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Atmospheric Chemistry and Physics Discussions

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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This is a draft/interactive response to the reviewer's comments, a more formal response will follow as per ACPD/ACP procedures. We're hoping that this draft may lead to feedback on the approaches we plan to take in modifying the manuscript according to the reviewers'; suggestions.

We thank both reviewers for their insights on the work to date, and their suggestions, which we think will improve the paper. Some draft responses (read these as what we plan to do):

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 PM2.5 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 changes on PM2.5. The latter is the quantity with recommended limits for exposure, etc., hence we focused on the PM2.5 concentrations (and chemical analysis to explain their changes) as opposed to the speciated values. The speciated PM2.5 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 would help the explanation that comes later in the conceptual model section. Three additional figures will therefore be added, as recommended by the reviewer, and the text will be modified to include quantitative comparisons based on the figures.

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 will be modified to clarify this and the terminology will be made more specific. The essential idea was to try to simplify the interactions between ammonia/um and the sulphate and nitrate species in the same sense that "NOx limitation"; and "VOC limitation" are used to describe different reaction regimes for ozone production. 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 SO42–NO3–NH4+ system based on the ISORROPIA Algorithms, Atmos. Environ. (37): 2279-2294, 2003). As noted in the original ACPD manuscript, when there is insufficient ammonia/um to charge balance the anions, then the system is "ammonia-limited" in that changes to the total ammonia will directly affect the amount of particulate mass. If ammonia moles in excess of the sum of the anion moles are available, then changes to the ammonia concentration (unless reductions sufficient to be below the charge balance) will have little impact on the particulate matter mass. We went a bit further in the original manuscript to suggest "strongly" versus "weakly" ammonia limited environments;

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the former for the phase space where total ammonia to total sulphate moles (TA/TS) is < 2, the latter for TA/TS > 2. The sulphuric acid, ammonium bisulphate, letovicite, ammonium sulphate region of the phase diagram in the above reference has been defined as "strongly ammonia limited", in that reductions in ammonia emissions in this set of chemical regimes will always reduce the PM2.5 mass sulphate-ammonium-nitrate system. For TA/TS > 2, (where ammonium nitrate formation may occur), reductions in PM2.5 will also depend on the amount of total nitrate available, hence the phrase "weakly ammonia limited". The text in the revised manuscript will be clarified to include the above description. As well, we'll explicitly define strongly versus weakly ammonia-limited regimes throughout the text, noting that the distinction between the two helps define a local chemical regime (portion of the phase space; the type of chemistry happening locally) as opposed to necessarily describing how local changes in ammonia will affect changes in PM2.5. e.g. in a weakly ammonia limited regime, decreases in ammonia will decrease the PM2.5 if the total ammonia in excess of that required to charge balance sulphate is less than or equal to the moles of total nitrate present.

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...". $>>$ This was the intent of the conceptual model presented in the original manuscript. We'll rework that description making use of the references mentioned.

Re: "in Fig. 7 and 8, the changes of 5 ug/m3 at the high end of the distributions are huge, far exceeding the median and probably accounting for much of the total PM2.5. Some explanation of whether these large changes are possible, and under what conditions they result, would help. Likewise, although increases in PM2.5 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.

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The idea of checking it out in more detail is a good one: for the maxima and minima of these figures, we'll pull out the model species in the base case and emissions reduction scenario, and compare the chemical regimes. With regards to the local increases in PM2.5, a hypothesis: these may be due to upwind locations impacting a downwind measurement site location. For example, in Figure 7 and 8 of the original manuscript, two stations with largest magnitude of these infrequent increases are Saturna (an island between Vancouver Island and the mainland along the Canadian south-west coast) and Simcoe (near the shore of Lake Simcoe). Both of these sites are impacted by long range transport of sulphate and nitrate from urban sources (from Vancouver/Seattle and Detroit, respectively). The local agricultural ammonia emissions sources in both cases are known to be large. The increase in downwind PM2.5 with a reduction in ammonia emissions may result from a decrease in depositional loss en-route to the measurement site. That is, the growth is sufficiently rapid in the base-case 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. With regards to the phase diagram mentioned above, this may indicate that the reduction in ammonia has resulted in a shift of chemical regime to one in which less growth occurs en-route to the observation site. The composition extraction mentioned above should allow us to evaluate this hypothesis.

Re: "In Fig. 3, why do we see these seasonal and spatial patterns in ammonia/sulfate?" >> A large part of this is likely a combination of the temperature dependence of the ammonium nitrate equilibria with ammonia and nitric acid gases, and the seasonal dependence of the ammonia emissions. The ammonium nitrate (both solid and aqueous ions) side of the equilibrium is strongly favoured at low temperatures, hence in what we've called "weakly ammonia limited" regions there will tend to be more of the total ammonia in the form of particle ammonium nitrate. The loss of ammonium to deposition is less than the loss of ammonia due to deposition - hence the total ammonium concentration would tend to be higher in colder climates since its net lifetime is longer. Hence the total ammonium to sulphate ratio would tend to be higher in colder months.

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However, the emissions (Fig. 2) show that the winter emissions are much less than the other seasons. In summary: Summer TA/TS is low since the temperatures are higher and less ammonia is in the particle phase. Winter TA/TS is low since the emissions of ammonia are very low. Spring and fall TA/TS are higher since the ammonia emissions are relatively high, and the temperatures are sufficiently low that more of the ammonia is in the particle phase, hence has a longer atmospheric lifetime. This should be observable in the new speciated PM figures to be added in the revised manuscript.

Specific comments: use of PM2.5-NH4 will be changed to p-NH4; Figure captions will be corrected as suggested. We'll try to get ACP to expand the horizontal scale for Figure 8. Reference to figures 7 and 8 will be 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 PM2.5 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'll do some more analysis of the extrema of the figures to determine the chemical conditions under which the largest increases and decreases in the PM2.5 are occurring in the model. Tables 3 and 4 in the existing manuscript describe the model performance. 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 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 will at least be able to say which species are controlling the differences, and relate these species back to the average model performance in the tables. 2. "I strongly agree with reviewer 2 that the concept of "ammonia-limitation" as

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described in the introduction is not sufficient for explaining the change in PM2.5 due to a change in ammonia emissions". >> As noted in the response to the other reviewer, the essential idea was to try to simplify the interactions between ammonia/um and the sulphate and nitrate species in the same sense that "NOx limitation" and "VOC limitation" are used to describe different reaction regimes for ozone production. 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 SO42–NO3–NH4+ system based on the ISORROPIA Algorithms, Atmos. Environ. (37): 2279-2294, 2003). As noted in the original manuscript, when there is insufficient ammonia/um to charge balance the anions, then the system is "ammonia-limited" in that changes to the total ammonia will directly affect the amount of particulate mass. If ammonia moles in excess of the sum of the anion moles are available, then changes to the ammonia concentration (unless reductions sufficient to be below the charge balance) will have little impact on the particulate matter mass. We went a bit further in the original manuscript to suggest "strongly" versus "weakly" ammonia limited environments; the former for cases where total ammonia to total sulphate moles (TA/TS) is $<$ 2, the latter for TA/TS $>$ 2. The sulphuric acid, ammonium bisulphate, letovicite, ammonium sulphate region of the phase diagram in the above reference has been defined as "strongly ammonia limited", in that reductions in ammonia emissions in this set of chemical regimes will always reduce the PM2.5 mass sulphate-ammonium-nitrate system. For TA/TS $>$ 2, (where ammonium nitrate formation may occur), reductions in PM2.5 will also depend on the amount of total nitrate available, hence the phrase "weakly ammonia limited". The text in the revised manuscript will be clarified to include the above description. As well, we'll explicitly define strongly versus weakly ammonia-limited regimes throughout the text, noting that the distinction between the two helps define a local chemical regime (portion of the phase space; the type of chemistry happening locally) as opposed to necessarily describing how local changes in ammonia will affect changes in PM2.5. e.g. in a weakly ammonia limited regime, decreases in ammonia will decrease

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the PM2.5 if the total ammonia in excess of that required to charge balance sulphate is less than or equal to the moles of total nitrate present. "...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" >>As noted in the response to the other reviewer, the these fields will be plotted in the revised manuscript, and the text revised to take this into account. 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 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'll revise this section with reference to the new delta-particle sulfate, nitrate and ammonium plots, as well as making use of the references provided to compare to other work. We'll also follow the reviewer's suggestion with arrows (an alternative might be (+) and (-) symbols), as opposed to the font size changes, and correct the HNO3 gas deposition in the diagram 4. "The authors select a single sensitivity analysis of reducing Canadian beef

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cattle emissions by 50%. The impact of this change on PM2.5 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." >> The existing text will be modified to clarify this point. Figure 16 will be 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 is the southern half of the Canadian province of Alberta, with a population of several million. The field depicted, like the others in the 4-panel figures, is a 3 month average. 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. Re:"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 test 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'll provide this information in a table, or reference the work where it may be found: the issue here is that the emissions processing system used to spatially and temporally allocate the emissions (SMOKE) includes temporary files that can be used to deter-

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mine source amounts, but we're not sure (until we go through the files generated two years in the past) whether these will be of sufficient detail. The alternative will be to reference the documents describing the emissions inventory. 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%). re: "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 on the order of decades - a more exact figure and a reference to some of the latest estimates for this will be provided in the revised manuscript. We will also clarify the description of critical load exceedances to incorporate the above discussion.

Reviewer 1 Specific comments: P5732@L20: "possibly trans-oceanic consequences downwind". >> The effect is sufficiently small (max 0.25 ug/m3, in spring season over the ocean), that we've decided to remove the sentence. P5375@L17-22: "Several recent studies have examined the impact of ammonia emissions on PM2.5" >> The given references will be included and briefly discussed in the revised manuscript. P5376@L21: "What fraction of the total ammonia/ammonium emissions are as particle ammonium?" >> A very small amount (fraction of a percent) - insignificant by mass rel-

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ative to the gas-phase emissions. Any particles emitted would be immediately subject to thermodynamic equilibrium, however. The sentence will be clarified. 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. This reference will be added to the discussion in the paper. 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.

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." >> The table will be created and compared to figures with the nitrate deposition composition.

P5394@L6: "predicted decrease in median hourly PM2.5 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.

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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. 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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