NO₃⁻ to changes in surface processes, chemistry, and convection indicates that the global trends of NH₃ emissions may not be a suitable proxy to estimate the future forcing from NO₃⁻ aerosols (Heald and Spracklen, 2015). We conclude that in addition to improvements to NH₃ emission inventories (e.g., bidirectional exchange of NH₃ (Zhu et al.,

2015)), *observational constraints on the processes controlling the vertical redistribution of NH₃ and the response of NO₃⁻ to NH₃ in the free troposphere (e.g., magnitude of NH₃ emissions in the tropics (Aneja et al., 2012; Whitburn et al., 2015), biomass burning injection height (Val Martin et al., 2010), transport and removal of NH₃ in convective updrafts, heterogeneous chemistry on dust) and sensitivity studies to characterize their response to climate change are needed to improve estimates of present and future NO₃⁻ optical depth.*

Fig 2: by a black cross in the upper left panel.

corrected

Fig 9: “Across AM3N” It isn’t clear what is mean here. Across what? Seasons? Different model configurations?

we have specified that we refer here to the different AM3N configurations

25741.11: However, recent

corrected

25741.17: In this study

corrected

25747.3: It seems rather obvious that it would depend on the choice or reaction probability suggest rewording.

this subsection has been rewritten see above.

throughout: It is odd to present numbers as “X %” rather than “X%”.

this was done during typesetting by copernicus staff. Thus we have kept all percent numbers as “X %”

25747.16: slow, similar

corrected

25747.16: results

corrected

Other corrections

The following additional corrections have been made:

1. We corrected an error in the labeling of the tick marks in Fig. 8.
2. We have added seasalt and dust optical depths for the LMDz-INCA model in Fig. 9.
3. We have added that revisions to the convective removal of ammonia in the GISS model result in a much lower simulated present-day nitrate optical depth (0.005, S. Bauer, personal communication).

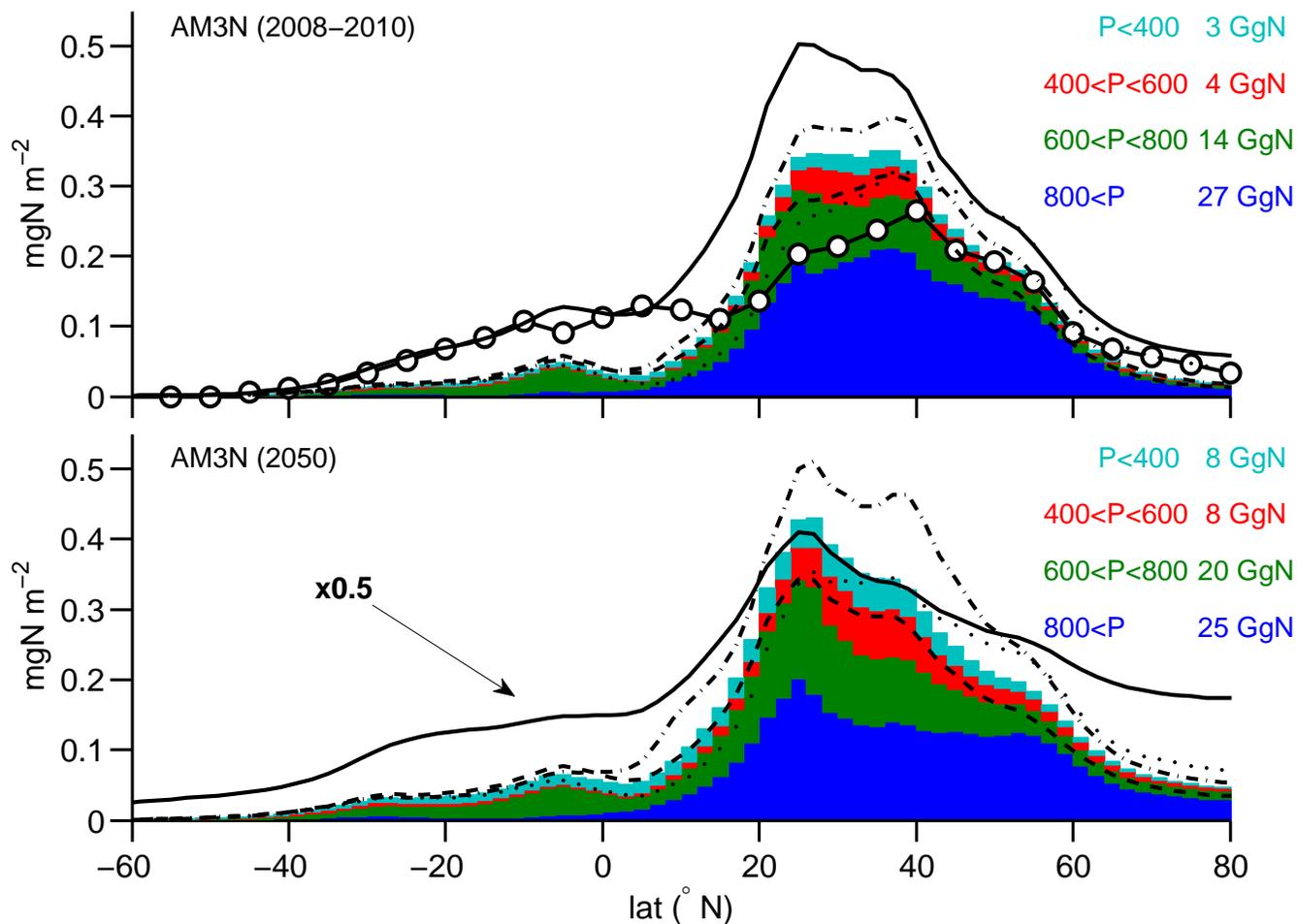


Figure 12: Annual zonal mean distribution of NO_3^- in AM3N with 2008-2010 anthropogenic emissions (top) and 2050 anthropogenic emissions (from RCP8.5 except for NH_3 , see text). The blue, green, red, and cyan regions denote the NO_3^- burden located above 800 hPa, between 600 and 800 hPa, between 400 and 600 hPa, and below 400 hPa, with the partial burden in each pressure range indicated inset. The annual mean zonal burdens of NO_3^- simulated using AM3N_fdep_diu (dash line), using AM3N with anthropogenic emissions from RCP8.5 for NH_3 (dotted line), using AM3N_ndust (dash dot line), and using AM3N with reduced convective removal of NH_3 (solid line) are also shown. The white circles in the top panel indicate the 2000 annual zonal mean NO_3^- burden simulated by Hauglustaine et al. (2014).

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Sensitivity of nitrate aerosols to ammonia emissions and to nitrate chemistry: implications for present and future nitrate optical depth

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Abstract

We update and evaluate the treatment of nitrate aerosols in the Geophysical Fluid Dynamics Laboratory (GFDL) atmospheric model (AM3). Accounting for the radiative effects of nitrate aerosols generally improves the simulated aerosol optical depth, although nitrate concentrations at the surface are biased high. This bias can be reduced by increasing the deposition of nitrate to account for the near-surface volatilization of ammonium nitrate or by neglecting the heterogeneous production of nitric acid to account for the inhibition of N_2O_5 reactive uptake at high nitrate concentrations. Globally, uncertainties in these processes can impact the simulated nitrate optical depth by up to 25 %, much more than the impact of uncertainties in the seasonality of ammonia emissions (6 %) or in the uptake of nitric acid on dust (13 %). Our best estimate for present-day fine nitrate optical depth at 550 nm is 0.006 (0.005–0.008). ~~We only find a modest increase of~~ In wintertime, nitrate aerosols are simulated to account for over 30% of the aerosol optical depth over western Europe and North America. ~~Simulated nitrate optical depth (< increases by less than 30 % (0.0061–0.010) in response to the projected changes in the emissions of SO_2 (anthropogenic emissions from 2010 to 2050 (e.g., –40 %) and ammonia (for SO_2 and +38 %) from 2010 to 2050. Nitrate burden is projected to increase in the tropics and in the~~ for ammonia). ~~This increase is primarily driven by greater concentrations of nitrate in the free troposphere, but to decrease at the surface while surface nitrate concentrations decrease in the midlatitudes because of lower nitric acid concentrations. Our results suggest following lower concentrations of nitric acid. With the projected increase of ammonia emissions, we show that better constraints on the heterogeneous chemistry its vertical distribution (e.g., convective transport and biomass burning injection) and on the sources and sinks of nitric acid on dust, on tropical ammonia emissions, and on the transport of ammonia to the free troposphere (e.g., heterogeneous reaction on dust) are needed to improve projections of aerosol estimates of future nitrate~~ optical depth.

1 Introduction

Ammonium nitrate (NH_4NO_3) aerosols are produced by the reaction of nitric acid (HNO_3), a photochemical product of NO oxidation, and ammonia (NH_3). Emissions of NH_3 and NO are primarily from anthropogenic origin: fossil fuel combustion for NO and agriculture for NH_3 (Bouwman et al., 1997; Paulot et al., 2014). (i.e., Bouwman et al. (1997); Paulot et al. (2014)). The formation of NH_4NO_3 is favored by cold temperatures and high relative humidity (Stelson and Seinfeld, 1982). NH_4NO_3 production competes with that of ammonium sulfate, which is generally more thermodynamically stable (Pinder et al., 2008), and that of coarse-mode nitrate via heterogeneous uptake of HNO_3 on dust and sea salt (Zhuang et al., 1999; Jacobson, 1999; Jordan et al., 2003). (i.e., Zhuang et al. (1999); Jacobson (1999); Jordan et al. (2003)).

NH_4NO_3 is an important component of surface particulate matter in the US (Malm et al., 2004; Hand et al., 2012; Kim et al., 2014), Europe (Schaap et al., 2004), and Asia (Pathak et al., 2009). (i.e., Malm et al. (2004); Hand et al. (2012); Kim et al. (2014)), Europe (i.e., Schaap et al. (2004)), and Asia (i.e., Pathak et al. (2009); Ying et al. (2014)), especially in winter. As NH_4NO_3 rapidly volatilizes away from sources of NO and NH_3 and with warmer temperature, it is only predicted to make an important contribution to aerosol optical depth (AOD) over polluted regions (Park et al., 2014), with global annual estimates of nitrate optical depth ranging from 0.0023 to 0.025 (Bellouin et al., 2011; Shindell et al., 2013; Myhre et al., 2013; Hauglustaine et al., 2014). However, recent modeling studies have shown that NH_4NO_3 may become the largest contributor to anthropogenic AOD by the end of 21st century (Hauglustaine et al., 2014), following the projected increase of NH_3 emissions and decrease of SO_2 emissions. Such an increase of NH_4NO_3 would offset some of the decline in anthropogenic aerosol radiative forcing over the 21st century (Adams et al., 2001; Liao et al., 2006; Bellouin et al., 2011; Shindell et al., 2013; Hauglustaine et al., 2014).

In ~~the~~ this study, we aim at characterizing the mechanisms controlling the response of NO_3^- optical depth to changes in anthropogenic emissions from 2010 to 2050. We focus in particular on how this response is modulated by the temporal and spatial variations

in NH_3 emissions, the heterogeneous chemistry of HNO_3 , and the surface removal of nitrate aerosols. In Sect. 2, we first describe a new configuration (AM3N) of the global chemistry-climate atmospheric model (AM3) from the Geophysical Fluid Dynamics Laboratory (GFDL), with revised treatments of sulfate and nitrate chemistry and aerosol deposition. We emphasize significant differences in the simulated budgets of SO_4^{2-} , NO_3^- , and $\text{NH}_x \equiv \text{NH}_3 + \text{NH}_4^+$ between AM3N and the version of AM3 used for the Coupled Model Intercomparison Project (CMIP) 5. In Sect. 3, we evaluate the simulated distribution of AOD, as well as SO_4^{2-} , NO_3^- , and NH_3 concentrations at the surface and in precipitated water. In particular, we evaluate AM3 and AM3N against the extensive set of aerosol composition and optical properties routinely measured at Bondville (40.1°N , 88.4°W). In Sect. 4, we examine the response of NO_3^- optical depth to projected changes in anthropogenic emissions in 2050 and its sensitivity to different treatments of removal and chemistry.

2 Method

2.1 Model description

We use the GFDL-AM3 chemistry–climate model to simulate gas and aerosol chemistry. In its standard form, AM3 uses a finite volume dynamical core on a cubed sphere grid with 200 km (c48) horizontal resolution and 48 hybrid sigma pressure vertical layers (Donner et al., 2011). AM3 simulations were conducted for ACCMIP (Naik et al., 2013b) and as the atmospheric component of the GFDL coupled climate model CM3 for CMIP5 in support of the IPCC AR5.

The chemistry of AM3 has been described by Naik et al. (2013a) with updates to the gas-phase [chemistry described in Mao et al. \(2013b, c\)](#) and [heterogeneous chemistry \(Mao et al., 2013b, c\)](#). Briefly, AM3 includes SO_4^{2-} formation from gas-phase oxidation and in-cloud reaction of SO_2 with O_3 and H_2O_2 (Tie et al., 2005). In-cloud production of SO_4^{2-} is sensitive to cloud pH, which is calculated as a function of the concentration of SO_4^{2-} (assumed to be entirely in cloud water), NH_3 , SO_2 , HNO_3 , and CO_2 . NH_4NO_3 formation is

calculated following Stelson and Seinfeld (1982), but is assumed irreversible. Dry deposition and wet scavenging by large scale and convective precipitation are described by Fang et al. (2011); Donner et al. (2011); Naik et al. (2013a).

Aerosol optical properties (i.e., extinction efficiency, single-scattering albedo, and asymmetry parameter) are described by Donner et al. (2011) and Strong et al. (2015). Sulfate is assumed to be fully neutralized by ammonium. Its size distribution is taken as log-normal following Haywood and Ramaswamy (1998) with hygroscopic growth based on pure ammonium sulfate (Tang and Munkelwitz, 1994) and capped at 95 % relative humidity. Aerosol activation into cloud droplets follows the parameterization of Ming et al. (2006). For radiative calculations, aerosols are assumed to be externally mixed except for sulfate and hydrophilic black carbon, which are assumed internally mixed (Donner et al., 2011). Nitrate is not considered for radiative calculations in AM3.

A new configuration of AM3 is introduced (referred to as AM3N hereafter) with the following changes aimed at improving the simulation of nitrate aerosols (see Sect. 3):

Aerosol chemistry – We use ISORROPIA to simulate the sulfate-nitrate-ammonia thermodynamic equilibrium (Fountoukis and Nenes, 2007). Equilibrium between gas and aerosol is assumed to be reached at each model time step (30 min), which is generally justified for $PM_{2.5}$ (Meng and Seinfeld, 1996). In-cloud oxidation of SO_2 is restricted to liquid clouds and we revise the calculation of cloud pH to account for the partitioning of HNO_3/NO_3^- and NH_3/NH_4^+ between the gas phase and cloud water.

Heterogeneous chemistry on dust – We include the heterogeneous uptake of HNO_3 , NO_3^- , N_2O_5 , SO_2 , and H_2SO_4 on dust particles (Table S1 in the Supplement). The uptake of HNO_3 , NO_3^- , and N_2O_5 is assumed to be limited by alkalinity (Song and Carmichael, 2001). Following Fairlie et al. (2010), dust alkalinity is comprised of calcium and magnesium carbonates, with calcium and magnesium constituting 3 and 0.6 % (by mass) of coarse dust emissions (radius > 1 μm), respectively. Observations suggest alkalinity is primarily found in the coarse mode (Claquin et al., 1999); we assume that fine dust carries half as much alkalinity per kg as coarse dust. [We also reduce the reaction probabilities \(\$\gamma\$ \) of \$N_2O_5\$, \$NO_2\$, and \$NO_3\$ on aerosols relative to AM3 \(Mao et al., 2013b\) \(see Table S1 and Sect. 2.3.2\).](#)

The implications of these changes for the budget of HNO_3 and aerosol NO_3^- are described in Sect. 2.4.

Nitrate optical depth – The optical properties and the mixing with black carbon of ammonium nitrate are assumed to be identical to those of ammonium sulfate. This approximation introduces an error in mass extinction at 550 nm of less than 20 % for $\text{RH} < 95\%$. ~~We neglect the optical properties~~ < 90 % and and by less than 10% between 90% and 95% (Fig. S1). The optical depth of NO_3^- on dust associated with dust is expected to be small relative to fine-mode NO_3^- (e.g., Hauglustaine et al. (2014)) and it is not considered here.

Dry deposition – Similar to AM3, the dry deposition of gases and fine aerosols are calculated based on a monthly climatology of deposition velocities. We update this climatology to account for recent observations of rapid deposition of H_2O_2 and some oxygenated volatile organic compounds (OVOCs), using the deposition velocities calculated in the GEOS-Chem chemical transport model as described by Nguyen et al. (2015).

Wet deposition – In AM3, aerosol removal by snow is treated like that by rain. In AM3N, water-soluble aerosols are not removed by snow, when the snow is formed via the Wegener–Bergeron–Findeisen mechanism (referred to as Bergeron mechanism hereafter), i.e., when water evaporates from liquid cloud droplets and condenses onto growing ice crystals. This treatment is consistent with observations (Henning et al., 2004) and similar to that used in other global models (Liu et al., 2011; Wang et al., 2011; Fan et al., 2012). Scavenging by snow formed via riming and homogeneous freezing is treated like that by rain. Gases are not scavenged by snow except HNO_3 (Neu and Prather, 2012). Convective plumes are discretized on a vertical grid that has finer vertical resolution than AM3 (Donner, 1993). The improved discretization of the convective plume has little impact on precipitation at the surface but increases the convective wet removal of tracers as we will show in Sect. 3.

2.2 Emissions

We use anthropogenic emissions from the Hemispheric Transport of Air Pollution v2 (HTAP_v2) task force regridded to $0.5^\circ \times 0.5^\circ$ for years 2008 and 2010 (Janssens-Maenhout et al., 2015). HTAP_v2 aircraft emissions are distributed vertically following Lamarque et al.

(2010). Daily biomass burning emissions are based on the NCAR Fire INventory (FINNv1, Wiedinmyer et al., 2011) and emitted in the model surface layer. Average dust emissions are parameterized following Ginoux et al. (2001), as:

$$F_p = CSs_p u_{10m}^2 (u_{10m} - u_t) \text{ if } u_{10m} > u_t \quad (1)$$

where C is a dimensional factor ($\mu\text{g s}^2 \text{ m}^{-5}$), S is the source function based on topography, u_{10m} is the horizontal wind at 10 m (m s^{-1}), u_t is the threshold velocity (m s^{-1}), and s_p is the fraction of total dust emitted in the size class p as defined by Li et al. (2008). Over the 2008–2010 period, dust emission is 1640 Tg a^{-1} . This includes 1230 Tg a^{-1} from natural sources (S from Ginoux et al. (2001), $C = 0.125 \mu\text{g s}^2 \text{ m}^{-5}$, $u_t = 1 \text{ m s}^{-1}$), similar to the AEROCOM multi-model mean (Huneeus et al., 2011), and 410 Tg a^{-1} from anthropogenic sources (primarily over cropland and pasture from Ginoux et al. (2012b) with updated MODIS collection 6, $C = 0.219 \mu\text{g s}^2 \text{ m}^{-5}$, $u_t = 3 \text{ m s}^{-1}$). Isoprene emissions are calculated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther et al., 2006; Ras-mussen et al., 2012). NO emissions from lightning are calculated as a function of subgrid convection (Horowitz et al., 2003). Differences in the treatment of convection in AM3N result in a greater NO emissions from lightning in AM3N (5.6 Tg N a^{-1}) compared to AM3 (5.2 Tg N a^{-1}), with both estimates within the range of emissions inferred from observations (Martin et al., 2007; Murray et al., 2012). Other natural emissions, including soil NO_x and soil and ocean NH_3 emissions, are described by Donner et al. (2011) and Naik et al. (2013a). Global total emissions of SO_2 , NH_3 , and NO_x are listed in Table 1.

2.3 Sensitivity simulations

Considering the large uncertainty in the simulated nitrate optical depth and surface concentrations, we design a set of sensitivity simulations based on AM3N to characterize the sensitivity of nitrate and sulfate to key uncertainties in chemistry and in NH_3 emissions (Table 2). All simulations are run from 2007 to 2010 using 2007 to spin-up the model. To facilitate the comparison with observations and limit meteorological variability across model configurations, the model horizontal wind is relaxed to 6 hourly values from the National

Centers for Environmental Predictions reanalysis (Kalnay et al., 1996) as described in Lin et al. (2012).

2.3.1 NH₃ emissions

Present-day – The largest source of NH₃ to the atmosphere is agriculture. Unlike anthropogenic emissions of other compounds, which are dominated by fossil fuel emissions, NH₃ emissions exhibit large seasonal variations, which reflect the seasonality of agricultural practices (e.g., fertilizer application) as well as the decrease of NH₃ solubility with temperature (Misselbrook et al., 2004; Pinder et al., 2006; Paulot et al., 2014). The HTAP_v2 inventory includes monthly variations in anthropogenic NH₃ emissions over North America, Europe, and parts of Asia, including Japan and China but excluding India. Anthropogenic emissions of NH₃ previously used in AM3 simulations for ACCMIP and CMIP5 are constant throughout the year (Lamarque et al., 2010). To evaluate the impact of the seasonality of NH₃ emissions on NO₃⁻, we remove all temporal variability in the anthropogenic emissions of NH₃ in simulation AM3N_ns. NH₃ emissions also exhibit diurnal variability (Pinder et al., 2006), which may affect the simulated concentrations of NH₃ and NH₄NO₃ (Zhu et al., 2013; Van Damme et al., 2014b; Schiferl et al., 2014) (Zhu et al., 2013; Van Damme et al., 2014). In AM3N_diu, we impose the NH₃ diurnal cycle of the regional LOTOS (Long Term Ozone Simulation) model globally (Schaap et al., 2004). The ratio between maximum emission (1–2 p.m. local time) and minimum emissions (3–6 a.m.) is 5.7.

2050 – Anthropogenic NH₃ emissions for 2050 are estimated by scaling HTAP_v2 surface anthropogenic NH₃ emissions with national projections from the Representative Concentration Pathway 8.5 (RCP8.5) from 2010 to 2050 (Fig. 1), while keeping natural and biomass burning emissions at their present-day levels. We use the RCP8.5 scenario for 2050 (van Vuuren et al., 2011) as it most closely resembles emissions from regional inventories over the 2000–2010 period (Granier et al., 2011). However, we do not use the RCP8.5 spatial distribution of NH₃ sources, as it differs notably from HTAP_v2 over many source regions such as India, the Nile delta, the Benelux, the California Central Valley, and the Saskatchewan (Fig. 1). These differences may reflect mapping errors for RCP8.5 NH₃

emissions from agriculture as noted by Lamarque et al. (2013). Our approach results in 18% more anthropogenic emissions (60 Tg N a^{-1}) than in RCP8.5 for 2050.

2.3.2 Heterogeneous chemistry

~~Wintertime production of HNO_3 can be produced by the reactive in the northern midlatitudes boundary layer is dominated by the uptake of N_2O_5 , NO_2 , and NO_3 on aerosols (Table S1). In winter, the heterogeneous reaction e.g., Dentener and Crutzen (1993); Tie et al. (2003); Lamsal et al. (2010)). The probability for the heterogeneous conversion of N_2O_5 has been shown to be the largest simulated source of HNO_3 in the boundary layer over the United States (Lamsal et al., 2010). Nitrate formation is expected to be sensitive to this reaction as both NH_4NO_3 and N_2O_5 are more stable under cold conditions. The impact of heterogeneous chemistry on NO_y depends on the choice of reaction probabilities to HNO_3 (γ ; Paulot et al., 2013; Macintyre and Evans, 2010), which remain uncertain (Chang et al., 2011). Field) remains uncertain (Chang et al., 2011) with field and laboratory observations show that N_2O_5 heterogeneous uptake is suppressed showing that it is inhibited by aerosol nitrate and organics (Brown et al., 2009; Brown and Stutz, 2012; Wagner et al., 2013; Gaston et al., 2014), but favored/enhanced by cold temperatures (Griffiths and Anthony Cox, 2009; Wagner et al., 2013). In AM3N, we use $\gamma_{\text{N}_2\text{O}_5} = 0.01$, one order of magnitude less than in AM3 (Mao et al., 2013c) and similar to the global mean value $\gamma_{\text{N}_2\text{O}_5} = 0.02$ derived by Evans and Jacob (2005). In AM3N_nhet To quantify the impact of the heterogeneous production of HNO_3 on aerosol NO_3^- , we neglect the heterogeneous production of HNO_3 via NO_3 , NO_2 , and N_2O_5 aerosol uptake, similar to Bellouin et al. (2011). in AM3N_nhet. We also neglect the productions of HNO_3 by NO_3 and NO_2 reactive uptake, as they may modulate the wintertime budget of NO_y in polluted region (Paulot et al., 2013). Note that previous characterizations of NO_3^- optical depth also neglected the heterogeneous chemistry of oxidized nitrogen (e.g., Bellouin et al. (2011)).~~

We also evaluate the impact of the heterogeneous chemistry on dust, as it is not included in all model (e.g., Pye et al. (2009); Bellouin et al. (2011)). In AM3N_ndust, we neglect the

uptake of HNO_3 , N_2O_5 , NO_3 , H_2SO_4 , and SO_2 on dust, ~~similar to Pye et al. (2009) and Bellouin et al. (2011).~~

2.3.3 Surface removal of fine NO_3^-

In AM3N, the dry deposition of NH_4NO_3 is slow, similar to other fine aerosols. Several field observations have reported steeper vertical gradients and faster deposition velocities (v_d) for NO_3^- than for SO_4^{2-} (Huebert et al., 1988; Wyers and Duyzer, 1997; Van Oss et al., 1998; Rattray and Sievering, 2001; Nemitz et al., 2004; Fowler et al., 2009; Wolff et al., 2010; Barbaro et al., 2015). This difference stems from gradients in temperature, RH, and HNO_3 within the boundary layer, which reduce the stability of NH_4NO_3 near the surface. The volatilization NH_4NO_3 may result in an underestimate of the surface deposition of $\text{TNO}_3 \equiv \text{HNO}_3 + \text{NO}_3^-$ since $v_d(\text{NH}_4\text{NO}_3) \ll v_d(\text{HNO}_3)$. As an upper bound, we assume that the surface removal of fine NO_3^- is limited by turbulent transport by setting $v_d(\text{NO}_3^-) = v_d(\text{HNO}_3)$ in AM3N_fdep.

2.4 Budget and global distribution

Table 1 shows the budgets of SO_4^{2-} , NH_x , and NO_y in AM3 and AM3N for 2010. Here NO_y is defined as the sum of all species that contained oxidized nitrogen. The budgets for all simulations are given in Table S2.

The lifetimes of SO_4^{2-} , NH_x , and NO_y are significantly shorter in AM3N than in AM3. This decrease is driven in part by greater convective removal associated with changes in finer vertical discretization of convective plumes. For instance, the lifetime of SO_4^{2-} with respect to convective removal decreases from 44 to 18 days.

For SO_4^{2-} , the increased effectiveness of convective removal is partly offset by reduction in the removal by snow (Sect. 2.2). The SO_4^{2-} lifetime in both AM3 and AM3N falls within the range of AEROCOM models (3–5.2 days Schulz et al., 2006). Unlike AM3, AM3N includes ammonium in the calculation of cloud pH, which reduces the acidity of cloud droplets and favors the production of SO_4^{2-} via in cloud oxidation of SO_2 by O_3 . The production of

Discussion Paper | Discussion Paper | Discussion Paper

SO_4^{2-} via $\text{SO}_2 + \text{O}_3$ is 4.5 Tg S a^{-1} in AM3N, greater than the recent estimate of Sofen et al. (2011) (1.5 Tg S a^{-1}). This discrepancy may reflect differences in cloud pH and lower H_2O_2 concentrations in AM3N because of faster dry deposition for H_2O_2 and efficient removal of HO_2 via aerosol uptake (Mao et al., 2013a). AM3N does not include production of SO_4^{2-} via aqueous reaction of SO_2 with O_2 catalyzed by iron and manganese or by the oxidation of SO_2 by stabilized Criegee intermediates (Mauldin III et al., 2012). The lifetime of SO_2 is 1.3 days in both AM3 and AM3N, similar to Sofen et al. (2011) and Lee et al. (2011). The overall conversion from SO_2 to SO_4^{2-} (excluding SO_4^{2-} on dust) is reduced compared to AM3 from 50 to 42 % and lower than the AEROCOM multi model mean (62 %).

In AM3, NH_3 uptake by SO_4^{2-} is solely controlled by kinetics without any thermodynamic limit, such that NH_3 burden is small (0.005 TgN) and NH_3 generally limits the formation of NH_4NO_3 . In AM3N, the uptake of NH_3 by SO_4^{2-} aerosols cannot exceed the thermodynamic limit calculated by ISORROPIA, which results in a greater NH_3 burden (0.11 TgN) and favors the production of NH_4NO_3 . The shorter lifetime of NH_x in AM3N than in AM3 reflects the change in the speciation of NH_x and the faster dry deposition of NH_3 relative to NH_4^+ . The lifetime of NH_x in AM3N (2.5 days) is similar to that derived by Xu and Penner (2012) and Hauglustaine et al. (2014) (2.3 days).

AM3N and AM3 differ most strikingly in their simulations of NO_y . The contribution of HNO_3 to the removal of NO_y decreases from 81 % (AM3) to 56 % (AM3N). In contrast, the contribution of aerosols to NO_y removal increases from 2 to 22 %. Recent studies (Hauglustaine et al., 2014; Xu and Penner, 2012) find an even greater contribution of aerosols to the removal of NO_y (> 30 %); this different may reflect the lack of HNO_3 uptake by seasalt in AM3N. Organic nitrogen contributes 10 % of NO_y removal in both AM3 and AM3N. The much lower fraction of NO_y deposited as HNO_3 in AM3N relative to AM3 reflects both the increased production of NH_4NO_3 and the uptake of HNO_3 on dust. The total heterogeneous production of HNO_3 by N_2O_5 (9.7 Tg N a^{-1}), NO_2 (0.6 Tg N a^{-1}), and NO_3^- (0.4 Tg N a^{-1}) uptake on fine aerosols is reduced by 50 % in AM3N relative to AM3. This decrease is primarily driven by reduced reaction probabilities for NO_2 and NO_3 uptake. In contrast, the change of $\gamma_{\text{N}_2\text{O}_5}$ from 0.1 (AM3) to 0.01 (AM3N) reduces the heterogeneous uptake of

N_2O_5 by only 20 % because of the large increase in the sulfate surface area in winter (see Sect. 3). The magnitude of the N_2O_5 source of HNO_3 in AM3N is three times as large as reported by Hauglustaine et al. (2014). This may reflect greater reactive aerosol surface area in AM3N, as N_2O_5 hydrolysis can take place on SO_4^{2-} , BC, OC, and NO_3^- aerosols, while only SO_4^{2-} is considered by Hauglustaine et al. (2014). Reduction in the simulated HNO_3 burden – driven by faster NO_3^- deposition (AM3N_fdep), heterogeneous uptake of HNO_3 on dust (AM3N_ndust), or reduced heterogeneous production of HNO_3 (AM3N_nhet) – increase cloud pH, which favors the oxidation of SO_2 by O_3 (Table S2).

Figure 2 shows the burden of fine NO_3^- , NO_3^- on dust, NH_4^+ , and NH_3 in AM3N. The simulated global burdens fall within the range of previous estimates (Bauer et al., 2007; Feng and Penner, 2007; Pye et al., 2009; Pringle et al., 2010; Bellouin et al., 2011; Xu and Penner, 2012; Hauglustaine et al., 2014) for fine NO_3^- (0.04–0.11 Tg N), NO_3^- on dust (0.07–0.41 Tg N), NH_4^+ (0.21–0.27 Tg N), and NH_3 (0.07–0.29 Tg N). The burden of fine NO_3^- peaks over China where it reaches over 5 mg N m^{-2} , with a secondary maximum over India. Fine NO_3^- burden is also elevated over northern Europe and the US Midwest, where agricultural activities are located close to large sources of oxidized nitrogen. Compared with the fine nitrate distribution from Hauglustaine et al. (2014) for 2000, AM3N simulates greater nitrate burden over Asia but lower burdens over Europe and the US. These differences may reflect different spatial distributions of NH_3 emissions (Fig. 1). AM3N simulates large enhancements in NH_3 column over source regions such as India (where the burden reaches 12 mg m^{-2}), northern China, the Netherlands, and the US Midwest, as supported by satellite observations (Van Damme et al., 2014a). This lends some support to the spatial allocation of anthropogenic NH_3 emissions in HTAP_v2 inventory, although observed enhancements in NH_3 burden over the Po Valley and California are not captured by AM3N.

3 Evaluation

3.1 Bondville

We first evaluate the model against an extensive suite of observations collected at Bondville (40.1° N, 88.4° W, 213 m a.s.l.). Bondville is located in the vicinity of large sources of NH_3 and NO_x , which result in elevated surface NO_3^- concentrations (Fig. 3) and make this site well-suited to evaluate the representation of nitrate aerosols in AM3 and AM3N. Here we compare the model against observations of surface NO_3^- and SO_4^{2-} concentrations (from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network), surface NH_3 concentrations (Ammonia Monitoring Network (AMoN)), SO_4^{2-} , NO_3^- , and NH_4^+ wet deposition (National Atmospheric Deposition Program (NADP)), surface dry aerosol extinction (NOAA Earth System Research Laboratory (ESRL), Delene and Ogren, 2002), and AOD (Aerosol Robotic Network (AERONET)). Vertical profiles of aerosol extinction were also collected by NOAA ESRL Airborne Aerosol Observing (AAO) program from 2006 to 2009 (Esteve et al., 2012; Sheridan et al., 2012). Temperature and humidity profiles are measured twice daily by the ESRL Surface Radiation Budget Network (SURFRAD).

Figure 3 shows the observed (black) and simulated monthly concentrations in surface air (left column) and in precipitated water (right column) for NO_3^- , SO_4^{2-} , and NH_3 (NH_4^+ for wet deposition) for AM3 and different AM3N configurations. Both NO_3^- and NH_3 concentrations are higher year round in AM3N than in AM3, as ISORROPIA enforces thermodynamic limitation to the uptake of NH_3 by SO_4^{2-} . Observations show a spring peak in surface NH_3 concentrations, while both AM3 and AM3N simulate a summer peak. Bondville is surrounded by corn and soybean fields and NH_3 emissions associated with spring fertilizer application may be underestimated (Paulot et al., 2014). In summer, more efficient convective removal of SO_4^{2-} in AM3N reduces the AM3 high bias for SO_4^{2-} surface concentration and low bias for SO_4^{2-} wet deposition. In winter, the low bias for surface SO_4^{2-} concentration in AM3 is reduced as a result of less efficient removal by snow and increased in-cloud oxidation of SO_2 . AM3N_nhet and AM3N_fdep produce greater SO_4^{2-} concentrations in winter than AM3N consistent with increased in-cloud oxidation of SO_2 by O_3 (Table S2).

NO_3^- shows a large positive bias in AM3N in winter ($> 70\%$ in February). This bias can be reduced by either neglecting the heterogeneous production of HNO_3 via NO_2 , NO_3 , and N_2O_5 (AM3N_nhet) or treating the deposition of fine NO_3^- like that of HNO_3 (AM3N_fdep). Conversely, neglecting the seasonality of NH_3 emissions (AM3N_ns), similar to simulations performed for ACCMIP and CMIP5, increases the bias for NO_3^- in winter.

To analyze the factors controlling NH_4NO_3 in the model, we calculate the gas-ratio (GR) at each model time step. GR was first proposed by Ansari and Pandis (1998) to diagnose the sensitivity of NH_4NO_3 to its gas-phase precursors NH_3 and HNO_3 and is defined as:

$$\text{GR} = \frac{[\text{NH}_3] + [\text{NH}_4^+] - 2[\text{SO}_4^{2-}]}{[\text{HNO}_3] + [\text{NO}_3^-]} \quad (2)$$

GR defines three different regimes: (a) $\text{GR} > 1$, in which NH_4NO_3 formation is limited by the availability of HNO_3 , (b) $0 < \text{GR} < 1$, in which NH_4NO_3 is limited by the availability of NH_3 , and (c) $\text{GR} < 0$, in which NH_4NO_3 is inhibited by SO_4^{2-} . We define the degree of limitation of NH_4NO_3 by HNO_3 ($\mathcal{L}(\text{HNO}_3)$) as the fraction of the time when $\text{GR} > 1$. In winter, NH_4NO_3 is most frequently limited by HNO_3 ($\mathcal{L}(\text{HNO}_3) = 78\%$ in AM3N). Figure 4 (bottom panel) shows $\mathcal{L}(\text{HNO}_3)$ binned by NO_3^- concentrations. NH_4NO_3 is most limited by HNO_3 availability at low $[\text{NO}_3^-]$, while NH_3 becomes more limiting at high $[\text{NO}_3^-]$. This suggests that even in an environment that is generally NH_3 -rich with respect to NH_4NO_3 formation, NH_3 emissions modulates NO_3^- production during high- NO_3^- episodes (AM3N_ns).

Figure 4 also shows that AM3N_nhet and AM3N_fdep produce different distributions of daily $[\text{NO}_3^-]$ although they have similar mean monthly $[\text{NO}_3^-]$ (top panel). AM3N_fdep reproduces observations at low NO_3^- concentrations well but underestimates the frequency of high NO_3^- events, when NH_4NO_3 exhibits significant sensitivity to NH_3 . Under these conditions, less volatilization of NH_4NO_3 near the surface is expected as NH_3 is not depleted near the surface like HNO_3 . AM3_nhet $[\text{NO}_3^-]$ is most consistent with observations at high $[\text{NO}_3^-]$, conditions under which N_2O_5 heterogeneous uptake has been observed to be inhibited both in laboratory and field settings (Bertram and Thornton, 2009; Wagner et al., 2013). The ability of AM3N_fdep and AM3N_nhet to capture NO_3^- under different condi-

tions emphasizes the need to represent the dynamic nature of $\gamma(\text{N}_2\text{O}_5)$ and TNO_3 surface removal.

Figure 5 shows the observed and simulated monthly AOD at Bondville. Observed AOD peaks in summer and reaches a minimum in winter. This seasonality is well captured by AM3 (top panel), while AOD in AM3N_fdep_diu (bottom panel) peaks in spring and is biased high in winter and fall. Biases in AOD may be caused by errors in aerosol abundance and speciation but also by errors in aerosol hygroscopic growth. Their relative contribution can be estimated by comparing observed and simulated aerosol extinction profiles, under dry conditions ($\text{RH} < 40\%$) (Delene and Ogren, 2002; Sheridan et al., 2012; Esteve et al., 2012). Figure 6 shows that AM3N overestimates aerosol dry extinction in spring and fall, which suggests that the simulated aerosol abundance is overestimated. This bias may be caused by organic carbon or dust, which contribute over 30% of the simulated aerosol dry extinction throughout the column in spring, summer, and fall (Fig. S1S2 in the Supplement). In winter and summer, AM3N is more consistent with the observed aerosol dry extinction profile than AM3. In particular, AM3 exhibits a low bias in winter and a high bias in summer, consistent with the biases for surface $[\text{SO}_4^{2-}]$ and with the lack of extinction from NO_3^- , the largest contributor to AM3N dry aerosol extinction below 1000 m in winter (Fig. S1S2). The different biases of AM3 and AM3N against AOD and dry extinction in winter and summer suggest errors in the hygroscopic growth of aerosols. This is consistent with comparisons with twice daily soundings of temperature (Fig. S2S3) and relative humidity (Fig. S3S4) over Bondville, which show that AM3N is on average too humid in winter and spring and too dry in summer. In particular, AM3N overestimates the occurrence of high-humidity periods ($\text{RH} > 90\%$, Fig. S4S5), when aerosol hygroscopic growth is especially large. Modeled AOD would be especially sensitive to positive RH biases in winter since AOD winter is primarily controlled by SO_4^{2-} and NO_3^- , which have stronger hygroscopic growth than organic carbon and dust.

3.2 Global evaluation

We broaden our evaluations of AM3 and AM3N using observations of surface $[\text{NO}_3^-]$, $[\text{SO}_4^{2-}]$, and $[\text{NH}_3]$ in the US (IMPROVE and AMoN) and Europe (European Monitoring and Evaluation Programme (EMEP)), $[\text{NH}_x]$ and $[\text{HNO}_3]$ (EMEP), and SO_4^{2-} , NO_3^- , and NH_4^+ concentrations in precipitated water (NADP and EMEP). We compare the model monthly means from 2008 to 2010 to the average monthly observations from 2006 to 2012. For AMoN, we consider all observations (2007–2014) to take advantage of the ongoing expansion of the network. We apply Grubbs' test (Grubbs, 1950) for each station to filter out possible outliers (95 % critical value). Table 3 shows the normalized mean bias (ratio of the mean difference between model and observations to the mean observed value) and the correlation between model and observation for each dataset for AM3, AM3N. Evaluations of all AM3N configurations and seasonal comparisons (Table S3 and Figs. [S5 to S17](#)[S6 to S18](#)) are provided in the Supplement.

Table 3 shows that AM3 and AM3N exhibit similar normalized mean biases for SO_4^{2-} surface concentrations and wet deposition in the US and Europe. However AM3N exhibits better correlation with observations, which reflects a large improvement in the simulated seasonality of surface of SO_4^{2-} (Figs. [S5 and S11](#)[S6 and S12](#)). As previously noted, the improvement in the simulated $[\text{SO}_4^{2-}]$ in AM3N reflects increased removal in summer by convective precipitation, greater production of SO_4^{2-} via $\text{O}_3 + \text{SO}_2$, and less efficient removal by snow in winter. The increased removal of SO_4^{2-} by convective precipitation in AM3N improves the simulation of summer wet deposition in the US, although it remains biased low (Fig. [S8](#)). [Similar improvements to summer time wet deposition are found S9](#). [Increased convective removal of \$\text{HNO}_3\$ and \$\text{NH}_3\$ also reduce the low bias in simulated summer wet deposition for \$\text{NO}_3^-\$ \(-50% to -23%, Fig. S10\) and \$\text{NH}_4^+\$ \(Figs. \[S9 and 46% to -16%\]\(#\), Fig. S10\). Greater in-cloud oxidation of \$\text{SO}_2\$ by ozone in AM3N_fdep and AM3N_nhet \[result in lower-reduces the low\]\(#\) biases for surface \$\[\text{SO}_4^{2-}\]\$ \[than relative to AM3N \\(from -11 % to -5% in the US and -22 % to -13 % in Europe\\)\]\(#\).](#)

Surface $[\text{NO}_3^-]$ is generally overestimated in AM3N, especially over the US (+100%). Recent studies using a range of NH_3 emissions and different representations of aerosol thermodynamics and heterogeneous chemistry also found large positive biases in simulated surface $[\text{NO}_3^-]$ (Heald et al., 2012; Walker et al., 2012; Hauglustaine et al., 2014). Figure 7 shows the annual distribution of $\mathcal{L}(\text{HNO}_3)$ in AM3N. At the surface, NH_4NO_3 formation is primarily limited by the availability of HNO_3 over continental regions, such as Europe, India, or Northern China. Under HNO_3 -limited conditions, our analysis at Bondville suggests that increasing the deposition of TNO_3 (AM3N_fdep) can improve the simulation of surface $[\text{NO}_3^-]$. On a continental basis, we also find that AM3N_fdep_diu better captures surface $[\text{NO}_3^-]$ (+17% bias in the US) and we will focus on this configuration in the following. Note that the diurnal cycle of NH_3 emissions has a small effect impact on the simulated $[\text{NO}_3^-]$ concentration on a continental scale mean surface $[\text{NO}_3^-]$ concentration, but reduces surface $[\text{NH}_3]$ and increases the export of NH_3 and increases its export to the free troposphere. Fig. S20 shows the observed and simulated diurnal cycle of $[\text{NO}_3^-]$ at the YRK SEARCH site. NO_3^- exhibits a pronounced diurnal cycle with a maximum in the early morning and a minimum in the late afternoon (as a result of both thermodynamics and boundary layer height). AM3N and AM3N_diu capture the timing of the diurnal cycle well. As NH_3 emissions peak in the afternoon, the magnitude of the NH_4NO_3 diurnal cycle in AM3N_diu is lower than in AM3N. Higher daytime concentrations of NH_4NO_3 in AM3N_diu suggest that accounting for the diurnal cycle of NH_3 emissions may increase the magnitude of the radiative forcing associated with NH_4NO_3 .

Figure 8 shows the average monthly variation of AOD from 2008 to 2010 over different regions as observed by MODIS (Remer et al., 2008) and MISR (Kahn et al., 2009) and simulated by AM3 and AM3N_fdep_diu. Although AM3 does not exhibit a large bias on a global scale (-0.03 for MODIS and 0.09 for MISR), it fails to capture the seasonality of AOD over most continental regions. Over North America, AOD is biased low in winter and high in summer in AM3, consistent with the biases in surface $[\text{SO}_4^{2-}]$. The spring bias may be exacerbated by insufficient transport of aerosols from Asia. AM3 is biased high over tropical land masses, consistent with insufficient convective removal of aerosols. AM3N_fdep_diu

AOD shows improved correlations with observations over most continental regions (see also Fig. S18S19). The increased AOD in winter and spring can be partly attributed to nitrate optical depth, which accounts for up to ~35% over 30% of AOD over North America.

Following Lee and Adams (2010) and Shindell et al. (2013), we further evaluate the performances of AM3 and AM3N in locations within the top decile of simulated NO_3^- and SO_4^{2-} burden against observations from MODIS, MISR, and AERONET. AM3 AOD is biased high over high SO_4^{2-} regions (+30 to 50%) and low over high NO_3^- regions (-10 to -50%) consistent with the analysis of Shindell et al. (2013). The bias over high SO_4^{2-} regions is greatly reduced in AM3N (<10%), while the model exhibits a high bias against satellite AOD observations (10–20%) but little bias against AERONET observations in high NO_3^- regions. More detailed comparisons with AERONET show that AM3N better captures AOD at high latitude in spring (Fig. S18S19), which lends support to the changes made to the representation of in-cloud sulfate production and wet deposition.

4 Sensitivity of nitrate optical depth

4.1 Present-day emission

Figure 9 compares the contributions of SO_4^{2-} , NO_3^- , OC, BC, dust, and sea salt to the global mean AOD in AM3 and AM3N_fdep_diu, with previous estimates (Shindell et al., 2013; Hauglustaine et al., 2014). Present-day global mean AOD in AM3N_fdep_diu is 0.136, 16% less than in AM3. AOD from all components decrease as a result of more efficient convective removal, with the largest decrease for SO_4^{2-} (-36%). SO_4^{2-} optical depth decreases most from AM3 to AM3N_fdep_diu over tropical regions, while it increases at high latitude, consistent with changes in SO_4^{2-} chemistry and removal. NO_3^- optical depth ranges from 0.0052 (AM3N_nhet) to 0.0078 (AM3N_ndust). Our best estimate is 0.0060 (AM3N_fdep_diu). The different treatment of reactive nitrogen result in similar changes in SO_4^{2-} (0.002) and NO_3^- optical dep (0.003). The range of NO_3^- optical depths derived from AM3N (0.0052–0.0078) encompasses recent estimates by Hauglustaine et al. (2014) and

Bellouin et al. (2011), but differs significantly from the GISS (0.023) and CICERO (0.002) models. Shindell et al. (2013) reported that convective transport of NH_3 to the free troposphere, where NH_4NO_3 is stable and sensitive to NH_3 (Fig. 7), is responsible for the elevated nitrate in the GISS model. [Revisions of the treatment of \$\text{NH}_3\$ convective removal in GISS reduce the simulated present-day \$\text{NO}_3^-\$ optical depth to 0.005 \(S. Bauer, personal communication\).](#)

Shindell et al. (2013) also showed that CICERO may overestimate SO_4^{2-} optical depth, which would inhibit the production of NH_4NO_3 by decreasing the amount of free ammonia ($[\text{NH}_x] - 2[\text{SO}_4^{2-}]$).

Figure 10 shows the annual AM3N nitrate optical depth and its sensitivity to the treatment of NH_3 emissions and NO_3^- chemistry in AM3N. The sensitivity of NO_3^- optical depth to NH_3 seasonality is small and follows the patterns of NH_4NO_3 limitations by NH_3 , with largest sensitivity over the Eastern US and in the outflow of continents. The global sensitivity to NH_3 seasonality is a lower bound, since the seasonality of anthropogenic NH_3 emissions is not represented in important source regions (e.g., India, South America) in HTAPv2. We find greater sensitivity to the diurnal cycle of NH_3 emissions, which is attributed to increased transport of NH_3 into the free troposphere, where NH_4NO_3 is more sensitive to NH_3 (Fig. 7) and more stable because of colder temperature. Decreasing HNO_3 production, either by neglecting its heterogeneous production (AM3N_nhet) or increasing the deposition of NO_3^- (AM3N_fdep) reduce the annual mean NO_3^- optical depth by 25% globally. Regionally, NO_3^- in polluted regions is more sensitive to the heterogeneous production of HNO_3 because of the large aerosol surface area in these regions. Neglecting heterogeneous chemistry on dust results in a large relative increase of NO_3^- optical depth in dusty regions but the increase of the global mean NO_3^- optical depth is small (13%). This muted response is caused by low NH_3 sources near major natural dust sources. A notable exception is anthropogenic dust, whose sources are primarily associated with agriculture (Ginoux et al., 2012a). The proximity of NH_3 and anthropogenic dust sources result in 35% greater sensitivity of NO_3^- optical depth to anthropogenic dust than to natural dust (per kg of dust).

4.2 2050 emissions

Figure 9 shows the contributions of sulfate, nitrate, organic carbon, black carbon, dust, and sea salt to the global mean AOD in AM3 and AM3N_fdep_diu using 2050 emission as described in Sect. 2.2. Sulfate optical depths decrease by 20 % from 2010 to 2050 in both AM3 and AM3N_fdep_diu, similar to Hauglustaine et al. (2014). In all configurations, AM3N produces a ~~modest~~ small increase of the global mean NO_3^- optical depth in response to changes in anthropogenic emissions from 2010 to 2050 (< 30 %). ~~The~~ , with NO_3^- optical depth ranging from 0.0061 (AM3N_fdep) to 0.01 (AM3N_ndust). In AM3N, the conversion rate from NH_3 to NO_3^- (excluding dust) defined as the molar ratio of the fine NO_3^- burden to NH_3 emissions decreases by 10 % from 0.34 day^{-1} to 0.29 day^{-1} . NH_4NO_3 lifetime with respect to deposition increases by 25 % under the 2050 emissions, which suggests that the increase in NO_3^- optical depth in AM3N is driven by reduced sinks rather than increased production. ~~In contrast~~ The response of NO_3^- to changes in anthropogenic emissions is weaker than reported in recent studies. For instance, Hauglustaine et al. (2014) reported a ~~doubling of NO_3^- optical depth from 2000 to~~ NO_3^- optical depth of 0.01 for 2050 under the RCP8.5 scenario as well as an increase in ~~and an increase of~~ the conversion rate from NH_3 to NO_3^- from 0.36 day^{-1} to 0.57 day^{-1} from 2000 to 2050. Using the same anthropogenic emissions, the simulated NO_3^- optical depth in AM3N in 2050 (the configuration closest to that used by Hauglustaine et al. (2014)) is 0.077 and the conversion rate from NH_3 to NO_3^- is 0.33 day^{-1} .

Figure 11 shows that the simulated NO_3^- optical depth decreases in all AM3N configurations over Europe and China, increases over India, and exhibits little change over the US. In all regions SO_2 emissions are projected to decrease. This results in greater sensitivity of NO_3^- optical depth to HNO_3 , which is reflected in the increase of the sensitivity of NO_3^- optical depth to the uptake of HNO_3 by dust and lower sensitivity to temporal variations of NH_3 emissions (seasonality, diurnal cycle). The sensitivity of NO_3^- optical depth to the heterogeneous production of HNO_3 is reduced despite the increased sensitivity of NO_3^- to

HNO_3 . This follows the decrease in aerosol surface area associated with the reduction of the SO_4^{2-} burden.

The simulated changes in NO_3^- optical depth from present-day to 2050 over the US, China, and Europe are consistent with surface NH_4NO_3 limitations. For instance, surface NH_4NO_3 is primarily limited by HNO_3 in Europe and China and the decrease of NO_3^- optical depth is driven by the reduction of NO emissions. In these regions, AM3N simulates similar NO_3^- optical depth using different anthropogenic emissions of NH_3 for 2050, which is also consistent with the reduced sensitivity to NH_3 emissions. However, surface NH_4NO_3 limitation patterns cannot explain the increase of NO_3^- optical depth over India.

Figure 12 shows that the NO_3^- burden is projected to shift equatorward in the Northern Hemisphere in response to changes in anthropogenic emission from present-day to 2050. This shift is less pronounced when using anthropogenic NH_3 emissions from NH_4NO_3 increases in the free troposphere but decreases near the surface, a vertical redistribution also noted by Hauglustaine et al. (2014). The decrease of surface NO_3^- in the midlatitudes is primarily driven by lower NO emission. Large differences in the seasonality, spatial distribution, and magnitude of anthropogenic NH_3 emissions in RCP8.5 (dotted line) and scaled HTAPv2 for 2050 because of lower NH_3 emissions over India. The lower NH_3 emissions in RCP8.5 over India also result in opposite trends for NO_3^- optical depth in this region (Fig. 11). have little impact on the simulated NO_3^- burden (<10%), which reflects the diminishing sensitivity of surface NH_4NO_3 to NH_3 . However, NO_3^- remains sensitive to NH_3 in the free troposphere, where it can persist longer than in the boundary layer thanks to lower temperature. The solid line in Figure 12 also shows that the meridional redistribution of NO_3^- is associated with an increase of shows the free tropospheric burden of NO_3^- , while NO_3^- near impact of lower convective removal of NH_3 (achieved by neglecting the impact of pH on NH_3 solubility) on the NO_3^- burden. Over the 2008–2010 period, this results in a 40% increase of the NO_3^- burden with a near quadrupling in the tropics, qualitatively matching the results of Hauglustaine et al. (2014) in this region. In 2050, the impact is much more pronounced and the simulated burden is more than twice as large as in 2010, a similar response to that found by Hauglustaine et al. (2014). Note that increasing NH_3 emissions

from biomass burning and distributing these emissions vertically (Naik et al., 2013a) also increases tropical NO_3^- (not shown) but to a much lower degree (<50%). These results suggest that differences in the transport of NH_3 to the surface decreases. A similar vertical redistribution of NO_3^- was also noted by Hauglustaine et al. (2014). In the free troposphere, NH_4NO_3 formation is limited by NH_3 (Fig. 7), which suggests that the increase of the NO_3^- burden in AM3N from present-day to 2050 is primarily driven by an increase of the NH_3 flux to the free troposphere associated with greater tropical emissions. The lower tropical NO_3^- free troposphere across models contribute to the variability in the projected NO_3^- burden and optical depth. Such differences may arise from differences in the parameterizations of convection (Folkens et al., 2006) as suggested by the much lower tropical NO_3^- burden in AM3N compared to the estimate of Hauglustaine et al. (2014) likely results from a lower flux of NH_3 to the free troposphere in AM3N than in LMDz-INCA model (Hauglustaine et al., 2014) but also from changes in the tropical circulation in response to climate change (e.g., from different biomass burning injection heights, convective schemes). Our study suggests that changes in this flux due to changes in emission and climate will play a large role in determining future NO_3^- optical depth. (Ma et al. (2012)).

5 Conclusions

We have developed a new configuration of AM3 (AM3N) with revised treatment of nitrate and sulfate chemistry and deposition. We showed that AM3N better captures observed AOD than a configuration of AM3 similar to that used for ACCMIP and CMIP5. AM3N overestimates surface NO_3^- concentration especially in the US. This bias may reflect neglect in AM3N of the dynamic nature of N_2O_5 uptake and near-surface volatilization of NH_4NO_3 .

We have evaluated the sensitivity of NO_3^- optical depth to poorly constrained aspects of NO_3^- chemistry (heterogeneous production of HNO_3 , uptake of HNO_3 by natural and anthropogenic dust, surface removal of NH_4NO_3) and NH_3 emissions (diurnal cycle, seasonality). Globally, the formation of NH_4NO_3 is more limited by HNO_3 than NH_3 , such that NO_3^- optical depth is more sensitive to the representation of the heterogeneous chemistry

of HNO_3 than to uncertainties in NH_3 emissions. Simulated present-day NO_3^- optical depth ranges from 0.0054 to 0.0082, depending on the treatment of reactive nitrogen. Differences in the treatment of reactive nitrogen alone are unlikely to account for the large spread in estimates of present-day NO_3^- optical depth (0.0023–0.025).

We have examined the response of simulated NO_3^- optical depth to projected changes in anthropogenic emissions from 2010 to 2050 in RCP8.5. Depending on the configuration of AM3N, NO_3^- optical depth varies from 0.0061 to 0.01 in 2050. The increase of NO_3^- (< 30%) under present-day climate conditions. This weak response reflects increasing limitation of NH_4NO_3 production by HNO_3 relative to 2008–2010 is partly inhibited by greater limitation of NH_4NO_3 production by HNO_3 at the surface due to lower NO emissions, more efficient removal of HNO_3 by dust, and a large decrease in the heterogeneous production of HNO_3 by N_2O_5 (associated with lower aerosol surface area). Increasing limitation of NH_4NO_3 formation by HNO_3 suggests that the global trends of NH_3 emissions may not be a suitable proxy to estimate the future NO_3^- radiative effect (Heald and Spracklen, 2015). In the Northern Hemisphere, the NO_3^- burden is projected to shift southward, following the increase of tropical NH_3 emissions and the decrease of NO emissions in the midlatitudes. This shift is associated with an increase of the NO_3^- burden in the free troposphere, where NH_4NO_3 formation is limited by NH_3 . We suggest that the convective transport of NH_3 and its response to climate change (not considered here) play an important role in modulating the response of NO_3^- optical depth to changes in anthropogenic emissions. The complexity of the response of NO_3^- to changes in surface processes, chemistry, and convection indicates that the global trends of NH_3 emissions may not be a suitable proxy to estimate the future forcing from NO_3^- aerosols (Heald and Spracklen, 2015).

We conclude that in addition to improvements to NH_3 emission inventories (e.g., bidirectional exchange of NH_3 (Zhu et al., 2015)), observational constraints on the processes controlling the flux of NH_3 into the tropical vertical redistribution of NH_3 and the response of NO_3^- to NH_3 in the free troposphere (e.g., magnitude of NH_3 emis-

sions in the tropics (Aneja et al., 2012; Whitburn et al., 2015), biomass burning injection height (Val Martin et al., 2010), ~~convective transport of NH_3~~ [transport and removal of \$\text{NH}_3\$ in convective updrafts, heterogeneous chemistry on dust and sensitivity studies to characterize their response to climate change](#) are needed to improve estimates of present and future NO_3^- - NO_3^- optical depth.

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Table 1. Simulated budget of SO₄, NH_x, and NO_y in 2010.

	AM3	AM3N
SO₄*		
Production (Tg S a ⁻¹)	37.3	33.1
OH	10.4	7.7
H ₂ O ₂	26.7	16.2
O ₃	0.1	4.5
dust	0.0	1.9
Loss (Tg S a ⁻¹)	37.4	33.3
Dry deposition	4.7	4.6
SO ₄	4.7	3.8
SO ₄ on dust	0.0	0.8
Wet deposition	32.7	28.7
SO ₄	32.7	27.5
SO ₄ on dust	0.0	1.1
Lifetime (days)	4.9	3.8
NH_x		
NH ₃ emission (Tg N a ⁻¹) [†]	54.5	54.5
Loss (Tg N a ⁻¹)	54.8	55.0
Dry deposition	14.4	23.5
NH ₄ ⁺	14.3	3.6
NH ₃	0.1	19.9
Wet deposition	40.4	30.7
NH ₄ ⁺	39.4	20.7
NH ₃	1.0	10.1
Gas oxidation	0.0	0.8
Lifetime (days)	5.5	2.5
NO_y		
NO emission (Tg N a ⁻¹)	51.4	51.8
Loss (Tg N a ⁻¹)	51.3	51.0
Dry deposition	25.4	23.1
HNO ₃	18.3	10.7
NO ₃ on dust	0.0	3.4
NH ₄ NO ₃	0.7	0.8
Organic nitrogen	3.9	4.0
Wet deposition	25.6	27.6
HNO ₃	23.4	17.8
NO ₃ on dust	0.0	3.7
NH ₄ NO ₃	0.5	3.5
Organic nitrogen	1.7	2.6
Lifetime (days)	22.7	13.4

* SO₂ emissions are 74.0 Tg S a⁻¹ including 16.0 Tg S a⁻¹ from DMS oxidation.

[†] including 39.9 Tg N a⁻¹ from anthropogenic sources, 3.9 Tg N a⁻¹ from biomass burning, and 10.7 Tg N a⁻¹ from natural sources (primarily from the ocean)

Table 2. Configurations of AM3N used in this study.

	Temporal variation of NH ₃ emissions	Heterogeneous chemistry on dust	Heterogeneous production of HNO ₃	Dry deposition of NH ₄ NO ₃
AM3N	Monthly	Yes	Yes	SO ₄ ²⁻
AM3N_fdep	Monthly	Yes	Yes	HNO ₃
AM3N_diu	Monthly+Diurnal	Yes	Yes	SO ₄ ²⁻
AM3N_ns	No	Yes	Yes	SO ₄ ²⁻
AM3N_nhet	Monthly	Yes	No	SO ₄ ²⁻
AM3N_ndust	Monthly	No	Yes	SO ₄ ²⁻
AM3N_fdep_diu	Monthly+Diurnal	Yes	Yes	HNO ₃

Table 3. Normalized mean bias and correlation coefficient (in parentheses) of monthly model results vs. measurements of surface concentrations of SO_4^{2-} , NO_3^- and HNO_3 , NH_3 and NH_x , concentrations of SO_4^{2-} , NH_4^+ , and NO_3^- in rain, and total aerosol optical depth at 550 nm from AERONET, MISR and MODIS.^a

		AM3	AM3N	AM3N_fdep_diu
SO₄				
Aerosol	US	0.07 (0.81)	-0.11 (0.89)	-0.06 (0.89)
	Europe	-0.43 (0.24)	-0.22 (0.62)	-0.13 (0.64)
Wet deposition				
	US	0.00 (0.42)	-0.07 (0.59)	-0.08 (0.57)
	Europe	-0.18 (0.53)	-0.32 (0.57)	-0.32 (0.53)
NO₃				
Aerosol	US	-0.61 (0.64)	1.03 (0.64)	0.17 (0.65)
	Europe	-0.78 (0.62)	0.32 (0.62)	-0.30 (0.58)
Gas + Aerosol				
	Europe	-0.18 (0.61)	0.17 (0.75)	-0.29 (0.57)
Wet deposition				
	US	0.14 (0.33)	0.23 (0.52)	0.11 (0.54)
	Europe	-0.32 (0.57)	-0.29 (0.54)	-0.39 (0.54)
NH_x				
Gas	US	-0.75 (0.50)	-0.10 (0.54)	-0.22 (0.53)
	Europe	-0.65 (0.48)	0.23 (0.54)	0.17 (0.50)
Gas + aerosol				
	Europe	0.69 (0.66)	0.18 (0.64)	0.02 (0.64)
Wet deposition				
	US	-0.20 (0.50)	-0.20 (0.69)	-0.15 (0.69)
	Europe	-0.23 (0.52)	-0.36 (0.58)	-0.32 (0.58)
AOD				
MODIS				
	World	0.09 (0.57)	-0.08 (0.68)	-0.08 (0.68)
	high NO ₃	-0.15 (0.83)	0.11 (0.87)	0.09 (0.87)
	high SO ₄	0.57 (0.83)	0.06 (0.87)	0.06 (0.87)
MISR				
	World	-0.03 (0.53)	-0.16 (0.59)	-0.16 (0.59)
	high NO ₃	-0.12 (0.84)	0.21 (0.87)	0.18 (0.87)
	high SO ₄	0.54 (0.86)	0.12 (0.88)	0.12 (0.88)
AERONET				
	World	-0.03 (0.72)	-0.10 (0.82)	-0.11 (0.82)
	high NO ₃	-0.50 (0.87)	-0.01 (0.76)	-0.07 (0.70)
	high SO ₄	0.33 (0.47)	-0.10 (0.74)	-0.10 (0.71)

^a Model results are averaged from 2008 to 2010, while we use observations from 2006 to 2012, except for MODIS and MISR (2008–2010) and NH₃ observations in the US (2007–2014). Detailed seasonal comparisons are presented in the Supplement.

Figure 1. Average annual emissions of NH_3 for 2010 (top row) and 2050 (bottom row) based on anthropogenic NH_3 emissions from HTAP_v2 (left column) and from RCP8.5 (right column). Non anthropogenic emissions (including biomass burning) are the same in all scenarios. Total annual emissions are indicated inset.

Figure 2. Annual mean burden of NO_3^- , NO_3^- on dust, NH_4^+ , and NH_3 in mg N m^{-2} in AM3N from 2008 to 2010. Global burdens are indicated inset. The location of the Bondville site is indicated by a black cross [in the upper left panel](#).

Figure 3. Observed (black) and simulated monthly concentrations of NO_3^- , SO_4^{2-} , and NH_3 at Bondville (40.1°N , 88.4°W) in surface air (left panel) and precipitated water (right panel). Observations are averaged from the 2006 to 2012, while model output is from 2008 to 2010. The vertical bars denote one standard deviation of the mean monthly observations. The different model sensitivity experiments are described in Table 2.

Figure 4. Observed and simulated distribution of daily NO_3^- concentration at Bondville (40.1°N , 88.4°W) in winter (top panel) from 2006 to 2012 (observations) and 2008 to 2010 (model). The degree of HNO_3 limitation for NH_4NO_3 formation ($\text{GR} > 1$) is shown in the bottom panel. The different model sensitivity experiments are described in Table 2.

Figure 5. Observed and simulated aerosol optical depth at 550 nm at Bondville (40.1° N, 88.4° W) in AM3 and AM3N_fdep_diu. Observations (black crosses) are averaged from 2006 to 2012 and the thin vertical black bars denote one standard deviation of the mean. Thick color bars show the simulated optical depth of SO_4^{2-} (red), NO_3^- (cyan), OC (green), BC (purple), dust (brown), and sea salt (blue) for AM3N_fdep_diu (2008–2010 average).

Figure 6. Mean seasonal observed (black dots) and simulated surface and vertical profiles of aerosol dry extinction at Bondville (40.1° N, 88.4° W). The vertical profile show the average of all observations by the Airborne Aerosol Observatory from 2006 to 2009 collected during daytime (10 a.m.–4 p.m. local time). Surface observations reflect the average of all daytime observations at the ESRL BND station from 2006 to 2012 with no local pollution. Model is averaged for daytime from 2008 to 2010. Horizontal lines show the 25th to 75th percentiles of observed dry aerosol extinctions. Dry extinctions are reported at standard temperature and pressure (273.15 K, 1 atm). We multiply the modeled nitrate extinction by 0.8 to account for the evaporation of ammonium nitrate in the nephelometer (Bergin et al., 1997). The different model sensitivity experiments are described in Table 2.

Figure 7. Simulated degree of limitation of NH_4NO_3 formation by HNO_3 ($\text{GR} > 1$) weighted by NH_4NO_3 concentration at different pressure levels in AM3N for 2010.

Figure 8. Observed and simulated monthly AOD at 550 nm in different regions averaged over the 2008–2010 period. Circles show observations from MODIS (open circles) and MISR (filled circles). The solid and dash black line show the AOD simulated by AM3N_fdep_diu and AM3 respectively. We also show the simulated optical depths of sulfate (red), nitrate (cyan), dust (brown), organic carbon (green), black carbon (purple), and sea salt (blue) in AM3N_fdep_diu. The model is sampled to match the the location and time of valid measurements by both MODIS and MISR in each region. Correlations between simulated and observed AOD are shown inset for AM3N_fdep_diu and AM3 (in parenthesis).

Figure 9. Contribution of different aerosol types to the global mean annual aerosol optical depth at 550 nm in AM3, AM3N, and other climate models considering NO_3^- aerosol. ~~Note that (all-sky except clear-sky AOD is used for the GISS model).~~ AM3 and AM3N AOD are representative of 2010 conditions, while other models reflect 2000 conditions. The range of SO_4^{2-} , NO_3^- , and total AOD across AM3N configurations are shown by red, light blue, and black horizontal bars respectively. Note that changes in the parameterization of NH_3 convective removal reduce the simulated NO_3^- optical depth by GISS to 0.005 (S. Bauer, personal communication).

Figure 10. Annual mean NO_3^- optical depth at 550 nm in AM3N (top left panel) and its relative sensitivity to the treatment of NH_3 emissions, NO_3^- production, and loss in % for 2008–2010 conditions. The change in NO_3^- optical depth relative to AM3N is indicated in the bottom left for each configuration. The sensitivity is only shown in regions, where NO_3^- optical depth is greater than 0.005.

Figure 11. Nitrate optical depth at 550 nm over the United States, Europe, China, and India for 2008–2010 (white bars) and 2050 (black bars) anthropogenic emissions for different configurations of AM3N. The thin red bar indicates the nitrate optical depth calculated using RCP8.5 2050 NH_3 emissions in AM3N. The relative changes between 2008–2010 and 2050 in NO_3^- optical depth and surface emissions of NH_3 , SO_2 , and NO are indicated for each region.

Figure 12. Annual zonal mean distribution of NO_3^- in AM3N with present-day 2008–2010 anthropogenic emissions (top) and 2050 anthropogenic emissions (from RCP8.5 except for NH_3 , see text). The blue, green, red, and cyan regions denote the NO_3^- burden located above 800 hPa, between 600 and 800 hPa, between 400 and 600 hPa, and below 400 hPa, with the global fraction–partial burden in each pressure range indicated inset. The black solid line in the top panel indicates the 2000 annual zonal mean NO_3^- burden simulated by Hauglustaine et al. (2014). The using AM3N fdep diu (dash black line), using AM3N with anthropogenic emissions from RCP8.5 for NH_3 (dotted line), using AM3N ndust (dash dot line), and using AM3N with reduced convective removal of NH_3 (solid line) are also shown. The white circles in the bottom-top panel indicate the 2000 annual zonal mean NO_3^- burden simulated by AM3N using 2050 anthropogenic emissions from RCP8.5 for all compounds. Hauglustaine et al. (2014)