

Interactive comment on “Modelling the impacts of ammonia emissions reductions on North American air quality” by P. A. Makar et al.

P. A. Makar et al.

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We thank both reviewers for their insights on the work to date, and their suggestions, which we think will improve the paper.

Reviewer 2:

Re: "I don't think that the paper gives a clear answer to how the different components of PM respond to the change in ammonia emissions. Does PM decrease because ammonium nitrate, sulfate or other components decrease?", and on page S1098, "On p. 5374...A more clear way to to present the results might be through separate tile plots for the change in PM_{2.5} sulfate, nitrate and ammonium (all in ug/m³). "

A very good point, and echoed by the other reviewer. The original work was funded under a Canadian government initiative to investigate the impact of ammonia emissions

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Discussion Paper



changes on PM_{2.5}. The latter is the quantity with recommended limits for exposure, etc., hence we focused on the PM_{2.5} concentrations (and chemical analysis to explain their changes) as opposed to the speciated values. The speciated PM_{2.5} was included in the model outputs, however, and figures have been created for them. Looking at the paper with fresh eyes, we agree - including the speciated inorganic components for each season helps the explanation that comes later in the conceptual model section. Three additional figures (revised manuscript figure numbers 6,7,8) have been added to the manuscript, following immediately after the original Figure 5 for total average PM_{2.5} change, for the seasonal average change in PM_{2.5} ammonium, sulphate, and nitrate. Two additional paragraphs of text have been added to explain the figures (starting "The seasonal change in PM_{2.5} ammonium...") in the revised manuscript. As expected from our conceptual model, most of the reductions in PM_{2.5} mass result from reductions in the ammonium and nitrate components of PM_{2.5}. The sulphate response was interesting; depending on season and location, the PM_{2.5}-sulphate could either increase or decrease. Additional model diagnostics have allowed us to determine the cause of these variations; competition between the different equilibrium and oxidation pathways for sulphur in the aqueous phase chemistry portion of the model. We've also included quantitative mass composition changes for the 98th and 2nd percentile PM_{2.5} mass changes at the monitoring station locations (described below).

Re: "Ammonia limitation...What is not clear from the presentation is what is being limited by the lack of ammonia"

Answer: the formation of inorganic particulate matter, and the text has been extensively modified to clarify this and the terminology has been made more specific. In the revised version, we've started from Blanchard et al. (1999)'s definition of ammonia limitation, then noted that this definition is appropriate to bulk mode chemistry while the ambient atmosphere tends to have sulphate and the base cations separated into fine and coarse modes, respectively. This in turn is used to give rise to a modified definition, of strongly and weakly ammonia limited environments, the former for situa-

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tions in which there is insufficient total ammonium to charge-balance the sulphate, and the latter in which there is insufficient excess total ammonium, subsequent to sulphate charge balancing, to charge balance the difference between the remaining cations and anions. The essential idea here is to note that total ammonia may have an impact on particle formation even when the base cations are present, due to the size segregation of sulphate from those cations. Further impacts of total ammonia on particle formation will depend on the relative amounts of the other anions and cations, hence the "weakly ammonia limited" definition. We're well aware of the complexities of the system (cf. phase diagram associated with the ammonium-sulfate-nitrate system, Figure 1, Makar, P.A., Bouchet, V.S., and Nenes, A., Inorganic Chemistry Calculations using HETV : A Vectorized Solver for the SO₄–NO₃–NH₄⁺ system based on the ISORROPIA Algorithms, Atmos. Environ. (37): 2279-2294, 2003, and the competition between coarse and fine mode chemistry for the available nitrate, cf. Makar, P.A., Wiebe, H.A., Staebler, R.M., Li, S.M. and Anlauf, K. Measurement and modeling of particulate nitrate formation. J. Geophys. Res. (D) (103, (D11)): 13095-13110, 1998.). We've explicitly defined strongly versus weakly ammonia-limited regimes where appropriate in the text.

Re: "The authors could divide their thinking in two steps: what is the response of gas-aerosol chemistry to changes in ammonia, and second, given those changes ...what is the effect on the lifetime and concentrations of the different species given different removal rates...discussed at length in several papers that the authors do not reference - although the focus is on changes in sulfate rather than ammonia, similar concepts would apply..."

We have revised the text making use of the references, in a number of places. We've also revised the conceptual model description to make more quantitative use of the new new and existing figures.

Re: "...in Fig. 7 and 8, the changes of 5 $\mu\text{g}/\text{m}^3$ at the high end of the distributions are huge, far exceeding the median and probably accounting for much of the total PM_{2.5}. Some explanation of whether these large changes are possible, and under

what conditions they result, would help. Likewise, although increases in PM_{2.5} are rare, can the authors provide a theoretical basis why this would happen?"

The changes are "possible" to the extent that the model is right, and the model is predicting them. We have added two new figures (12 and 13 in the revised manuscript) which show the speciation of the change in PM_{2.5} mass for the 98th and 2nd percentile mass changes of the original manuscript's station-location PM-2.5 mass change figures (figures 10 and 11 in the revised manuscript). These figures show that the large mass decreases associated with reductions in ammonia emissions (98th percentile mass decreases) result from reductions in particle ammonium and nitrate mass, while the small increases that sometimes occur (2nd percentile mass decreases) are often associated with increases in particle sulphate. An additional paragraph describing these new figures has been added to the manuscript. Our original hypothesis for the slight increases in PM_{2.5} mass in the 2nd percentile in the on-line version of the response to the reviewers has been largely replaced by our subsequent analysis of the sulphate portion of the mass (see above discussion of new figures 6 through 8): this describes the increases in PM_{2.5} mass observed in the eastern USA. We've also added a reference to Tsimpidi et al (2007): they noted that a 50% reduction in ammonia had no impact on the sulphate in the summer, in contrast, our results suggest that the sulphate concentration may increase slightly, due to the pH and temperature dependence of HSO₃-(aq) oxidation to SO₄²⁻(aq) within the aqueous phase. Outside of the Eastern USA, our hypothesis for the mass increases from the on-line response to the reviewers has been put forward: these may be due to upwind locations impacting a downwind measurement site location. The non-sulphate increases in mass at some locations are linked to particle nitrate. The growth in the base case may be sufficiently rapid that the particles tend to be lost to deposition prior to their arrival at the measurement site. Reducing the ammonia emissions en-route to the measurement site may reduce the in-transit depositional losses.

"In Fig. 3, why do we see these seasonal and spatial patterns in ammonia/sulfate?"

S2603

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Interactive Discussion

Discussion Paper



Upon reading over our original on-line response, we realized that there is a much simpler explanation: the variations are due to (1) seasonal variations in the ammonia emissions (Figure 2, which shows the lowest ammonia emissions occurring in the winter, the highest in the spring, summer and fall), and (2) increased levels of sulphate production in the summer due to higher oxidation of SO₂ to SO₄ in the gas and aqueous phases. The low winter ammonia emissions help reduce the ratio in the winter; the high summer sulphate production helps reduce the ratio in the summer. The net result is Figure 3, with summer and winter having lower TA/TS ratios than the other two seasons. This explanation has been added to the text relating to Figure 3.

Specific comments: - The use of PM_{2.5}-NH₄ has been changed to p-NH₄; - Figure captions: we tried modifying the existing bitmaps to remove the text blocks at the top of the page, but this did not improve the images. The alternative would be to regenerate all of the images from scratch, with just, e.g. "MAM" on the top of each figure. The existing in-panel text includes MAM as well as supplementary information: we're not sure that this really improves the figures, after giving it a try. So the figures are unchanged in that regard relative to the original manuscript - Horizontal size of figure 8 (figure 11, revised manuscript) We've changed the view for this page to landscape in our original submission to improve readability, and will request a similar rotation for the final version in the journal. - Reference to figures 7 and 8 in the conclusions has been modified as requested.

Reviewer 1:

1. "In figures 7 and 8...times when the impacts are much larger. This is an important point: at the time when the PM_{2.5} is most sensitive to ammonia emissions, does the model accurately represent the nitrate, sulfate and meteorological conditions when compared with the data from the measurement stations? This is critical to building confidence in the results."

As noted above in the response to Reviewer 2, we've done more analysis of the ex-

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trema of the figures to determine the chemical conditions under which the largest increases and decreases in the PM_{2.5} are occurring in the model (see figures 6,7,8 and 12 and 13 in the revised manuscript). The large decreases in PM_{2.5} are shown to be due to decreases in the ammonium and nitrate portion of the particle mass. Table 3 in the original manuscript shows that the model is biased low in its base-case predictions for both ammonium and nitrate. Evaluating the model for specific stations for these cases doesn't make sense, though, due to the sparseness of the measurement data: the stations measure 24 hour averages, spaced out once every 3 to 6 days, depending on the network. Figures 7 and 8 in the original manuscript (10 and 11 in the revised manuscript) are showing the distributions from hourly model differences. We'd have to be lucky to capture one of the extreme events at one of the stations, and it would be averaged out in the measurement record if we did. However, by extracting the model composition at the extrema we are able to say which species are controlling the differences, and relate these species back to the average model performance in the tables. We've added some caveats in the conclusions regarding the model predictions and limitations. One of the most significant of these is the lack of coarse-mode chemistry in the model: given that a large part of the mass reduction is in p-NO₃, which, as described in the revised manuscript, will also depend on the other base cations present in the ambient atmosphere, the model may be showing a greater sensitivity to ammonium nitrate formation than occurs in the ambient atmosphere. We've therefore stated in the revised conclusions and the abstract that the changes depicted with the version of the model used here should be considered upper limits.

2. "I strongly agree with reviewer 2 that the concept of "ammonia-limitation" as described in the introduction is not sufficient for explaining the change in PM_{2.5} due to a change in ammonia emissions".

This section has been completely re-written, starting from Blanchard et al,'s 1999 description of ammonia limitation, and discussing its limitations due to the size segregation of sulphate into fine and base cations into coarse mode particles. This in turn

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leads to a better description of the need for a revised definition that includes "strongly" and "weakly" ammonia limited environments, the former for situations in which there is insufficient total ammonium to charge-balance the sulphate, and the latter in which there is insufficient excess total ammonium, subsequent to sulphate charge balancing, to charge balance the difference between the remaining cations and anions. The essential idea here is to note that total ammonia may have an impact on particle formation even when the base cations are present, due to the size segregation of sulphate from those cations. Further impacts of total ammonia on particle formation will depend on the relative amounts of the other anions and cations, hence the "weakly ammonia limited" definition. We've also mentioned in the conclusions the potential impacts of the lack of base cation chemistry on our results in a number of locations throughout the text.

"...the metrics plotted in Figures 3, 9, 10, 11, and 12 are not as helpful to understanding the changes as simply plotting the change in sulfate, nitrate, and ammonium aerosol"

We have added the requested plots (Figures 6,7,8) in the revised manuscript, as well as 98th and 2nd percentile mass composition change diagrams (Figures 12 and 13) that accompany the station location PM2.5 mass change histograms of Figures 10 and 11. The text in the manuscript has been revised to include descriptions of these figures.

3. "The conceptual model in Figure 16 is a useful construct, but on in the way it is currently presented. My sense is that the authors are working to explain why the PM2.5 sensitivity in the industrial Midwest of the US and southern Canada is larger than most locations on the continent. This is a valuable goal, but to be useful, some important details are necessary."

While the region identified by the reviewer is certainly one place the conceptual model could apply, other regions could be used as well. Our intent here was not to be quantitative, but to give a qualitative description of the processes that may lead to the model results. At any given instant in time the actual atmosphere will be more complicated (the

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conceptual model is built along a single Lagrangian trajectory, for example, whereas the 3D atmosphere will have the potential for horizontal mixing and local reversals of wind direction). The conceptual model is intended to be a sufficiently generic, idealized, description of the relevant chemistry, to allow its application as an aid in understanding the chemical processes, as opposed to a detailed mass budget exercise for a specific case. With regards to such an exercise, the devil would be in the details: arbitrary decisions would have to be made, such as deciding on the boundaries of the three regions, and deciding on the circumstances under which fluxes are to be calculated (e.g. if the winds reverse direction along some part of the two boundaries between the domains, are the fluxes not calculated?). As noted in the response to the other reviewer, we've revised the conceptual analysis section with reference to the new delta-particle sulfate, nitrate and ammonium plots (Figures 6-8, 12, 13, revised manuscript), as well as making use of the references provided to compare to other work elsewhere in the manuscript. Rather than use font size changes, we've made use of changes to the colours of the fonts in order to show the differences between the base case and the scenario simulations. HNO₃ gas deposition has been included in the revised diagram.

4. "The authors select a single sensitivity analysis of reducing Canadian beef cattle emissions by 50%. The impact of this change on PM_{2.5} is very small in magnitude and limited in spatial extent, especially compared to the 30% decrease in all ammonia sources. Furthermore, the locations impacted by this sensitivity test are not areas identified with a critical load. I am puzzled then why the authors conclude that further research on Canadian cattle emissions are of higher priority than other sources."

As was noted in the original manuscript, the purpose of the additional sensitivity analysis (beyond the 30% agricultural ammonia emission reduction sensitivity analysis) was to examine the extent to which uncertainties in the Canadian emissions data could affect the model results. The point, which may not have been clear from the accompanying figure, is that the impact of the uncertainty from this single specific source type is the same as the first sensitivity test of a 30% reduction in agricultural ammonia

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sources, for some parts of Canada. Hence the conclusion that further improvements to the ammonia emissions data are needed. Figure 16 (revised manuscript figure 22) has been replaced with an expanded view 8 panel figure focusing on the given region and comparing the 50% reduction in beef cattle emissions to the same expanded view taken from the 30% across the board reduction of Figure 5.

Re: "very small in magnitude and limited in spatial extent"

The region affected by the change are the Canadian Prairie provinces (the areal extent of the affected region is similar to that of the state of Texas), with a population of several million. The fields depicted, like the others in the original 4-panel figures, are 3 month averages. The previous discussion in the paper showed that the main effect of emissions reductions will occur in short term but high concentration episodes that will be much larger in magnitude than averages. Particulate matter is known to have human health impacts: critical load exceedance estimates are not the only impact of ammonia emissions changes.

"These sources are likely to have the same uncertainty and greater impact"

Our choice of the beef cattle emissions for a sensitivity run was based on recommendations from the team of researchers who built the new Canadian inventory. The sensitivity run showed that in the given region, the uncertainty in the locally dominant emissions source of ammonia was sufficient to be equivalent to a 30% reduction in ammonia emissions. Hence our conclusion that further work is needed on this emissions sector, since the uncertainty in the emissions input is equivalent to a large reduction in across-the-board ammonia emissions.

5. "Ammonia emissions are uncertain in their magnitude and timing. For comparison with other work, it would be very helpful to list the magnitude of the ammonia emissions used in this work, divided by month and source category."

We have provided this information in tables in an appendix at the end of the revised

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manuscript. Note that the tables add 14 pages to the length of the manuscript due to the variety of sources.

6. "The change in critical load exceedances in Section 4.2.5 should be explained in more detail. From reading the text and looking at Figure 15, the 30% reduction in NH₃ caused at most a 10% reduction in the magnitude of the exceedance. Is this because most of the exceedance is due to sulfate?"

No. Critical load exceedances were calculated separately for sulfate alone, and were found to have a minimal impact (only two grid squares changed color scale, for the equivalent figure as 15a for S alone). The reviewer's estimate of the maximum reduction being 10% is incorrect: for example, Figure 15b shows that southern Ontario would have a reduction > 150 eq/hectare/yr, while the same location in Figure 15a shows individual base-case grid squares of > 100 to < 700 eq/ha/year (i.e. anywhere from 100% to 21%).

"Does this mean that currently, such emission reductions are not necessary?"

Yes - the current rate of ecosystem damage (primarily due to sulfur) is such that reductions in ammonia emissions will not slow the rate of ecosystem damage, as of yet. However, once the ongoing sulfur-induced ecosystem damage is sufficient, ammonia emissions reductions would be one means of slowing the rate of additional ecosystem damage after that point in time.

"At current deposition rates, how many years until this occurs?"

The expected time scale for this to occur in Canada is uncertain, based on the available references, but on the order of decades: an exact figure is not available; the sources we consulted suggested a range of response times.

Specific Comments:

P5732@L20: "possibly trans-oceanic consequences downwind".

Full Screen / Esc

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Interactive Discussion

Discussion Paper



The effect is sufficiently small (max 0.25 ug/m³, in spring season over the ocean), that we've decided to remove the part of the sentence mentioning trans-oceanic consequences.

P5375@L17-22: "Several recent studies have examined the impact of ammonia emissions on PM_{2.5}"

The Pinder et al and Tsimpidi references have been included and briefly discussed in the revised manuscript.

P5376@L21: What fraction of the total ammonia/ammonium emissions are as particle ammonium?

Double-checking the split factors used in the model, we found that the particle ammonium emissions are actually zero " the text has been corrected.

P5379@L13: What are the biogenic emissions of ammonia?

A good example comparison may be found in Table 7.7 of the most recent IPCC report (AR4, 2007). Soils under natural vegetation emit a small amount of ammonia, as do the oceans, as a result of bacterial activity and decomposition processes. These amounts are very small relative to the amount due to agriculture, on a global basis. The sentence referred to in the original manuscript, however, refers to the emissions of all species used in the model, not specifically the ammonia emissions. This has been clarified in the revised text, and the given reference added.

P5382@L19-26: "This manuscript frequently points out that the response to a change in ammonia emissions is non-linear with respect to the concentrations of the inorganic anions. How serious are these modeling errors at the times and locations where the model predicts the largest sensitivity to ammonia emissions, and what are the implications for interpreting the modeling results?"

The time resolution of the available monitoring network data makes it very difficult to assess this - see the above discussion on individual station observations. We

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have included a discussion of model uncertainties in the conclusions of the revised manuscript, in addition to the existing error analysis comparing the model results to observation stations

P5387@L1: "due to chemistry: a shift in chemical" perhaps "due to aerosol thermodynamics: a shift in phase" is more specific.

The page number is 5388 in our copy: The line will be changed as recommended.

P5390@L24: "This point that nitrogen deposition decreases because near-source p-NO₃ decreases seems unusual to me... It would be helpful to have a table of the total deposition of NH₃, HNO₃, p-NO₃, and p-NH₄, separated by wet and dry deposition, before and after the emission change, or simply the % change due to the emission change."

A number of corrections were made to the text here: most of the change in deposited nitrogen (75%) is from decreases in aqueous-phase ammonium (which includes both washout of p-NH₄ and NH₄⁺ resulting from uptake into cloud water and subsequent rainout, and is not just p-NH₄ as stated in the original text). Dry deposition of NH₃(g) makes up another 10% of the total nitrogen deposited, and the remaining 10% of the total N deposited is from all forms of nitrate (not just p-NO₃, as was stated in the original text. The revised manuscript has been corrected.

P5394@L6: "predicted decrease in median hourly PM_{2.5} mass of less than or equal to 1 ug m⁻³" Where is the decrease equal to 1 ug m⁻³? All of the monitors have median changes less than 1 ug m⁻³. It would be more helpful to describe when and where the largest changes occur. "

We're glad the reviewer caught this: that should be "less than", not "less than or equal to", with reference to the figures presented.

Technical comments: "Figure 8 is extremely difficult to read. Is it possible to make these plots wider or exclude some of the less relevant data? "

The strength of the figures is that they show all of the stations for the given monitoring network. In the context of the electronic form of the journal, one can always expand the view of the figure to examine portions of it in more detail. In our revised submission, the figures have been converted to landscape format (in the submitted pdf). We'll see if the journal will allow a larger/wider format for the figure (another option would be to split the two figures into four; e.g. stations west versus east of Kentucky).

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 5371, 2009.

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9, S2600–S2612, 2009

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