Response to Reviewers 1 & 3

Reviewer comments are in italic font, and author responses start with [CW]

Response to Reviewer # 1

Thank you for your thorough review of our paper. We have taken into account all of your suggestions, and it has greatly improved the revised manuscript. Please see below for item-by-item responses to each comment.

Citations of non-available papers are given (cited as "this issue" but non available in the special issue). This stands for example for description of measurements (Wentworth et al), deposition of N and S (Makar et al), parameterizations (Akingunola et al), fire emissions (Zhang et al.).

[CW] This is one of the difficulties with having a number of linked papers being submitted at the same time. We have modified the text to only refer to the papers which have been submitted at the time these revisions have been carried out. Some of these citations have been submitted to the special issue (e.g., Makar, Zhang), and should appear on ACPD soon. When they are not (e.g., Akingunola, Wentworth), the references were removed.

NH3 concentrations are really low in the region of study and the reader may wonder why this region is worth studying, in the light of what is written in the introduction, (NH3 may be harmful for air, water quality, or ecosystem and human health). A sentence or 2 on the relevancy of studying regions where concentrations remain low for the moment would be useful.

[CW] While the NH3 concentrations are relatively low (0.6 ppbv), the impact on atmospheric chemistry may be large, via the formation of particle ammonium nitrate and ammonium sulphate, and through acidifying emissions. It has been shown that ecosystems in Northern Alberta and Saskatchewan are sensitive to nitrogen deposition, and that dry deposition of NH3 and NO2 dominate the near-source N deposition, while wet deposition of ammonium ions dominate the long-range transport ammonia budget (Makar et al 2017, this ACPD issue). The amount of gaseous ammonia in the atmosphere is thus crucial for accurate estimation of the deposition of nitrogen in the region. It has also been shown the emissions of other pollutants from the AOSR are comparable to that of a city (e.g., Liggio et al, *Nature*, 534, 91-94, 2016), thus, even where NH3 concentrations are relatively low, it is important to understand if the OS facilities are causing critical levels of NH3, and if not, if any other kinds of sources (e.g., fires, re-emissions) are. This justification has been added to the revised manuscript (lines 63-69).

Some citations are given for satellite measurements of NH3 concentrations at a large scale, but nothing is said about orders of magnitude. Do the model results of this study match with previous satellite measurements? More values of ambient concentrations should be cited.

[CW] The model results of this study match the magnitude of NH3 given by TES in the Shephard et al (2015) paper. The model values in southern part of our domain also match the high end of values reported by NH3 reports (e.g., ref AMoN report for NH3 levels in agricultural and other regions). We have added this additional discussion to the revised manuscript (lines 80-85, 484-486).
Clarisse et al (2009) and Van Damme et al (2014) report on IASI NH3 global measurements – however these are total columns, thus harder to compare to the CrIS profiles and surface concentrations in ppbv. Zhu et al (2013) also use TES, but their measurements focus on the U.S., thus would be redundant and less relevant study than the Shephard et al (2015) study mentioned above. Similarly Beer et al (2008) also use TES and focus on the U.S. and China. Low NH3

observations were also shown in the Supplemental Information of Kharol et al (2017, GRL), but these were for Alaska and Yukon, and from the CrIS satellite, so would be redundant to mention.

This is also true for bidirectional exchanges: some papers are cited, but only as a list of papers, and no quantified values are given to be compared with what is found in this study. The papers should be cited with precise examples of measured fluxes is the same area or in regions with the same type of ecosystems.

[CW] Zhu et al (2015) found with GEOS-Chem that the re-emission of NH3 added around 1 ppbv to NH3 concentrations globally in the month of July in North America (but decreased concentrations during the cooler months), and that bidirectional flux did not increase NH4 wet deposition. Wichink Kruit et al (2010) found something more similar to us in their 2007 European study, which was a decrease in NH3 deposition, but an increase in wet NH4 deposition. We have added this information, along with some quantitative comparisons to other sources in the literature (e.g., Kharol et al (2017); Behera et al (2013), into our discussion in Section 5 (lines 603-607, 631-362, and 644-652).

A meteorological description of the site would be useful all along the study. Indeed, emissions have their impact on NH3 concentrations, but wind speed, humidity, temperature have also a significant impact on exchange fluxes. This part of dynamical interpretation on deposition fluxes is missing.

[CW] The meteorological description and discussion of the region and its impact on bidirectional flux is now added to the revised manuscript, in Sections 2.2 (bidi description), 3.1 (surface site description), Section 5.2 (effect on deposition), and the conclusions.

A discussion about why the addition of bidirectional flux is so important in improving the model is missing in terms of processes. The discussion is only about ppb and %, and not about processes.

[CW] Section 2.2 described the bidirectional flux process, and where the temperature dependency comes in (e.g., equation 3), but a lot of the dynamics/meteorology was hidden in the resistance terms (R_i). We have added additional discussion about how meteorology plays a role to this section (lines 218-230) as well as when discussing deposition in the results section (Section 5.2, lines 639-641). We also added a better explanation of the process at the beginning of Section 2.2, lines 174-179.

2- Does the paper present novel concepts, ideas, tools, or data?: not really, bidirectional exchanges of NH3 is already known to be important, tools and data have already been used in Shepard et al (2015)

[CW] We would argue that our paper presents novel tools (GEM-MACH-Bidi) and data (CrIS observations, and FireWorks emissions): The Shephard et al (2015) study used TES satellite observations and a version of GEM-MACH that did not have bidirectional flux or forest fire emissions. Whereas, in our study, we have used new CrIS satellite observations and the GEM-MACH-Bidi model, which is a new version of GEM-MACH that has the bidirectional flux scheme (previous GEM-MACH versions had no NH3 re-emission process). GEM-MACH-Bidi is the new tool, which we evaluate with cutting edge NH3 satellite data (from CrIS). We note that ours is the first study to use the CrIS satellite observations of NH3 for model evaluation. Our study is also the first to use the FireWorks forest fire emissions at such high spatial resolution. We have updated the abstract, introduction, and conclusion to emphasize these novel features of our study so that they are clearer for the reader.

11- Is the language fluent and precise? Not always

[CW] The language was made more precise in the revised manuscript, where the reviewer mentioned problems in the detailed comments.

13- Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? Yes, mentioned in specific comments. 14- Are the number and quality of references appropriate? Not always

[CW] When specific comments were made relating to these issues, they were addressed in the responses below.

Specific comments
Line 42: As you write that NH3 is a contaminant, precise in what order of concentration it has negative effects.

[CW] While NH3 is poisonous if inhaled in great quantities, these are much greater than found in the atmosphere. For example, there is an Alberta Ambient Air Quality Objective for NH3, which is 2000 ppbv 1-hour average; the basis for this is odour http://aep.alberta.ca/air/legislation/ambient-air-quality-objectives/documents/AAQO-Summary-Jun29-2017.pdf , but this is not relevant to the outdoor atmospheric conditions we are talking about in our study.
The reason NH3 was listed as a Criteria Air Contaminant is because of its secondary effects as a PM precursor (Environment Canada, 2001), as discussed in this paragraph of the original manuscript. Therefore, one cannot say what ambient concentration of NH3 would cause negative health effects because it is complicated by the atmospheric conditions (meteorological and concentrations of other chemical species) for PM formation. Thus, there is no federal Canadian Ambient Air Quality Standard for NH3, however, there is for PM2.5 (in Canada, the PM2.5 guideline is 28 ug/m3, 24 hour average).
Another negative affect of NH3 is its contribution to nitrogen deposition (discussed in the Makar et al companion paper) – wet ammonium ion deposition dominates N deposition in the regions hundreds of km downwind from the anthropogenic sources, for example. The amount of nitrogen deposition which may cause an exceedance of critical loads is highly dependent on the local ecosystem characteristics, and varies by over 3 orders of magnitude in the region examined here. Thus, no particular NH3 concentration can be cited to cause an exceedance in critical loads.

Precise somewhere in your introduction that despite negative effects of high concentrations, low concentration regions are also worth studying.

[CW] It is still important to study this region because the modelled background NH3 must be correct in order to understand the relative impacts of the oil sands operations, and because even a small amount may cause a critical load exceedance for deposition to sensitive terrestrial and wetland ecosystems. This explanation was added to the introduction, lines 63-69.

Line 44: Modeling provides: : :: this could be true if inventories are correct and with fine resolution, which is hardly feasible in most models. Remove this first part of the sentence.

[CW] Done.

Line 55: reformulate your sentence because reading “the AOSR is a large source of air” is a bit weird.

[CW] Done.

Line 58: why are NH3 concentrations so low, despite local pollution?

[CW] The anthropogenic emissions of the AOSR take place in a relatively small region compared to all of "northern Alberta and Saskatchewan", which is where we've said that NH3 concentrations are low. We were basically saying that the area surrounding the AOSR has very few sources of NH3, and as a result, background concentrations of NH3 in that area are low (b/c of little population and lack of agriculture, compared to the southern part of the province. The low background concentration puts into context the ~0.5 ppbv model bias that existed before the addition of the missing sources. We've reformulated those sentences in the revised manuscript (lines 63-65) to better get that point across.

Line 61: give mean concentrations of cited agricultural areas.

[CW] In our reformulation, this reference is removed.

Line 66: give values of the fraction of deposited NH3 compared to NO2 and HNO3.

[CW] Since our references were based on atmospheric concentrations rather than deposition measurements, we have revised the wording here, and given ratios of NH3 to other N gases in the air. See lines 72-76 in the revised manuscript.

Line 114: precise what species are used from the inventories.

[CW] List of 25 species was added to the manuscript (lines 128-131).

Line 121: A word about the importance of carefully design stack parameters would be useful to understand why this part is so important for your study.

[CW] On line 128 of the original manuscript we mentioned that ill-designed stack parameters resulted in "erroneous short term plume events", causing "NH3 levels up to 2 orders of magnitude higher than ground observations", which should be explanation enough for the importance of stack parameters. However, we have added a note in the revised manuscript (line 148) that this stack is in the AOSR, thus it is important to get right for our study.

Line 167: give reference values of realistic NH3 concentrations consistent with findings from the literature, and explain why you use low end values.

[CW] We referenced annual AMoN values for "realistic NH3 concentrations" (line 209). The explanation of why the low end values were chosen was already given – to get realistic NH3 concentrations compared to observations.

Line 191: what do you mean by "major point emissions?"

[CW] An explanation of area and major point emissions has been added to the Emissions Section (Sec 2.1), lines 137-140.

Line 220: what is ECCC?

[CW] Acronym is now defined upon first use.

Line 259: you mention +/- 15% of uncertainty for measurements, with a mean measured value of 0.63 ppb (line 59). The model/measurements bias is 0.3-0.85 for bidi, what is the real impact on modeled concentration? What is the range of possible concentration? Is the measured concentration included in this range?

[CW] For the AMS-13 model evaluation (a single site heavily influenced by local anthropogenic sources), a 15% error on the measured 0.63 ppbv average is only 0.0945 ppbv, giving the range of 0.536 ppbv to 0.725 ppbv for the average measured concentrations there. The median model bias of the base case is -0.35 ppbv, meaning that the model reports only 0.28 ppbv NH_3 in that area – well below the bottom of the measurement range. The bidi model had a +0.3ppbv bias, meaning that the model reports 0.96 ppbv in that area, which is well above the range in the measurement average. Taking the standard deviation of the model biases at that specific location into account, and they all overlap with the measurements (e.g., the vertical range in the whiskers in Figure 5). However, we see in Figure 6, that the real improvements come in the form of better correlation and slopes with the bidi and fire+bidi models. We have not added any new text, as the existing text covers all of this.

Line 299: Figure 3 should not be placed here. It is only used later in the text, and should be included before figure 9. Furthermore, if placed here, it is not understandable why these three dates are chosen (not explained in the caption).

[CW] We have removed the reference to Figure 3 early on, and moved the figure to the appropriate place in the results/discussion.

Line 324: You mention fig 5 and then you talk about fig 4. Place fig 5 after fig 4 and give a description on interpretation of it.

[CW] That sentence about Fig 5 is removed, and figure 5 discussion is now appropriately placed.

Line 326: what are the background times?

[CW] Changed to "when NH_3 concentrations are relatively low (< 0.5 ppbv in the base model)".

In figure 4, NH_3 is in ppb, but NH_4^+, NO_3^- and SO_4^{2-} are not in ppb. Please correct the caption

[CW] Done.

Line 335: what is the increase of concentration with the influence of a local plume? 0.5 ppb seems to be very very low, and more included in the measurement noise than in a local pollution signal.

[CW] The 0.5 ppbv reference is in regard to the base model (line 334 of original manuscript) -- not in the measurements. The base model has very very low background concentrations (which we are correcting in this work), thus any time the base model goes above 0.5 ppbv, we can assume a nearby source, such as a plume. Note that even the measurements did not exceed 3 ppbv, and had a mean of 0.6 ppbv during this time period. Thus 0.5 ppbv is not low in relation to that. Discussion of these concentrations can be found in lines 387-392 of the revised manuscript.

Line 337: 0.08 ppb is less than the 15% measurement uncertainty. Is it really significant?

[CW] No, you are correct, it isn't. Therefore, we have removed the discussion about removing the plume influence to see "better" results, since they are not significantly better.

Line 339: R=0.1 and 0.4. Are these coefficients significant? Could you give a significance (p-value) of your correlation calculation everywhere it is necessary?

[CW] We have done a paired t-test on the AMS13 surface NH_3 data, and found that none of the three model simulations can be considered statistically indistinguishable from the measurements at the hourly time scale ($t>1$, $p<0.05$), although the weekly-averaged bidi simulation comes close, with $t=1.9$, $p=0.15$ (for model to be considered the same as the measurements, t should be <1, and p should be >0.05). These statistics are now included in Table 2 and discussed in the revised manuscript. Since the AMS13 results are just for a single gridpoint at the surface (where local variability due to point sources makes getting a good match closer to sources difficult), we have also added statistics for the aircraft and satellite results as well. The satellite results cover a much larger domain (all of Alberta and Saskatchewan, and throughout the troposphere).

For the particulate species, none of the correlations are significant either. Most air quality models do not model PM species well, and this is an area of on-going study.

Line 340: Fig 6a: what is the unit of NH3 concentration?

[CW] Fig 6a has units of ppbv in the axis labels, and the slope of the model/measurement line is unitless. Nothing changed.

Line 368: SO_4^{2-} *is influenced by anthropogenic emissions, why not by fire emissions?*

[CW] Added “and fire emissions” here.

Line 375: Why did you choose this precise flight? By the way, it would be useful to give some average values of meteorological conditions when describing the area of study (mean temperature, humidity, rainfall, wind speed, etc: : : all parameters that have a possible influence on NH3 concentration)

[CW] This flight was chosen as an example because this flight sampled mainly background NH3 concentrations (rather than facility plumes), and it is the modelled background NH3 that this study aims to improve (lines 448-450 in revised manuscript). Meteorological conditions for the AOSR were added to Section 3.1, lines 317-329.

Line 376: can you explain why fire+bidi does not improve the results compared to bidi?

[CW] In Figure 7c and d, there is very little difference in concentrations because the flight did not pass through a fire plume. We have added this explanation to the revised manuscript (lines 456-457).

Line 404: Figure 3 is used in this paragraph. It should appear in the text at this time, and not before.

[CW] Done: Fig. 3 of the original manuscript, is now Fig. 8 in the revised manuscript.

Line 430: specify at the lowest level.

[CW] Done.

Line 446: remove “that” before the fire+bidi model

[CW] Done.

Line 451: You suppose that the conversion of NH3 to NH4+ is underestimated: did you have a look at the NH4+ pool in that case?

[CW] Unfortunately, there were no NH4+ measurements in that region to compare to.

Line 453 to 459: this explanation is very confused. Please rephrase.

[CW] It has been rephrased and put into point form, making clear which part of the discussion is for which explanation (a, b, c) of the bias (lines 549-569).

Line 507: this sentence is not useful. Obviously if bidirectional parameterization is used it will balance deposition with emission and not increase deposition fluxes.

[CW] We agree with the reviewer that using a bidirectional scheme can only decrease net deposition for NH3 compared to a traditional unidirectional deposition scheme if all the other model components/parameters remain the same, e.g., the Zhang et al. (2010) bidirectional scheme versus the unidirectional scheme of Zhang et al. (2003), because the former was built on the later. However, the original unidirectional scheme used in our model was not exactly the same as in Zhang et al. (2003), but a hybrid of Wesely (1989) (for stomatal uptake) and Zhang et al. (2003) (for non-stomatal uptake). Thus, we cannot completely exclude the possibility that the new bidirectional scheme might produce higher deposition under certain circumstances without a model validation.

Line 517 and elsewhere: the unit for the flux is not appropriate. Please homogenize throughout the paragraph and use preferably ngN.m^{-2}.s^{-1}.

[CW] Units of moles/m2/day are now consistently used throughout.

Lines 584 and 587 use another unit which is not a flux unit. In this paragraph needs bibliography values need to be included for equivalent ecosystem or region.

[CW] Do you mean lines 582-583, which talked about % contributions to atmospheric concentrations? No numerical values were written on lines 584 and 587. However, we had included references to reported deposition and discussed them in Section 5.2, lines 524-531 of the original manuscript, using appropriate units. The revised manuscript has flux in moles/m^2/day throughout.

Figure 12 and 13 are redundant.

[CW] Figure 12-14 were removed, and replaced with a new Figure 12 that is the total NHx deposition.

Figure 13 is not necessary in my opinion.

[CW] Figure 12-14 were removed, and replaced with a new Figure 12 that is the total NHx deposition.

Line 539: again this sentence is not useful. Obviously wet deposition is only deposition. Again flux units are not correct and should be homogenized.

[CW] Any mention of μmoles/m2 should have been moles/m^2/day. This was corrected in the revised manuscript. Also, most of the discussion is now about total NHx deposition, rather than of wet and dry deposition discussed separately.

Line 550: how do wet deposition fluxes compare with literature?

[CW] It has been difficult to find relevant wet deposition fluxes in the literature, as many of those studies report on ammonium concentrations in rainwater without giving the precipitation flux. Or they report on locations that are not appropriate to compare to Alberta/Saskatchewan (e..g, Murano et al, 1998 found average values of 1E-4 moles/m2/day in Japan). We have however, added a couple of references, including a technical report in the United States, which reported about 2E-5 moles/m2/day average in the U.S. (lines 668-671). Our results are in between the values reported in those two studies.

Line 570-571: this sentence has already been written above. The conclusion should mention the possible influence of meteorological conditions on NH3 concentration, as well as in the text.

[CW] The fact that the NH3 emission factors need to be revisited for further model improvements is an important conclusion of our study, and that is why we have highlighted it again in our conclusion. The meteorological discussion of the region and its impact on bidirectional flux is now added to the revised manuscript, in Sections 2.2 (bidi description), 3.1 (surface site description), Section 5.2 (effect on deposition), and the conclusions.

Line 574: “miniscule”: please quantify.

[CW] 0.02 ug/m3 for each. This was added to the sentence (lines 698-696).

__Technical comments__
Line 16: remove , aftertime period.

[CW] Done.

Line 108: write covers instead of covering, twice in the line.

[CW] Done.

Line 109: remove “And” at the end of the line.

[CW] Done.

Line 117: remove (before Zhang and put (before 2017.

[CW] Done.

Line 163: replace “in” by “from” before Wen et al.

[CW] Done.

Line 228: Time period “from”

[CW] Done.

Line 296: a verb is missing in the sentence.

[CW] The verb was “compute”, but it should have been part of the list. We have fixed the sentence.

Line 321: include “to” after compared.

[CW] Done.

Line 352: remove italics for “should”, same line 488 for “total” and line 507 for “more”

[CW] Done.

Line 454: a) is missing after 10c

[CW] Done.

Line 493: problem with the sentence, please rephrase

[CW] Done.

Line 507 and 509: remove , after 11.

[CW] Done.

Line 526: replace x by times

[CW] Done.

Response to Reviewer #3

Thank you for your thorough review of our paper. We have taken into account all of your suggestions, and it has greatly improved the manuscript. Please see below for item-by-item responses to each comment (reviewer comments in italic font).

Serious concern: In the authors' implementation of the bidirectional NH3 flux, they assumed that there was an infinite soil pool of NH4+. This is an unreasonable assumption that is recognized and discussed by the authors. However, due to this or other assumptions in the implementation of the NH3 bidirectional flux mechanism, the NH3 emission/reemission flux is similar to or greater than the total (wet + dry) NHx deposition. This implies that the ecosystems are taking up little to no deposited NHx, which does not seem to be a reasonable result during the growing season. This casts doubt that any improvements in model performance is for the "right reasons" and on the value of the source apportionment results. I think that the authors should investigate and discuss the net total reduced nitrogen deposition, and if they cannot justify the high emission/reemission rates of ammonia, then I question the value of the final source attribution results.

[CW] As you say, we recognized that this simplification (using empirical average emission potentials) means that the soil and canopy pools of NH4+ are "infinite", which is not realistic. First, we note that Zhu et al (2015) use this method for their canopy pool of NH4+ in GEOS-Chem (used empirical average stomata emission potentials, which essentially makes for an infinite canopy pool). While they more realistically model the soil pool, they required a 3-month spin up to get the soil pool stable. This means that the soil pool is very large, and that over the shorter time scales we use in our study, assuming that the pool won't get depleted is a valid assumption. This is further supported by Wentworth et al (2014, Biogeosciences), who calculated the approximate relative abundances of NH_x in the boundary layer versus NH_4^+ in the soil pool to assess whether surface-to-air fluxes were sustainable. They found that soil NH_4^+ >> boundary layer NH_x (by over two orders of magnitude), further supporting the assumption in our bidirectional flux scheme. In addition, the turnover time for soil NH_4^+ is on the order of 1 day, and the majority of soil NH_4^+ comes from org-N decomposition (Booth et al., 2005, Ecol. Monogr.), hence it is unlikely that NH_3 bi-directional fluxes would significantly deplete/enhance soil NH_4^+ pools over shorter time scales such as the month simulated here.

Second, we have replotted the modelled deposition, combining the dry NH3 deposition + the wet NH4+ deposition to get a total NHx deposition. For the base, bidi, and fire+bidi, the results of the total deposition are shown below:

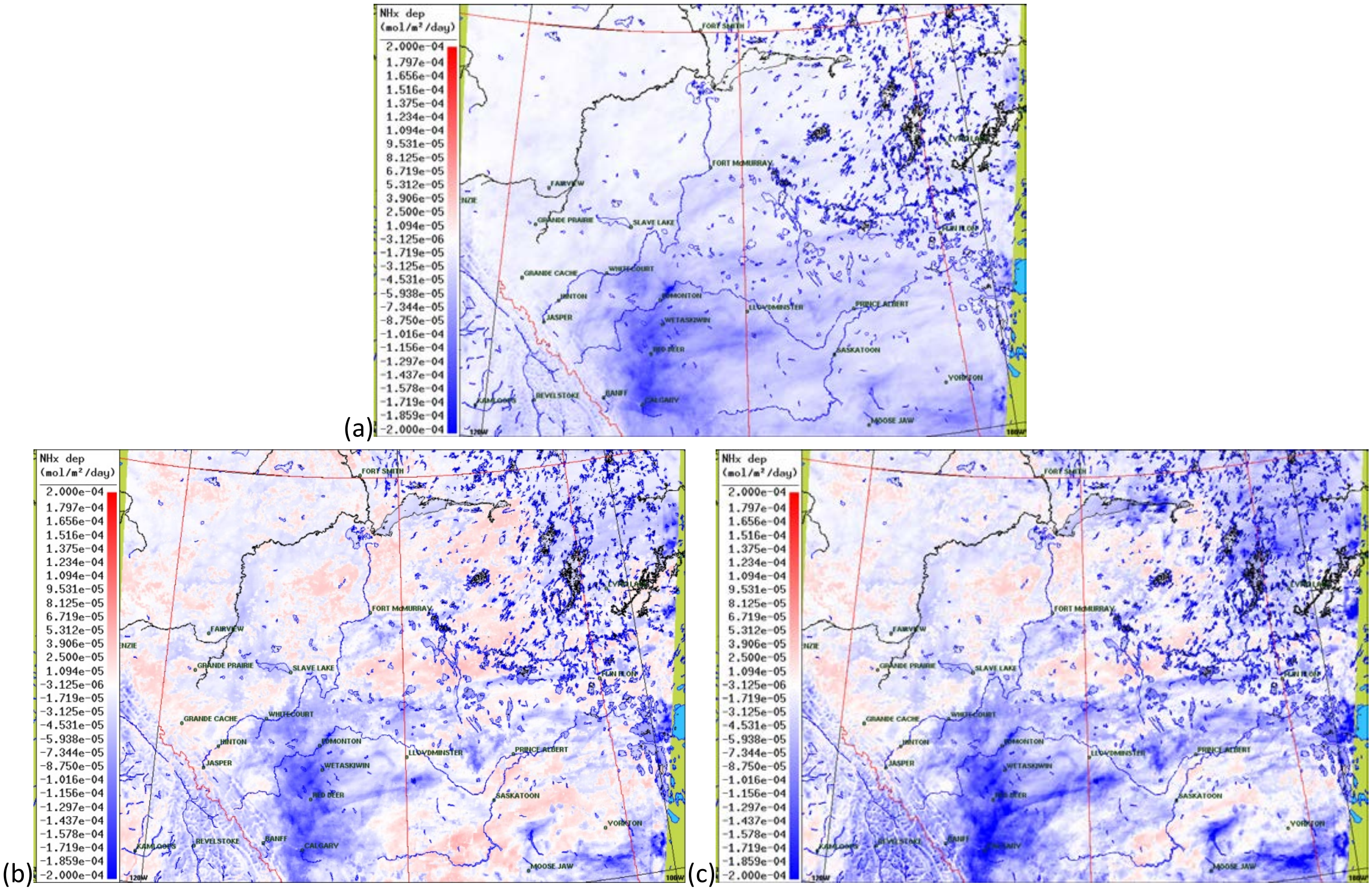

Figure R.1: Total deposited NHx (dry NH3 + wet NH4+) in (a) base, (b) bidi, and (c) fire+bidi. Red regions indicate net NHx emissions; and blue regions indicate net deposition.

Here we can better see that the ecosystems are in fact taking up deposited NHx over most of the domain (anywhere that's blue is net deposition, anywhere that's red is net upward flux) – which was not easy to see when the deposition maps were presented separately (e.g., Figures 12 & 14 for dry and wet dep, respectively, in the original manuscript). In the revised manuscript, we will present and discuss Figure R.1 as the new Figure 12, instead of showing the two separately since the total deposited NHx is the more important and relevant value. The average NHx flux values across the domain are:

NET FLUX (mol/m2/day)	**Base**	**Bidi**	**Fire+bidi**
Mean	-3.025E-5	-1.811E-5	-3.765E-5
Median	-2.061E-5	-1.299E-5	-2.843E-5

From these numbers you can see that in fact, the mean net flux of NHx across the domain from each simulation is similar and is net *downward* (negative). In fact, the fire+bidi has the largest mean net flux downward. Thus, our bidi scheme – even with a soil pool that can't be depleted – does not cause unrealistic net upward flux. In fact, Figure R.1c, shows that there is net deposition where NHx atmospheric concentrations are highest, but in parts of the domain where NHx atmospheric concentrations are low there is a net upward flux.

Addressing those "red" areas which are still visible in Figure R.1b and c; While the red areas in Figure R.1 have net upward flux <u>during our study's time period</u>, it is important to note that our study occurred during August and September, which are very warm months (discussion of meteorological conditions in the region was added to the revised manuscript), and the compensation point increases exponentially with temperature (Figure R.2 showing an example for one of the land use categories in the northern part of the domain).

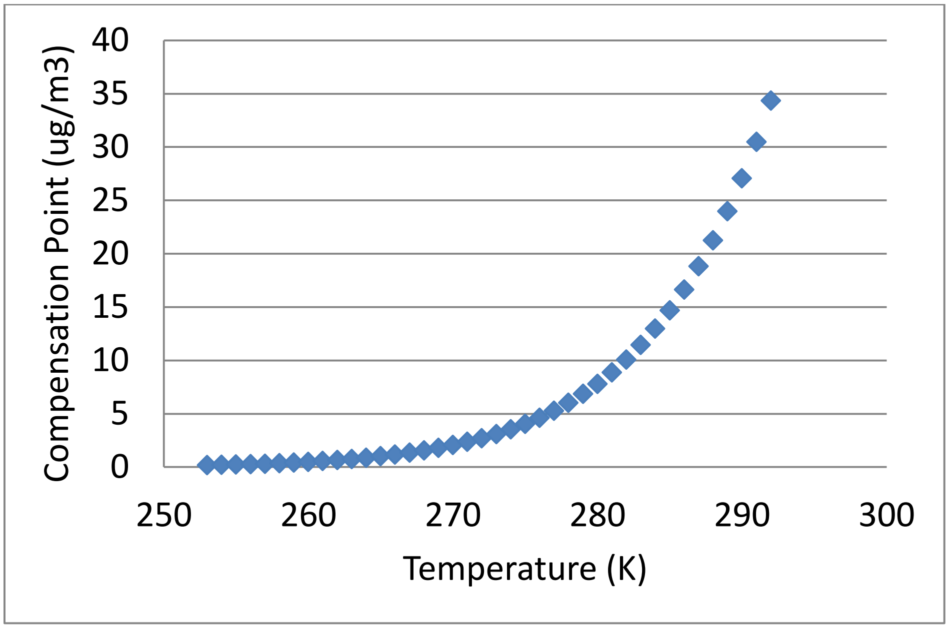

Figure R.2: Compensation point (Cg) relationship to temperature; Cg for evergreen needleleaf LUC shown as example.

The higher the compensation point, the more likely there will be upward flux, and the lower it is, the more likely there will be deposition. Therefore, during the colder part of the year (e.g., the preceding winter and spring), the compensation point is much lower than during our study, increasing the likelihood of net deposition, even for the regions shown as emitters in the summer in northern Alberta/Saskatchewan in Figure R.1. While we did not run our bidirectional flux simulation for the whole year, a standard (non-bi-di) GEM-MACH run for a full year, yielded a cumulative NHx (wet NH4 + dry NH3) deposition that was greater than our upward flux for Aug/Sept. This means that we can expect the soil pool to be replenished during cooler times of the year, rather than depleted. Thus, our modelling assumptions in this study – especially given that we modelled a short time period in the summer – are justified. This discussion, figure, and table have been added to the manuscript in Sections 2.2 and 5.2 of the revised manuscript.

The authors pursued the incorporation of ammonia bidirectional flux and wildfire emissions into the model due to significant underestimations of ammonia concentrations in a previous modeling exercise. While reasonable, they do not discuss potential issues with other modeling inputs and processes, including the underestimation of emissions from other sectors, e.g., agricultural regions and NH3 slip in fossil fuel combustion systems, as well as potentially overestimating NH4 wet deposition. Early in the manuscript it would be good to discuss why these other factors are not likely significant contributors to the initial model underestimation. This could include evaluation of the model NH4 wet deposition simulation against measured wet deposition or through fall data. If NHx wet deposition is also underestimated, then this would certainly point toward biases in the dry deposition rates and/or emissions.

[CW] We presented evidence in our study that agricultural emissions of NH3 are likely overestimated. We know GEM-MACH's NH4 deposition is not overestimated because of work in Makar et al (2017, in this special issue of ACPD), where they showed a small underestimation of NHx deposition in the base (non-bi-di) GEM-MACH model (model to observation slope of wet deposited nitrogen of 0.89, $R^2 = 0.76$). We've added this point to introduction, lines 85-89, in the revised manuscript.

Near the end of the manuscript, the authors do show that the base-case model simulation performed well near agricultural activity and that it underestimated NH3 when wildfire emissions impacted the area. This information supports the authors' premises, and I suggest that these results be discussed before the model comparison to the surface and aircraft measurements.

[CW] The following text was added to the introduction (lines 85-89 in the revised manuscript) to motivate the two changes we made to the GEM-MACH model in this study:

Having too much modelled NHx deposition is a cause that was ruled out when Makar et al (2017) showed that GEM-MACH actually underestimates NHx deposition. Underestimating anthropogenic and agricultural emissions in southern Alberta and Saskatchewan was also ruled out as a cause because the GEM-MACH model performs well in southern Canada and the U.S when compared to the U.S. Ambient Ammonia Monitoring Network (AMoN). NH3 sources known to be missing from the GEM-MACH model were forest fire emissions and re-emission of deposited NH3 from soils and plants (the latter referred to as bidirectional flux, hereafter), which would have the greatest impact in background areas, such as northern Alberta and Saskatchewan. Therefore, these two sources were added to an updated version of GEM-MACH…

Last, the oil sands region is an area of intense energy development, and some discussion of the ammonia emission from this activity and its uncertainty is warranted.

[CW] In another companion paper being submitted to the special issue the emissions are discussed in detail (Zhang et al). In the province of Alberta, the reported oil sands emissions represent 1% of the province's total anthropogenic NH3 emissions.

The oil sands have two different emissions inventories: the National Pollutant Release Inventory (NPRI) annual inventory, and Continuous Emissions Monitoring (CEMS) hourly emissions data. The CEMS emissions have relatively low uncertainties because they are based on measurements in the stacks. However, only some of the facilities measure NH3 emissions. Those that do would base their reported NPRI emissions on those CEMS measurements. Those that don't have higher uncertainty on the NH3 emissions they report. For example, the Syncrude facility has CEMS-based NH3 emissions in the NPRI inventory, so it should have relatively high quality (see http://www.ec.gc.ca/inrp-npri/donnees-data/index.cfm?do=substance_details&lang=En&opt_npri_id=0000002274&opt_cas_number=NA%20-%2016&opt_report_year=2013 for NH3 emissions for this facility and http://www.ec.gc.ca/inrp-npri/donnees-data/index.cfm?do=substance_details&lang=En&opt_npri_id=0000002274&opt_cas_number=NA%20-%2016&opt_report_year=2013 for the Basis of Estimate Codes. "M1" means "Continuous Emission Monitoring - In use from 2003 and onward"). However, because we don't have hourly CEMS NH3 emissions for 2013, it is hard to tell the difference between CEMS and NPRI values. Some of this discussion has been added to the manuscript, lines (142-147).

Specific comments In the abstract and introduction
it is noted that the Alberta oil sands region has relatively low ammonia concentrations. Please put this into some context. These concentrations are not low compared to many rural western North American sites.

[CW] The low NH3 concentrations are mainly across northern Alberta/Saskatchewan, but not necessarily within 10 km of the AOSR industries. We have modified the text to reflect that distinction (lines 63-71), however, 0.6-1.2 ppbv range that we find in the AMS13 measurements are on the low end of the NH3 2012 annual averages reported in this AMoN data summary: http://nadp.sws.uiuc.edu/amon/ . We have added some reported NH3 concentrations across different areas to the revised manuscript (measured via the AMoN network) in the introduction and Section 4.1 (lines 387-392).

Also, can anything be said about the estimated deposition rates in these regions compared to the reactive nitrogen critical loads? If the deposition rates are near or above the critical loads, then this work could have important policy implications.

[CW] The issue of acidic exceedances of critical loads of sulphur and nitrogen is the focus of the Makar et al study that has been submitted to the oil sands special issue of ACPD, currently awaiting assignment and initial recommendations from reviewers. The modelling carried out there was similar to our base case, but for an extended period of one year (a more relavant time scale for deposition to ecosystems). There, it was shown that anthropogenic sources in the region create sufficient *sulphur* deposition to exceed aquatic ecosystem critical loads over a large region; nitrogen deposition was not needed to result in exceedances. In that sense, the additional policy implications of nitrogen deposition may be moot. However, the exceedances were higher when N and S were considered together, but the key point with reference to the bi-directional fluxes is that sulphur alone was already sufficient for exceedances. Nevertheless, we are interested in following up the potential for bi-directional fluxes to influence exceedances, in future work.
With regards to nutrient N critical loads (i.e., eutrophication critical loads), to our knowledge, there have not been any N-critical loads developed specifically for the oil sands region.

<u>*Specific comments*</u>
Lines 173-175: "the bidirectional flux acts effectively as an additional source of NH3 gas, releasing stored NH3 until and unless the ambient concentration rises to the compensation point concentration." It would be good to discuss the origin of the NH3 in these emissions. That is, is the NH3 originating from the natural processes of the ecosystem or from previously deposited NH3 or a combination of both? Presumably, it is from both. This also has implications when discussing natural versus anthropogenic NH3. The authors assume that all NH3 bidirectional flux emissions are natural; however, if the deposited NH3 originating from anthropogenic sources was reemitted, then this NH3 would have anthropogenic origins. Consequently, not all of the reemitted ammonia due to the bidirectional flux processes is necessarily natural.

[CW] Since the re-emissions are from soils and plants, we have called them natural in the original manuscript, however, you are correct that the sources of NHx available for re-emissions are from increased deposition because of anthropogenic sources, as well as from natural N_2-fixation, organic decomposition, and microbial action. Vile et al (2014, Biogeochemistry) found that in boreal bogs, 90-95% of the NHx pool is from these natural processes, but that's not necessarily true for other land-types. So it's correct to say that the re-emissions are both natural and anthropogenic in origin. Similarly, forest fires provide another source of NHx which may be classified as natural and/or anthropogenic in origin. With the current GEM-MACH-Bidi model, we can't distinguish how much is from each. However, we have revised the text so that the re-emissions are no longer called "natural", but rather "semi-natural" (lines 10-12, and lines 178-179).

Line 186: "it is not desirable for our bidirectional flux scheme to have to rely in advance on another model's output. Therefore, we use this simplified version, and assess whether its results provide a good enough improvement to simulated NH3 for less cost in run time." The authors did not discuss what constitutes a "good enough" model simulation or whether the studied model satisfied this criterion.

[CW] This is a good point, and the phrase "good enough" was removed from the manuscript. The ultimate goal is to have model biases of zero within measurement errors bars, but this is not always possible given the complexities of an air quality model (e.g., there can be errors in modelled meteorology, emissions inventories, emissions spatial and temporal allocations, atmospheric chemistry, etc., etc.). Furthermore, a zero model bias may be achieved, but for the wrong reasons (e.g., knowing certain process/sources are missing, but compensating errors causing the model values to be close to measurements anyway). Thus, a quantitative *threshold* for "good enough" is not necessarily comprehensive.
We do consider the fire+bidi simulation to have satisfied our objective of "improving NH3 predictions" because it has better statistics when compared to a variety of measurements than the base case has (now summarized in Table 2 for all simulations and measurements), and because it contains all of the known missing sources of NH3 for the region. We have revised that text in Section 2.2 (lines 246-247).

In addition, as discussed in the general comments, I question whether the high NH3 emissions resulting from the bidirectional flux mechanism are reasonable or not and suggest further investigation and discussion.

[CW] The simplification in the soil and stomata emission potentials is an appropriate parameterization for reasons stated our response to reviewer#3's first comment (see above).

Line 307: "Figure 4 shows the time series of the concentrations of NH3 and its reaction products, fine-particulate NH4+ and NO3-" This is a confusing sentence.

[CW] Thank you for pointing out the unclear sentence. It has been revised (lines 384-386).

Also please specify if NO3- is only particulate nitrate or if it includes nitric acid.

[CW] It is only particulate NO3-.

Section 4.1: Reproducing the measured hourly ammonia concentrations is very challenging. It would be good to see how the model performs on an aggregated basis as well, e.g., can it reproduce the 24-hour average NH3 values and the average diurnal cycles?

[CW] Figure R.3 below is the timeseries of daily averages, which is clearer and doesn't need to be in log scale. We have replaced Figure 4 of the original manuscript with Fig R.3, and doing so does not much change the discussion that was there previously. We have kept the following two figures the same (with hourly data) in the revised manuscript.

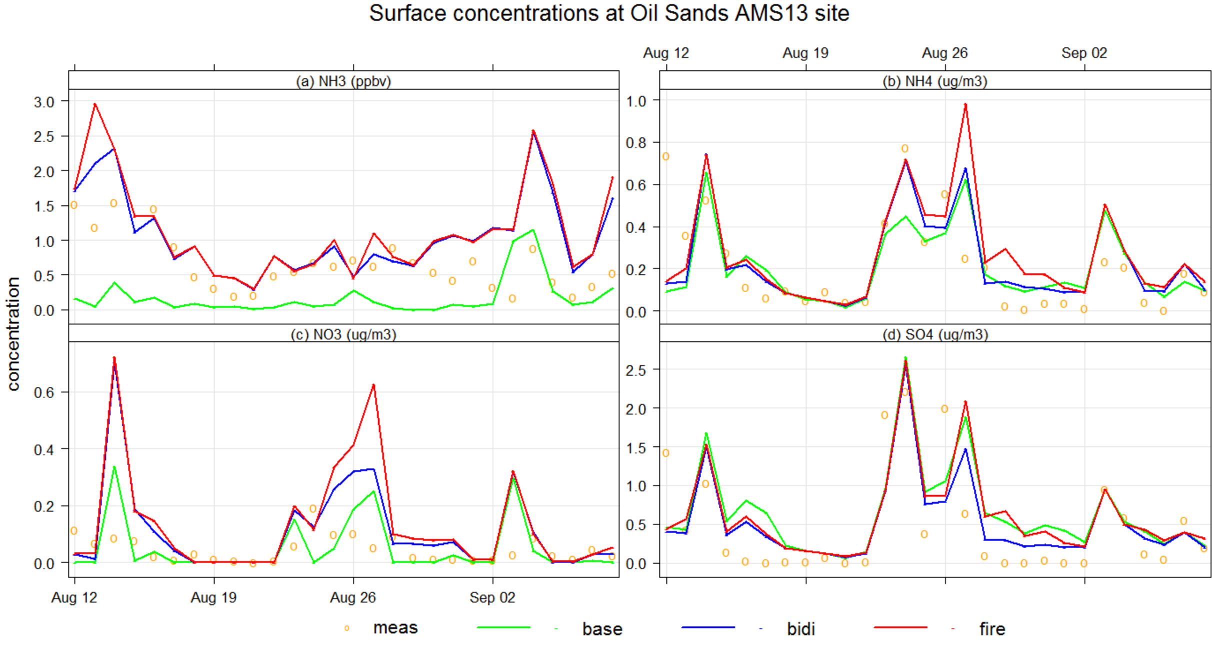

Figure R.3: daily average times series at the AMS13 ground site.

Figure R.4 below shows the analysis of day of week, diurnal cycle, etc. that the R openair package provides – here just for NH3. We see that while the bidi and fire+bidi models now over-predict NH3 concentrations at this single location which is influenced by local anthropogenic sources, the diurnal cycle is better represented in those simulations, compared to the base simulation, which is just spiky at certain hours. The bidi simulation is more similar to the measurements, although the amplitude of the cycle is still underestimated. Similarly the bidi simulation has the closest agreement with the August monthly average (lower-middle panel), and the average of most of the week days (lower-right panel). We have not added Fig. R.4 to the revised manuscript, however, we have added additional text describing these findings (lines 410-414).

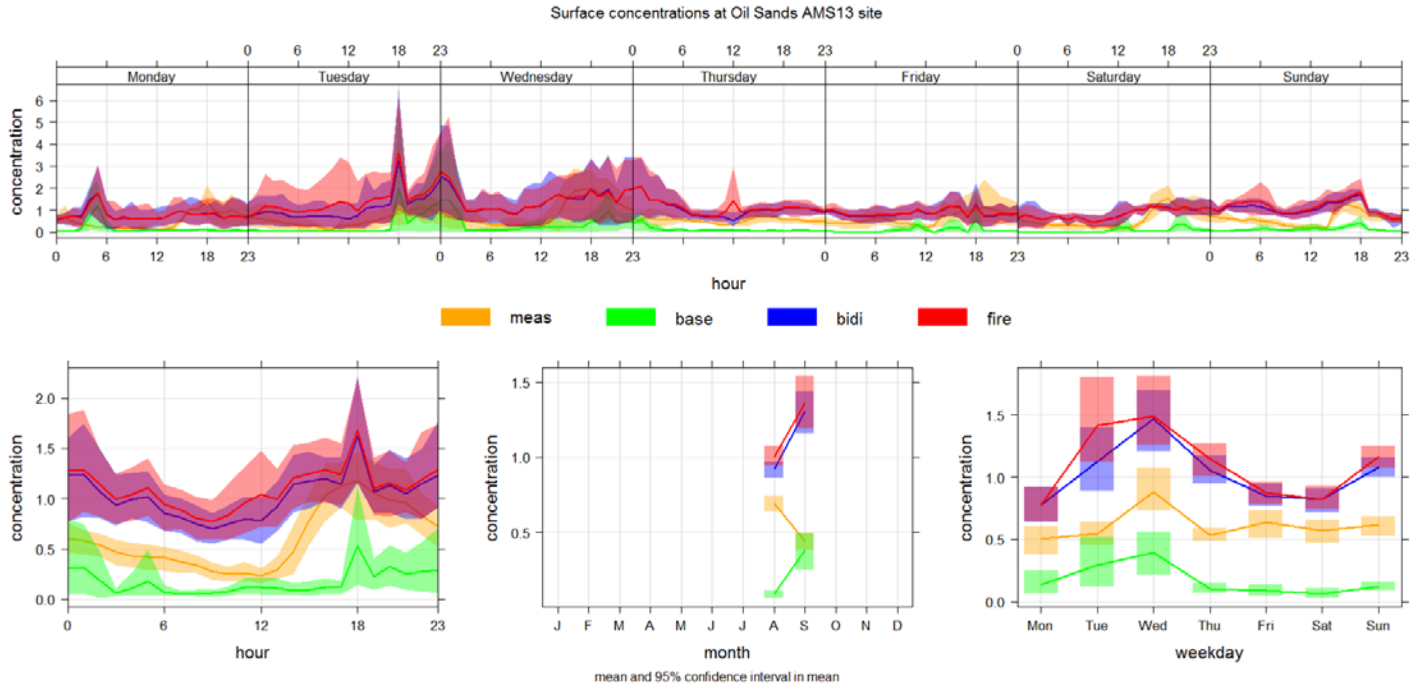

Figure R.4: time series analysis for NH3 at the AMS13 ground station. Hours are in UTC (subtract 6 to get local time).

It would be good to include estimates of the model error such as the RMS and fractional errors and bias in the model performance statistics.

[CW] RMS model error and fractional errors have been calculated and added into Table 2. For almost all comparison statistics, the fire+bidi simulation has the best results.

Line 333: "(from R=0.2 to 0.4)..." From Figure 6 it looks like the improvement in correlation should be from 0.1 to 0.4.

[CW] Yes, that's been corrected, as were the slopes.

Line 372: "However, we clearly see that for this flight, the bidirectional flux has increased NH3 concentrations, bringing them closer to the measured values." It is not clear from the figure that the model performance has improved, only that the simulated NH3 has increased. It would be good to add performance stats to panels b–c in Figure 7.

[CW] The improvement can be seen by the fact that the bidi and fire + bidi colours now match the colours in the measurement panel (they all use the same colour scale). The median concentrations of each panel are now mentioned in the text (line 455-456).

Lines 425-435: I think this discussion is very important for justifying the modeling refinements and should be moved up front.

[CW] We added to the introduction, lines 85-89.

Technical comments
The fonts used in the figures are very small, making text difficult to read. This is particularly the case in Figures 3, 11, 12, 13, and 14 and supplemental material.

[CW] These figures and their fonts were made larger.

Figures 12 and 13 are missing panels.

[CW] To address another reviewer comment, we have remade Figure 12 (which is Fig 13 in the revised manuscript), and eliminated Figures 13 and 14 from the original manuscript.

Manuscript prepared for Atmos. Chem. Phys.
with version 2015/04/24 7.83 Copernicus papers of the LaTeX class copernicus.cls.
Date: 19 December 2017

Contributions of natural and anthropogenic sources to ambient ammonia in the Athabasca Oil Sands and north-western Canada

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Abstract. Atmospheric ammonia (NH_3) is a short-lived pollutant that plays an important role in aerosol chemistry and nitrogen deposition. Dominant NH_3 emissions are from agriculture and forest fires, both of which are increasing globally. ~~The Alberta Oil Sands region has~~ Even remote regions with relatively low ambient NH_3 concentrations~~because of its remote location~~ , such as northern Alberta and Saskatchewan in northern Canada ~~; however, a~~ may be of interest because of industrial Oil Sands emissions, and a sensitive ecological system. A previous attempt to model NH_3 in the region showed a substantial negative bias compared to satellite profiles and aircraft observations. Known missing sources of NH_3 in the model were re-emission of NH_3 from plants and soils (bidirectional flux), and forest fire emissions, but the relative impact of these sources on NH_3 concentrations ~~and column totals~~ was unknown. Here we have used a research version of the high-resolution air quality forecasting model, GEM-MACH, to quantify the relative impacts of ~~natural~~ semi-natural (bidirectional flux of NH_3 and forest fire emissions) and direct anthropogenic (Oil Sands operations, combustion of fossil fuels, and agriculture) sources on ammonia concentrations, both at the surface and aloft, with a focus on the Athabasca Oil Sands region ~~,~~ during a measurement-intensive campaign in the summer of 2013. The addition of fires and bidirectional flux to GEM-MACH has improved the model bias, slope and correlation coefficients relative to ground, aircraft, and satellite NH_3 measurements significantly.

By running the ~~GEM-MACH~~ GEM-MACH-Bidi model in three configurations and calculating their differences, we find that averaged over Alberta and Saskatchewan during this time period ~~;~~ an average of 23.1% of surface NH_3 came from direct anthropogenic sources, 56.6% (or 1.24 ppbv) from bidirectional flux (re-emission from plants and soils), and 20.3% (or 0.42 ppbv) from forest fires. In the NH_3 total column, an average of 19.5% came from direct anthropogenic sources, 50.0%

from bidirectional flux, and 30.5% from forest fires. The addition of bidirectional flux and fire emissions caused the overall average net ~~flux of NH_3~~ deposition of NH_x across the domain to be ~~positive (upward). It also increased the NH_4^+ wet deposition by nearly a factor of three during the period simulated~~increased by 24.5%. Note that forest fires are very episodic and their contributions will vary significantly for different time periods and regions.

This study is the first use of the bidirectional flux scheme in GEM-MACH, which could be generalized for other volatile or semi-volatiles species. It is also the first time CrIS satellite observations of NH_3 have been used for model evaluation, and the first use of fire emissions in GEM-MACH at 2.5-km resolution.

1 Introduction

Ammonia (NH_3) is a short-lived pollutant that is receiving global attention because of its increasing concentrations. Emissions of NH_3 – which are in large part from agricultural fertilizer, livestock (Behera et al., 2013; Environment and Climate Change Canada, 2016), and biomass burning (Olivier et al., 1998; Krupa, 2003) – have not been regulated to the same extent as other nitrogen species. NH_3 is the only aerosol precursor whose global emissions are projected to rise throughout the next century (Moss et al., 2010; Lamarque et al., 2010; Ciais et al., 2013).

NH_3 has an atmospheric lifetime of hours to a day (Seinfeld and Pandis, 1998; Aneja et al., 2001). It is a base that reacts in the atmosphere with sulphuric acid (H_2SO_4) and nitric acid (HNO_3) to form crystalline sulphate, nitrate salts (e.g., $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3) and aqueous ions (SO_4^{2-}, HSO_4^-, NO_3^-), (Nenes et al., 1998; Makar et al., 2003) which are significant components of fine particulate matter ($PM_{2.5}$) (e.g., Jimenez et al., 2009, Environment Canada, 2001), thus causing health (Pope III et al., 2002; Lee et al., 2015) and climate impacts (IPCC, 2013). A large portion of NH_3 is readily deposited in the first 4-5 km from its source, but when in fine particulate form (as NH_4^+), its lifetime is days to several weeks (Galperin and Sofiev, 1998; Park et al., 2004; Behera et al., 2013; Paulot et al., 2014) and can be transported hundreds of kilometers (Krupa, 2003; Galloway et al., 2008; Makar et al., 2009). Deposition of NH_3 and these aerosols can lead to nitrogen eutrophication and soil acidification (Fangmeier et al., 1994; Sutton et al., 1998; Dragosits et al., 2002; Carfrae et al., 2004). ~~Thus,~~ NH_3 is listed as a Criteria Air Contaminant (Environment and Climate Change Canada, 2017) in order to help address air quality issues such as smog and acid rain.

Modelling ~~provides information on NH_3 concentrations where there are no measurements, and~~ can be used to better understand NH_3 processes. Recent NH_3 models have focused on improving bidirectional flux processes and impacts of livestock. Measurements of NH_3 bidirectional flux include those in Farquhar et al. (1980); Sutton et al. (1993, 1995); Asman et al. (1998); Nemitz et al. (2001), with indirect support for bidirectional flux also in Ellis et al. (2011). Thus, these studies were the motivation for the recent design of parameterizations to describe this important process (Wu et al., 2009;

Wichink Kruit et al., 2010; Massad et al., 2010; Zhang et al., 2010; Zhu et al., 2015; Fu et al., 2015; Hansen et al., 2017). Additionally, satellite observations are providing valuable insight on ammonia concentrations and emissions both on regional and global scales (Beer et al., 2008; Clarisse et al., 2009; Shephard et al., 2011; Shephard and Cady-Pereira, 2015; Van Damme et al., 2014; Zhu et al., 2013).

The Athabasca Oil Sands region (AOSR), located in the north-eastern part of the province of Alberta, Canada, is a large source of ~~air (Gordon et al., 2015; Liggio et al., 2016; Li et al., 2017), ecosystem (Kelly et al., 2009; Kirk et al., 2014; Hsu and Clair, 2015) and greenhouse gas (Charpentier et al., 2009) pollution~~ pollution to air (Gordon et al., 2015; Liggio et al., 2016; Li et al., 2017) and ecosystems (Kelly et al., 2009; Kirk et al., 2014; Hsu and Clair, 2015), as well as a source of greenhouse gases (Charpentier et al., 2009) due to mining and processing by the oil industry. ~~However~~ While NH_3 concentrations surrounding the AOSR in northern Alberta and Saskatchewan remain relatively low ~~(e.g., averaging 0.63 ± 0.57 ppbv at the surface,~~ – around 0.6-1.2 ppbv background (this study ~~); and averaging 1.2 ± 0.2 ppbv aloft (Shephard et al., 2015) compared to agricultural areas in the south of the provinces~~ and Shephard et al., 2015) – due to low population and lack of agriculture, the northern Alberta and Saskatchewan ecosystems are sensitive to nitrogen deposition (Clair and Percy, 2015; Wieder et al., 2016a, b; Vitt, 2016; , and the modelled background NH_3 must be correct in order to understand the relative impacts of the oil sands operations. It is important to understand if the AOSR facilities are causing critical levels of NH_3, and if not, if any other kinds of sources (e.g., ~~Makar et al., 2009) . However, a~~ fires, re-emissions) are. A monitoring study from 2005 to 2008 found NH_3 concentrations near Fort McMurray and Fort McKay (population centers in the vicinity of the oil sands facilities) to be highly variable in space and time with a range of 1.1 to 8.8 ppbv ~~(Bytnerowicz et al., 2010) .~~ (where the upper end corresponds to NH_3 levels found in agricultural regions of Canada and the U.S.), with NH_3 concentrations 1.5-3× higher than HNO_3 concentrations (Bytnerowicz et al., 2010) . Hsu and Clair (2016) also found NH_3 concentrations in the AOSR to be much higher than HNO_3, NO_3^-, and NH_4^+ concentrations (by 5, 23, and 1.8×, respectively). Thus, NH_3 may contribute the largest fraction of deposited nitrogen in the AOSR compared to other nitrogen species~~like NO_2 and HNO_3^- (Bytnerowicz et al., 2010; Hsu and Clair, 2015; Kharol et al., 2017)~~. Estimates of deposition of nitrogen ~~and sulphur~~ compounds in the AOSR are described in Makar et al. (2017) in this issue, however they did not include NH_3 bidirectional flux or forest fires in their model simulations.

In a previous study by Shephard et al. (2015) it was found that the GEM-MACH air quality forecasting model (Moran et al., 2010, 2013; Makar et al., 2015a, b; Gong et al., 2015), using a domain covering the Canadian provinces of Alberta and Saskatchewan, at 2.5-km resolution, under-predicted summertime tropospheric ammonia concentrations by 0.4-0.6 ppbv (which is 36-100 % depending on altitude - see Fig. 16 in Shephard et al., 2015) in the AOSR when compared to Tropospheric Emission Spectrometer (TES) satellite measurements and aircraft measurements. ~~NH~~Having too much modelled NH_x deposition is a cause that was ruled out when Makar et al. (2017) showed that GEM-MACH actually underestimates NH_x deposition. Underestimating anthropogenic and agricultural emissions was also ruled out as a cause because the GEM-MACH model performs well in southern Canada and the U.S when compared to the U.S. Ambient Ammonia Monitoring Network (AMoN). NH_3 sources known to be missing from the GEM-MACH model were forest fire emissions and re-emission of deposited NH_3 from soils and plants (the latter referred to as bidirectional flux, hereafter)~~. These~~ , which would have the greatest impact in background areas, such as northern Alberta and Saskatchewan. Therefore, these two sources were added to an updated version of GEM-MACH and model simulations were repeated for a 2013 summer period (12 August to 7 September 2013) during which an intensive measurement campaign occurred. We utilize ground, aircraft and satellite measurements of NH_3 and related species to evaluate the model and to quantify the impacts of the different sources on atmospheric NH_3 and its deposition.

Section 2 provides the model description. Section 3 provides a brief description of ammonia measurements during the campaign. Section 4 presents the evaluation of three model scenarios against three different types of measurements (surface, aircraft, and satellite), and Section 5 presents our quantitative assessment on the impacts of different sources of NH_3 to ambient concentrations and NH_x deposition in the region. Our conclusions appear in Section 6.

2 GEM-MACH model description

GEM-MACH (Global Environment Multiscale-Modelling Air quality and CHemistry) is an on-line chemical transport model, which is embedded in GEM, Environment and Climate Change Canada (ECCC)'s numerical weather prediction model (Moran et al., 2010). This means that the chemical processes of the model (gas-phase chemistry, plume rise emissions distribution, vertical diffusion and surface fluxes of tracers, and a particle chemistry package including particle microphysics, cloud processes, and inorganic heterogeneous chemistry) are imbedded within the meteorological model's physics package, this component in turn is imbedded within the meteorological model's dynamics package, which also handles chemical tracer advection. A detailed description of the process representation of GEM-MACH, and an evaluation of its performance for pollutants such as ozone and particulate matter (PM) appears in ~~Moran et al. (2013); Makar et al. (2015a, b); Gong et al. (2015); Akingunola et al. (2017)~~ Moran et al. (2013); Makar et al. (2015a, b); Gong et al. (2015).

GEM-MACH is used operationally to issue twice-daily, 48-hour public forecasts of criteria air pollutants (ozone, nitrogen oxides, PM), as well as the the Air Quality Health Index [https://ec.gc.ca/cas-aqhi/]. Any improvements to NH_3 in the model may result in better AQHI predictions, since NH_3 is a major precursor of $PM_{2.5}$, as mentioned in the introduction. We start with a similar, research version of GEM-MACHv2 to make the bidirectional flux modifications. The key differences between this and older versions are the use of a more recent meteorological package (GEMv4.8), the capability to nest in the vertical dimension as well as the horizontal dimension, and improvements to the treatment of fluxes, vertical diffusion, and advection~~(Akingunola et al. (2017), this issue)~~.

GEM-MACH can be run for many different spatial domains, at various spatial resolutions, and in 2-bin or 12-bin aerosol size distribution modes. For this study we run the model in the 2-bin mode (for computational efficiency), using a nested set of domains. The outer domain at 10-km resolution ~~covering~~ covers North America, and the inner domain at 2.5-km resolution ~~covering~~ covers the provinces of Alberta and Saskatchewan. The latter is referred to as the 2.5-km Oil Sands domain. ~~And this~~ This set up, along with the emissions described in the next section is hereafter called our “base" simulation.

2.1 Emissions

The emissions of 25 species (SO_2, SO_4 (gas), sulphate, nitrate, NH_4^+, NO, NO_2, NH_3, CO, nitrous acid, benzene, propane, higher alkanes, higher alkenes, ethene, toluene, aromatics, formaldehyde, aldehydes, methyl ethyl ketone, creosol, isoprene, crustal material, elemental carbon, and primary carbon) used in GEM-MACH (base case) come from Canadian and U.S. emissions inventories: 2011 National Emissions Inventory (NEI) version 1 for U.S. emissions, and the Air Pollutant Emission Inventory (APEI) 2013 for Canadian emissions (2010 for onroad and offroad emissions). Emissions were processed with SMOKE (Sparse Matrix Operator Kernel Emissions, https://www.cmascenter.org/smoke/) to convert the inventories into model-ready gridded hourly emissions files for modeling, separated into major point emissions (typically industrial emissions from stacks, emitted into the model layers that correspond to the stack height, at the reported temperature and velocity in the inventory's stack parameters), and area emissions (emissions from spread-out sources, such as transportation and agriculture, emitted into the first model layer). For more details about these emissions, see Moran et al. (2015) and ~~(Zhang et al. ,~~ Zhang et al. (2017, this issue).

The emissions data for NH_3 from oil sands sources are reported to the Canadian National Pollutant Release Inventory (NPRI) on a “total annual emissions per facility" basis. NH_3 emissions are generally more uncertain than SO_2 and NO_x emissions because NH_3 emissions are not measured to the same extent as those two. The oil sands represent only 1% of total Alberta NH_3 emissions, at approximately 1438 tonnes in 2013. For comparison, about 18× more NO_x and 57× more SO_2 was emitted from the oil sands facilities that year (http://www.ec.gc.ca/inrp-npri/donnees-data/index.cfm?lang=En). However, we found an issue with NH_3 in this inventory that impacted our model evaluation in the region, which we describe below.

The emissions data for NH_3 from oil sands sources are reported to the Canadian National Pollutant Release Inventory (NPRI) on a “total annual emissions per facility" basis. NH_3 emissions are generally more uncertain than SO_2 and NO_x emissions because NH_3 emissions are not measured to the same extent as those two. The oil sands represent only 1% of total Alberta NH_3 emissions, at approximately 1438 tonnes in 2013. For comparison, about 18× more NO_x and 57× more SO_2 was emitted from the oil sands facilities that year (http://www.ec.gc.ca/inrp-npri/donnees-data/index.cfm?lang

However, we found an issue with NH_3 in this inventory that impacted our model evaluation in the region, which we describe below.

If stack parameters (e.g., stack height and diameter, volume flow rates, temperatures, etc.) are included as part of that data, then the emissions are allocated to large stacks in our configuration of the SMOKE emissions processing system. In the absence of this information, SMOKE will assign default stack parameters based on its source category code. For the Syncrude Canada Ltd. - Mildred Lake Plant Site, NPRI ID 2274 (a facility in the AOSR), the default stack parameters were: 18.90 m for the stack height (which is within the first model layer), 0.24 m for the stack diameter, 320.0 K for the exhaust temperature, and 0.58 m/s for the exhaust velocity. However, when these defaults were applied in initial model simulations, they were found to result in erroneous short term plume events with simulated surface NH_3 levels up to 2 orders of magnitude higher than ground observations~~(Wentworth et al., 2017)~~, and modelled concentrations aloft too low compared to aircraft measurements (see Section 3). Conversely, for species such as SO_2, for which stack parameters were reported, the model was able to correctly place the SO_2 enhancements in space and time, relative to observations. When the stack parameters of the main stack for this facility were used for NH_3 emissions as well (stack height=183 m, stack diameter=7.9 m, exit temperature=513 K, exit velocity=23.9 m/s, from the NPRI website), the simulation of surface NH_3 was greatly improved. All subsequent simulations reported here make use of this correction.

2.2 Ammonia bidirectional flux parameterization

~~The bidirectional flux~~ NH_3 can be both deposited from the atmosphere to the ground, and re-emitted from soils and plants back to the atmosphere. The two taken together are called bidirectional flux, since the flux of NH_3 can go both up and down. The source of NH_3 available for re-emissions are from the accumulated NH_x in the soil and stomatal water, which can arise from increased deposition from anthropogenic sources, as well as from organic nitrogen decomposition (Booth et al., 2005), N_2-fixation (Vile et al., 2014), and natural microbial action (McCalley and Sparks, 2008).

The bidirectional flux scheme of Zhang et al. (2010) was applied within the GEM-MACHv2 model, replacing the original deposition velocity for NH_3 only (deposition velocity of other gas species follows a scheme based on a multiple resistance approach and a single-layer “big leaf" approach (Wesely, 1989; Zhang et al., 2002; Robichaud and Lin, 1991; Robichaud, 1994)). The bidirectional flux scheme is described in detail in Zhang et al. (2010), but we summarize it here.

Bidirectional exchange occurs between air-soil and air-stomata interfaces. The bidirectional flux (F_t) equation is:

$$F_t = -\frac{C_a - C_c}{R_a + R_b} \tag{1}$$

where R_a and R_b are the aerodynamic and quasi-laminar resistances, respectively. C_a is the NH_3 concentration in the air, and C_c is the canopy compensation point concentration, given by Eq. (2).

$$C_c = \frac{\frac{C_a}{R_a+R_b} + \frac{C_{st}}{R_{st}} + \frac{C_g}{R_{ac}+R_g}}{(R_a+R_b)^{-1} + (R_{st})^{-1} + (R_{ac}+R_g)^{-1} + (R_{cut})^{-1}} \tag{2}$$

where C_{st} and C_g are the stomatal and ground compensation points, and R_i are the resistances in s/m of the ground/soil (R_g), stomata (R_{st}), cuticle (R_{cut}), and in-canopy aerodynamic (R_{ac}). All resistance formulas can be found in Zhang et al. (2003).

Stomata (st) and ground (g) compensation points are both calculated using Eq. (3):

$$C_{st,g} = \frac{A}{T_{st,g}} \underline{\exp\frac{-B}{T_{st,g}}} \exp(\frac{-B}{T_{st,g}})\Gamma_{st,g} \tag{3}$$

A and B are constants derived from the equilibria constants for NH_3(g) in leaves' stomatal cavities to NH_4^+ and OH^- in the water contained in the apoplast within the leaf and in the soil where NH_3(g) in the soil pore air space is in equilibrium with the NH_4^+ and OH^- dissolved in soil water (Pleim et al., 2013). A=161500 mol K/L (Nemitz et al., 2000), or 2.7457×10^{15} ugK/m^3 (Pleim et al., 2013) for NH_3 for both stomata and soil. B=10380 (Nemitz et al., 2000). $\Gamma_{st,g}$ is the emission potential of the stomata and ground, respectively and, in theory, is equal to the NH_4^+ concentration over the H^+ concentration in the apoplast water of the canopy leaves or soil water:

$$\Gamma_{st,g} = \frac{[NH_4^+]_{st,g}}{[H^+]_{st,g}} \tag{4}$$

However, since there are no modeled NH_4^+ and H^+ apoplast water concentrations to use, we use $\Gamma_{st,g}$ ~~in~~ from Wen et al. (2014), which are based on long-term empirical averages. Wen et al. (2014) gives a range of values for emission potentials for 26 land use categories (LUCs), and we use the low-end of the values in our model with the following exceptions: We further lower the Γ_g for agriculture LUCs to 800, and increase Γ_{st} of boreal forest LUCs to 3000, all of which were necessary in order to achieve realistic NH_3 concentrations ~~,~~ (e.g., compared to reported AMoN values), while staying consistent with Γ findings from the literature.

This version of the model, which we call GEM-MACH-Bidi (or just “bidi" hereafter) was quite sensitive to the selection of emission potentials, which are themselves highly uncertain (Wen et al., 2014). GEM-MACH-Bidi uses the exact same emissions as in the base case, described in the previous section. However, when the sign of F_t in Eq. (1) becomes positive (that is, when $C_a < C_c$), the bidirectional flux acts effectively as an additional source of NH_3 gas, releasing stored NH_3 until and unless the ambient concentration rises to the compensation point concentration. When the flux is negative, net deposition of NH_3 occurs.

It is important to note that $C_{st,g}$ values are exponentially dependent on temperature (Fig. 1 shows an example of this relationship for the dominant LUCs in the northern part of the domain), and the higher the compensation point is, the greater the likelihood there will be upward flux. The lower $C_{st,g}$

is, the more likely there will be deposition. Since our simulation occurred in August and September 2013, when the average temperature in the AOSR was about 18°C (agriculture.alberta.ca/acis/alberta-weather-data-viewer.jsp), we expect to have more NH_3 re-emission than at other times of the year. During the rest of the year (e.g., the preceeding winter and spring), the compensation point would be much lower, greatly increasing the likelihood to have net deposition, even in northern Alberta/Saskatchewan where ambient NH_3 concentrations are low. Other meteorological factors affect the magnitude of bidirectional via the resistance terms. For example canopy compensation points have been observed to decrease with decreasing wind velocity, and increased precipitation (Flechard and Fowler, 1998; Fowler et al., 1998; Biswas et al., 2005; Zhang . In other words, we expect more re-emission during higher winds and drier conditions.

Other chemical transport models, such as GEOS-Chem and CMAQ use a similar method as Zhang et al. (2010), however, instead of the constant average soil emission potentials used here, they utilize a CMAQ-agroecosystem coupled simulation to calculate a soil pool from which to estimate Γ_g (Bash et al., 2013; Pleim et al., 2013; Zhu et al., 2015). In this case, the emission potential will vary and can go to zero if the NH_4^+ in the pool is depleted. However, it was shown in Wen et al. (2014) that their $\Gamma_{st,g}$ worked well during the same time of year as this investigation (August and September). This time of year was also shown in Zhu et al. (2015) to not have a large effect on emissions from the NH_4^+ pool. ~~Our investigation also has a short time scale of about a month, thus it is expected that the the soil pool would not be depleted over this time period~~Additionally, Wentworth et al. (2014) calculated the approximate relative abundances of NH_x in the boundary layer versus NH_4^+ in the soil pool to assess whether surface-to-air fluxes were sustainable. They found that soil NH_4^+ were much greater than boundary layer NH_x (by over two orders of magnitude), further supporting the assumption made here. In addition, the turnover time for soil NH_4^+ is on the order of one day, hence it is unlikely that NH_3 bi-directional fluxes would significantly deplete/enhance soil NH_4^+ pools. Finally, given that GEM-MACH is used for real-time air quality forecasts at Environment and Climate Change Canada, it is not desirable for our bidirectional flux scheme to have to rely in advance on another model's output. Therefore, we use this simplified version, and assess whether its results provide ~~a good enough improvement to~~ an improvement (smaller biases and better correlations to measurements) to simulated NH_3 for less cost in run time.

2.3 Addition of forest fire emissions

Our third model scenario (called "fire+bidi" hereafter) uses the GEM-MACH-Bidi model, and the exact same area emissions and anthropogenic major point emissions as the base and bidi scenarios. However, in addition, we add hourly North American forest fire emissions for all species to the major point emissions. The forest fire emissions system for GEM-MACH (called "Firework") is described in detail in Pavlovic et al. (2016). Briefly, to calculate the fire emissions for input to FireWork, biomass burning areas are first identified in near real time by the Canadian Wildland Fire Information System (CWFIS), which is operated by the Canadian Forest Service (http://cwfis.cfs.nrcan.gc.ca/home). CWFIS uses fire hotspots detected by NASA's Moderate Resolution Imaging Spectroradiometer (MODIS) and NOAA's Advanced Very High Resolution Radiometer (NOAA/AVHRR) and Visible Infrared Imaging Radiometer Suite (VIIRS) imagery as inputs. Daily total emissions per hotspot are then estimated by the Fire Emission Production Simulator (FEPS) module of the BlueSky Modeling Framework (Larkin et al., 2009). SMOKE was then used to prepare model-ready hourly emissions of several species (including NH_3) in a point-source format for model input.

In Environment and Climate Change Canada's operational forest fire forecasts, these emissions are used at 10-km resolution for the domain encompassing North America, with forest fires being treated as point sources with specific plume rise (Pavlovic et al., 2016). We have added 2013 forest fire emissions which were originally created for the 2013 Firework forecasts to the anthropogenic point source emissions used in the base case simulation, and modified the GEM-MACH model to be able to accommodate the changing number of major point sources each day (as the fires are parametrized as major points, and their number changes daily). Fire plume rise is an ongoing area of investigation (e.g., Heilman et al., 2014; Paugam et al., 2016); smoldering emissions tend to be emitted directly at the surface, whereas flaming emissions can inject plumes to the upper troposphere. Here, we have set all fire emissions to be distributed evenly throughout the boundary layer, which is a simplification, but one that averages out smouldering and flaming plume heights. Different parameterizations of fire plume rise are currently under development in GEM-MACH. The Fireworks fire emissions are described in detail in Zhang et al., (2017, this issue), and this study represents the first time they have been used at a 2.5-km horizontal resolution.

2.4 Model setup for three scenarios

The base, bidi, and fire+bidi models were all run with the following input files: Analysis files, which are the products of meteorological data assimilation and provide optimized initial conditions for the 12 UTC hour of each day, were obtained from ECCC archives (Buehner et al., 2013, 2015; Caron et al., 2015), and the numerical weather prediction regional GEM model was run regionally at 10-km and the high resolution GEM model was run at 2.5-km resolution to produce meteorological files to drive the model simulation. The base, bidi, and fire+bidi scenarios were run from 1 August to 7 September, 2013, where the first 11 days were "spin up" in order to allow chemical concentrations to stabilize, and are not used in our evaluation. This is a sufficient amount of spinup time, given that the atmospheric lifetime of NH_3 is typically up to 1 day (Seinfeld and Pandis, 1998; Aneja et al., 2001), and given that it is close to the transport time of air crossing the larger North American domain. The time period ~~of~~ from 12 August to 7 September was chosen to coincide with the intensive measurement campaign described in Section 3.

The model was run in a nested setup, whereby the North American domain was run at 10-km resolution using "climatological" chemical initial and boundary conditions from a 1-year MOZART simulation for all pollutants (Giordano et al., 2015). The nested Oil Sands region (which covers most of Alberta and Saskatchewan) was run at 2.5-km horizontal resolution, using the initial and boundary conditions from the 10-km North American model run. Figure 2 shows the two model domains.

The model simulations for the pilot and nested domains were not run as a continuous multiday forecast, but rather following to the operational air quality forecast process, where the meteorological values are updated regularly with new analyses, in order to prevent chaotic drift of the model meteorology from observations. Consequently, our simulation setup comprises simulations on the North American domain in 30-hour cycles starting at 12 UTC, and the Oil Sands domain in 24-hour cycles starting at 18 UTC (the 6 hour lag being required to allow meteorological spinup of the lower resolution model). The next cycle uses the chemical concentrations from the end of the last cycle as initial conditions for the next 24-30 hours. This system of staggered meteorological driving forecasts with a continuous concentration record continues until the full time period completes.

We run GEM-MACH in the 2-bin particle mode, which means that particles fall in either fine mode (diameter 0-2.5 μm) or coarse mode (diameter 2.5-10 μm), for computational efficiency (although sub-binning is used in some particle microphysics processes in order to ensure an accurate representation of particle microphysics (Moran et al., 2010)), and in order to follow the setup used for the operational 10-km resolution GEM-MACH forecast.

3 Measurements

Our three model simulations (base, bidi, and fire+bidi) are evaluated with surface, aircraft, and Cross-track Infrared Sounder (CrIS) satellite measurements. We briefly describe each of these observations below.

3.1 AMS13 ground measurements

An extensive suite of instrumentation was deployed at monitoring site AMS13 (57.1492°N, 111.6422°W, 270 m.a.s.l., Fig. 3) from 7 August 2013 until 12 September 2013. Mining operations and bitumen upgrading facilities are 5 km to the south and north of the site. It is surrounded by boreal forest, with dominant winds from the west~~.~~, averaging 1.9 m/s throughout the year. The average temperatures in the region for August are highs in the low 20s°C, and lows around 10°C, which is warm enough to make upward NH_3 flux more likely (recall Fig. 1), but temperatures drop rapidly at the end of August, into September, where the September highs average around 15°C, lows around 5°C. The skies are the clearest during August, with at least partly clear skies 50% of the time. That said, the warm season (May through September) is the wetter season (20% chance daily average), with more precipitation than during the cold season (7% chance daily average), but year round precipitation, as well as relative humidity are both relatively low in the AOSR. During the cold season (November through February), the average temperatures range from -21°C to -5°C, when the forest and soils are more likely to be a deposition sink for NH_3. During November to April, it is also much cloudier, with February having cloudy conditions 77% of the time. (All weather data cited here are from the annual report at Fort McMurray, found here: https://weatherspark.com/y/2795/Average-Weather-in-Fort-McMurray-Canada-Year-Round).

NH_3, fine particulate ammonium and nitrate, and other species were measured by the Ambient Ion Monitor-Ion Chromatograph (AIM-IC), via an inlet 4.55 m off the ground~~(Wentworth et al., 2017)~~. The uncertainty of these measurements is ± 15%. These measurements ~~appear in this issue (Wentworth et al., 2017), and~~ are described in more detail ~~there~~in Markovic et al. (2012).

Data gaps sometimes appeared in the surface NH_3 time series for the following reasons: instrument zero (Aug 14/15 and 17/18), instrument maintenance (Aug 19) and a power outage (Aug 27/28).

3.2 Aircraft measurements

During the Oil Sands Monitoring Intensive campaign, there were a total of 22 flights spanning 13 August to 7 September 2013. These measurements are described in detail in Shephard et al. (2015); Gordon et al. (2015); Liggio et al. (2016); Li et al. (2017), and are summarized here. Aircraft NH_3 measurements were conducted with a dual quantum cascade laser (QCL) trace gas monitor (Aerodyne Inc., Billerica, MA, USA; McManus et al., 2008), collecting data every 1 s. Outside air was sampled through a heated Teflon inlet tube shared with a high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS); the flow rate through the QCL was 10.8 L min^{-1}. The 1 σ uncertainty for each measurement is estimated to be ±0.3 ppbv (±35%) (Shephard et al., 2015).

Particulate NH_4^+ and NO_3^- (0- <1 μm in diameter) were measured by the Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) instrument on board the same flights, which collected data every 10 s. The ambient air was drawn through a forward facing, shrouded isokinetic particle inlet from which the HR-ToF-AMS sub-sampled. The total residence time in the inlet and associated tubing was approximately 1 second. The error on these measurements is ±9%. (Liggio et al., 2016)

Figure 3 shows a sample flight path from the campaign from 13 August 2013 – one of the thirteen flights with valid NH_3 measurements. The others took place on 15-17, 19 (two this day), 22-24, 26, 28 August, and 5-6 September 2013. NH_3 data on the other nine flights were invalidated due to instrument issues (those on 14, 20-21, 29, 31 August, and 2-4 September 2013), but were successful for the NH_4^+ and NO_3^- measurements.

3.3 CrIS satellite measurements

CrIS was launched in late October 2011 on board the Suomi NPP platform. CrIS follows a sun-synchronous orbit with a daytime overpass time at 13:30 (ascending) and a night time equator overpass at 1:30 (descending), local time. The instrument scans along a 2200 km swath using a 3 x 3 array of circular pixels with a diameter of 14 km at nadir for each pixel. The CrIS Fast Physical Retrieval (CFPR) described by Shephard and Cady-Pereira (2015) is used to perform satellite profile retrievals of ammonia volume mixing ratio (VMR) given the infrared emission spectrum from the atmosphere. This retrieval uses an optimal estimation approach (Rogers, 2000) that provides the satellite vertical sensitivity (averaging kernels) and an estimate of the total errors (error covariance matrix).

We take the CrIS retrieved profile and match it up with the closest model profile in both distance and time~~. Compute~~ , compute the distance between the CrIS pixel and model field for each time step, and then select the time step that best matches the satellite overpass time. Since the model time steps are every hour with a 10-km spatial resolution they are always matched up to better than half an hour, and within 5 km. ~~Figure 10 shows a map with four boxed regions indicating where model-measurement pairs were sampled for this study. These and the corresponding satellite fields will be discussed later in the model evaluation section below.~~

4 Model evaluation

An older version of GEM-MACH (v1.5.1) has been compared to TES satellite and aircraft measurements of ammonia over the AOSR (Shephard et al., 2015). Simulations with that version of the model were shown to be biased low, by about -0.5 ppbv, throughout the lower-tropospheric vertical profile. This represented a substantial deficit in the model predicted sources of NH_3, prompting the current work. We now compare our three GEM-MACH simulations (base, bidi, and fire+bidi) against surface point measurements at the measurement site near an oil sands facility (AMS13), aircraft measurements over the broader AOSR, and satellite measurements over the Alberta and Saskatchewan area. We will discuss which simulation agrees best with measurements and where there may still be room for additional model improvement.

4.1 At the AMS13 ground site

Figure 4 shows the timeseries of the daily average (for clarity) concentrations of NH_3 and ~~its reaction products,~~ fine-particulate NH_4^+ ~~and~~ , NO_3^-, ~~as well as its aerosol sink~~ and SO_4^{2-} at the AMS13 Oil Sands ground site for the observations and three model simulations. ~~Note that the y-scale is logarithmic to better show the differences between the three model scenarios and the measurements - however, this means that when concentrations drop to zero in the model, the line becomes disjointed. This is mainly evident in the NO_3^- time series (Fig. 4c). Figure 4~~ The hourly data were also studied, but not shown in the time series.

We first note that the NH_3 concentrations seen in the measured time series are relatively low with mean, median, and maximum of 0.6 ppbv, 0.426 ppbv, and 2.98 ppbv, respectively in the hourly data, which are lower than the 1-8 ppbv range in Bytnerowicz et al. (2010), and the 2.7 ppbv summertime mean given in Hsu and Clair (2016). However, this may be due to the different time periods and locations measured. Our mean measured values at the AMS13 site are similar to the concentrations found at U.S. AMoN background sites (http://nadp.sws.uiuc.edu/amon/).

Figure 4a shows that the base model (green) background concentrations of NH_3 are ~~biased~~ very low (nearly 0 ppbv when there is no plume influence) compared to the measurements (orange). Only during the spike on September 3-4th does the base model exceed the measured values, probably indicating a local plume event fumigating to a lesser extent in the observations than was assumed in the model. The NH_3 concentrations of the base case are biased low compared to the surface measurements by a median of -0.35 ppbv (Fig. 5a) over the time period of the campaign – comparable to the bias observed in satellite observations in Shephard et al. (2015). ~~The model-measurement differences are shown in Fig. 5a. In Fig.~~ In Figure 4, the bidi model (blue line) and fire+bidi model (red line) show a significant improvement to the NH_3 concentrations ~~during the background times,~~ compared to the base ~~case~~ model (green line). Unfortunately, during some time periods, these two versions of the model overestimate NH_3: During August 13th, the model adds a significant level of NH_3 due to fire emissions, however the surface *in situ* observations show no evidence of fire impact. During other time periods (e.g., 30 August to 3 September, and 4-7 September), the bidi model appears to have put too much NH_3 into the system. Therefore, the bidi model bias (Fig. 5a) is now 0.30 ppbv too high (median), and the fire+bidi bias is 0.32 ppbv high (median) over the time period of the campaign, resulting in an overall improvement of only 0.03 ppbv in the model bias.

~~When the influence of local plumes (defined as the base model exceeding 0.5 ppbv) is removed from the time series, the median biases are as follows: -0.36 ppbv for the base model, +0.26 ppbv for the bidi model, and +0.28 ppbv for the fire model – corresponding to an overall improvement of 0.08 ppbv in model bias for background concentrations.~~

While the bias improvement is small, the bidi and fire+bidi both have greatly improved correlation coefficients (from R=~~0.2~~ 0.1 to 0.4) and slopes much closer to 1 (from ~~0.035 to 0.614~~0.1 to 0.7), showing that those added sources are important to improve model results (Fig. 6a). ~~The correlation coefficients and slopes were similarly improved when the plume influence was removed, and only background-level concentrations were examined.~~ Additionally, the diurnal cycle (not shown) was improved in the bidi simulation, with both it and the measurements shaped like a sine curve having a minimum at 3:00-4:00am local time, and a maximum at noon local time, although the amplitude of the cycle was underestimated. Whereas, the base model diurnal cycle was flat from midnight to noon local time, and spikey from noon to midnight.

While Fig. 4a to 6a show that the addition of bidirectional flux significantly improves the model correlation coefficient, slope, and bias, there is still room for improvement. Paired t-test results indicate that the fire+bidi and measurements are still significantly different (see Table 2 for comparison statistics of all three simulations). While inherent limitations from model resolution and uncertainties may be responsible for the remaining bias, it is likely that (a) the emission potentials for the land use categories (LUCs) in the region may be causing too much re-emission of NH_3, and need refinement, and (b) the fire emissions of NH_3 are not properly distributed in the vertical, placing too much NH_3 near the surface and/or the fire emission factors for NH_3 are too high.

Refinement needed for the emission potentials and LUCs may be a significant cause of the bidi and fire+bidi model biases. Rooney et al. (2012) have shown that about 64% of the AOSR are wetlands (fens, bogs and marshes), which ~~should~~ should be mapped to the swamp LUC. However, our model currently assigns the AOSR landscape to evergreen needleleaf trees, deciduous broadleaf trees, inland lake, mixed shrubs, and mixed forests (and none of the region to swamp). This would lead to an overestimation of re-emission given that bogs are fairly acidic and our swamp emission potential is lower than the aforementioned LUCs. Other evidence for these two explanations will be presented below in Section 4.3.

The time series, model-vs-measured correlations, and model biases of NH_4^+, NO_3^-, and SO_4^{2-} are also shown in Fig. 4 to 6 (b, c, and d, respectively). For NH_4^+ and SO_4^{2-} there is very little change despite the increase in NH_3 that the bidirectional flux yields. The bias is very small for all three model scenarios, and the correlation coefficients are all relatively poor. So while there is an improvement to modelled NH_3 with bidirectional flux, there is a neutral affect on fine particulate NH_4^+. This may be because the charge of NH_4^+ in the particles is already enough in the base model to balance the charge of $2\times SO_4^{2-} + NO_3^-$ in the aerosols, thus, causing any additional NH_3 (from bidi and fires) to remain in the gas phase. Or it could be due to additional wet scavenging of the additional ammonium, which will be discussed in Section 5.2. The change in NH_3 concentrations has no effect on SO_4^{2-} since particulate SO_4^{2-} is not sensitive to the amount of NH_3/NH_4^+ available, and is dominated by anthropogenic and fire emissions. For NO_3^-, the base model bias was quite small at 0.01 μm/m^3, however the addition of bidi and fire+bidi further reduced that bias to 0.0011 and 0.0004 μm/m^3, respectively, which is a significant improvement. The correlation coefficient for NO_3^- also improved from about 0.1 to 0.3 (Fig. 6c).

4.2 Along the OS campaign flight paths

There were 13 flights during the OS campaign that had valid (above detection limit, and no instrument error) NH_3 measurements, and 22 flights that had valid NH_4^+ (0-1 μm diameter) measurements. The flight path of the first flight, which occurred on 13 August 2013 is shown in Fig. 3; chosen as an example because this flight sampled mainly background NH_3 concentrations (rather than facility plumes).

Figure 7 shows the NH_3 concentrations along this flight path over time. Here the hourly model output is interpolated to the same time frequency as the measurements. The model also has spatial resolution limits when comparing to the aircraft. However, we clearly see that for this flight, the bidirectional flux has increased NH_3 concentrations, bringing them closer to the measured values ~~.~~ (median biases for this flight are -1.38, 0.68, and 0.69 ppbv in the base, bidi, and fire+bidi simulations). There is little change when fires are added (Fig 7d vs c) because this flight did not pass through a fire plume.

Figure 8 shows the ~~corresponding~~ model-measurement ~~difference~~ differences and the model vs measurement scatter plots for the combined set of all flight paths for hourly-average concentrations of NH$_3$ and NH$_4^+$. For NH$_3$ the median base model bias is -0.75 ppbv, comparable to the bias observed in Shephard et al., 2015, with the bidi model bias improving to -0.24 ppbv, and the fire+bidi bias to -0.23 ppbv. Also the best correlation coefficient and slope is achieved by the fire+bidi scenario. The use of the bidirectional flux has thus reduced the model bias relative to the aircraft observations by a factor of three. The fire+bidi simulation has the best statistics compared to measurements, as summarized in Table 2.

Again, the NH$_4^+$ results show little change despite the increase in NH$_3$ concentrations. The small bias from the base case gets insignificantly smaller, and the slope and correlation coefficients are all negligibly changed.

4.3 In the vertical profiles across the region

The CrIS satellite has many observations over North America during the 2013 Oil Sands campaign. We have evaluated the model with these observations in a number of ways:

1. ~~Daytime overall average in this area~~ All daytime data from Aug 12 - September 7th, 2013; model-measurement comparisons over a large region encompassing Alberta and Saskatchewan~~(blue box in Fig. 10~~, latitude range: 48-60 °N, longitude range: 100-122 °W), which contains agricultural areas, a number of cities, the northern boreal forest, and the Oil Sands facilities.

2. Case studies where we attempt to isolate fire emissions ~~(magenta box in Fig. 10),~~ and non-fire conditions ~~(cyan and black boxes in Fig. 10)~~ to evaluate both new components (fires and bidi) of the model.

The latitude and longitude ranges of our model-measurement pairs are given in Table 1. The satellite passes over these regions at approximately 1pm and 1am local time.

~~In the large box spanning northern Alberta and Saskatchewan, there~~ There were over 60 000 model-measurement pairs between the model and the CrIS satellite over the model domain during August 12th to September 7th, 2013. Figure ~~10 shows the surface NH$_3$ concentrations over that region on three sample days (3 Sept, 1 Sept and 12 Aug, 2013), as well as sample Aqua MODIS true colour composite map for that day. Figure 9presents statistics~~ 9top panel presents model biases for the entire dataset in a box and whiskers plot of the vertical NH$_3$ profiles at five vertical levels~~, along with the model–satellite bias for the base model, bidi model, and fire+bidi model. The~~. The left-most panel shows the NH$_3$ concentrations measured by CrIS, and the right-most panel shows the diagonal elements of the CrIS averaging kernels, illustrating the sensitivity of the satellite measurements to each vertical level. The NH_3 concentrations over Alberta and Saskatchewan measured by CrIS are very similiar to those found by TES in the Shephard et al. (2015) study for the AOSR region.

~~In Fig. 9 we see that the~~ The middle panels show the model biases from the three simulations. The fire+bidi model has the smallest bias in the highest three layers, but the bidi model has the smallest bias in the two lowest layers, whereas the fire+bidi model increases NH_3 concentrations further (though still a smaller absolute bias compared to the base case, Fig. 9top). This could be due to an overestimate of the bidirectional flux re-emissions or of the fire emissions, or to an underestimate of the altitude of the fire emissions, or a combination of all three factors. In order to distinguish between these possibilities, two case studies were examined further below. The statistics from the model-CrIS comparison can be found in Table 2. That summary shows that the fire+bidi simulation performs better than the base and the bidi simulations.

The spatial distribution of modelled NH_3 can also be evaluated with CrIS measurements, as shown in the bottom panel of Figure 9. These are maps of the average surface NH_3 concentrations from the base model, the fire+bidi model, and the CrIS satellite. The fire+bidi model over-predicts the effect of fires in the middle of northern Saskatchewan, but appears to be missing fires in north-western Manitoba. Other than fire influence, the spatial distribution in the fire+bidi model is the same as that of the base model, but with significant increases in overall concentrations. And the spatial distribution of the model simulations is different from the spatial distribution that CrIS measures. For example, the model predicts much higher NH_3 concentrations near the city of Edmonton than CrIS shows. That said, the addition of bidirectional flux has greatly improved the NH_3 concentrations in the northern part of the province, where there was almost none in the base model.

We selected three sample days (3 Sept, 1 Sept and 12 Aug, 2013) that we use for the case studies, and surface NH_3 concentrations over that region as well as sample Aqua MODIS true colour composite maps for those days are shown (Fig. 10). The four boxed regions on those maps indicate where model-measurement pairs were sampled for this study. The cyan and black boxes in Fig. 10a and b are the regions where we sample clear-sky, no-fire conditions on 3 and 1 September 2013, respectively. The magenta box in Fig. 10c is the region where we isolated our fire case study on 12 August 2013. The blue box is the region we discussed above, which we analysed for the full time period simulated (12 Aug - 7 Sep 2013, Fig. 9top).

4.3.1 Case study 1: clear-sky days with little fire influence - evaluating bidi

In order to evaluate the bidirectional flux component separately from the fire component, we selected September 1st (southern, agricultural region - black box in Fig. 10b), and 3rd (northern, boreal forest and AOSR region - cyan box in Fig. 10a), where the MODIS map (EOSDIS NASA World view map, worldview.earthdata.nasa.gov) shows very little hot spots from fires, and that the conditions were relatively cloud and smoke free (which yield the most CrIS observations). See Table 1 for the latitude and longitude ranges. Figure 10 also shows the surface NH_3 concentrations as observed by

CrIS on each of those days. Figure 11a shows that in the north, the bidi model improves the bias from -0.84 ppbv to -0.07 ppbv in the lowest vertical level, and smaller, but still significant, improvements to the bias at the other levels. The fire+bidi model has a nearly identical impact as the bidi model, which is expected in a fire-free zone. Therefore, the GEM-MACH-Bidi model performs very well in northern Alberta and Saskatchewan where there is mainly boreal forest, and background-level NH_3 concentrations. This also implies that the LUC assignment discussed in Section 4.1 may only apply to a small region around the AOSR, and not to the overall large region we've defined here.

In the southern region (Fig. 11b), the addition of bidirectional flux moves the bias from near-zero to +1.02 ppbv in the lowest level. In this case, the base model with no bidirectional flux appears to be the most accurate model in areas dominated by agricultural sources. There are two possible explanations: a) agricultural emissions are too high in the base model, and the addition of the bidirectional flux leads to an overestimation of the NH_3 amounts, or b) re-emissions from bidirectional flux from crops are not significant. The literature (Bash et al., 2010; Massad et al., 2010; Zhang et al., 2010; Zhu et al., 2015) indicate that crops do indeed re-emit NH_3, therefore, (a) is the more likely explanation. The agriculture NH_3 emission inventory we used was created by the NAESI (National Agri-Environmental Standards Initiative) project (Bittman et al., 2008; Ayres et al., 2009; Makar et al., 2009) have about 30-200% uncertainty associated with them (Bouwman et al., 1997; Asman et al., 1998). Therefore, with improved national NH_3 emission inventories, the GEM-MACH-Bidi should improve model results across the domain.

4.3.2 Case study 2: a clear day with significant fire influence - evaluating fires

In order to evaluate the fire component separately from the bidirectional flux, we selected August 12th (a northern region with little-to-no agricultural contributions) where the MODIS map shows numerous hot spots from fires and smokey conditions (Fig. 10c, magenta box). The base and bidi models underestimate NH_3 concentrations (Fig. 11c) by -6.22 and -5.84 ppbv, respectively (in the lowest vertical layer), but ~~that~~ the fire+bidi model overestimates NH_3 by +4.06 ppbv. The fire+bidi version of the model still has the lowest bias of the three simulations, however, either (a) the fire+bidi model does not distribute the fire emissions properly in the vertical, (b) the fire emissions of NH_3 are too high, and/or (c) the model is not properly representing NO_2 and SO_2 in the fire, and so the conversion of NH_3 to NH_4^+ is underestimated. ~~Both~~ It is potentially a combination of all three explanations, and we further elaborate below.

- For explanation (a), both fire plume rise and fire emission factors are on-going areas of study. ~~It is likely a combination of all three explanations; in~~ In the model the fire emissions are distributed evenly ~~through out~~ throughout the boundary layer (the first 3-4 layers ~~from~~ in Fig. 11c), however, Shinozuka et al. (2011) suggest that sometimes the fire plumes are ~~in a Gaussian distribution located in a~~ distributed normally in a thin layer aloft~~(which is an option for GEM-MACH that is currently under development)~~. However, should that be the case ~~, the~~

~~bias would move~~ for the real-life fires in this case study, the model bias would be negative at at least one of the levels in Fig. 11c, which it ~~does not (unless the fire plume is actually above 4 km, however, it was found that the plume heights for the Fort McMurray fires of 2016 reached only up to 3-3.5 km, shown by the lidar on CALIPSO satellite)~~is not. Figure 11c shows that the positive bias extends throughout the first three vertical layers, and in the top two vertical layers, the bias does not move further negative (as would happen in the fire plume were actually at those altitudes in real life).

- (a) Our bias would be very high at low levels if the real fire plumes were actually above 4 km (above the altitudes we studied), however, it was found that the plume heights for most of the Fort McMurray fires of 2016 reached only up to 3-4 km altitude range based on the NASA Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) and Multi-angle Imaging SpectroRadiometer (MISR) satellite observations. Therefore, this is not likely the case.
- Explanation (b) seems the most likely, as the uncertainty on emission factors for NH_3 from wildfires is very large (e.g., 50-100% depending on the fuel type Urbanski, 2014), and could easily be overestimated. ~~Similarly, the NO_x~~
- The NO_x and SO_2 ~~emission factors have~~ fire emission factors (c) have smaller uncertainties of 10-40% (Urbanski, 2014).

Unfortunately, there were no flights that captured the fine structure of the fire plumes during the 2013 monitoring intensive campaign that can be used to further corroborate the vertical distribution of the fire plumes. There will however be flight observations of fires during the planned 2018 AOSR measurement campaign. Therefore, the model may be further improved with reduced NH_3 emission factors for fires, and/or improved vertical distribution of fire plumes.

5 Impacts of bidirectional flux and forest fires on NH_3 concentrations

5.1 Effect on ambient concentrations

Given that the overall fire+bidi model agrees best with measurements in the greater Alberta/Saskatchewan region (discussed throughout Section 4) and contains all known missing sources of NH_3, we can use the model to answer one of our key questions: What percent contributions to total ambient NH_3 concentrations came from bidirectional flux and from forest fires during the study time period? We do so by subtracting the bidi model output from the fire+bidi model output to get the forest fire component, and subtracting the base model output from the bidi model output to get the bidi component. The absolute differences are calculated as follows:

$$bidicomponent = NH_3^{bidi} - NH_3^{base} \tag{5}$$

$$firecomponent = NH_3^{fire+bidi} - NH_3^{bidi}, \tag{6}$$

which tell us how many ppbv of NH$_3$ on average comes from re-emissions of NH$_3$ (upward component of bidirectional flux), and from fire emissions.

The percent differences are calculated as follows:

$$bidipercent = \frac{NH_3^{bidi} - NH_3^{base}}{NH_3^{fire+bidi}} \times 100\% \tag{7}$$

$$firepercent = \frac{NH_3^{fire+bidi} - NH_3^{bidi}}{NH_3^{fire+bidi}} \times 100\%, \tag{8}$$

which tell us what percent of ~~*total*~~ total NH$_3$ concentrations on average comes from re-emissions of NH$_3$ (upward component of bidirectional flux), and from fire emissions, assuming the NH$_3$ from our fire+bidi simulation is the true total NH$_3$.

~~Over the 2.5-km model domain (averaged over~~ We perform this calculation on the averaged model output (12 August to 7 September 2013) ~~, we do this calculation (See Fig. 12)~~ over the 2.5-km model domain, and get an average of 20.3% (or 0.42 ppbv) ~~of~~ and a median of 10.4% for ambient surface NH$_3$ concentrations ~~comes~~ that come from forest fires ~~– though the median amount is only 10.4% for fires.~~ (Fig. 12). The mean and median are so different because fires are sporadic, large contributions to NH$_3$ concentrations, and the mean value is more sensitive to the big outliers. We get an average of 56.6% (or 1.24 ppbv) from bidirectional flux (56.3%~~median). The~~ , median), and the remaining 23.1%~~(average)~~ , average (33.3 %~~(~~, median) comes from direct emissions from anthropogenic sources (agriculture, fossil fuel combustion, oil sands industry, etc). These numbers are summarized in Table 3. The increase in NH$_3$ concentrations due to the bidirectional flux scheme is of the same order of magnitude as that found in the Zhu et al. (2015) study using the GEOS-Chem model, during the month of July, in the United States (where they found 1 ppbv increase in surface concentrations due to bidirectional flux). It is also similar to values found in Europe in the Wichink Kruit et al. (2010) study.

Over the model domain, the minimum bidi influence on surface NH$_3$ is just north of Edmonton, where only 1% of NH$_3$ comes from bidi. Similarly, two AOSR facilities north of Fort McMurray stand out as having small bidi influence (12-40 %, surrounded by values in the 90s% - Fig. 12~~,~~ d). Also, any remote region with fire emissions will have a small percentage contribution from bidirectional flux during the fires, as they are in northern Saskatchewan (Fig. 12~~,~~d). This is expected given that the average concentrations in cities and near large sources are very close to, or exceed the compensation point. The absolute maximum in the bidi component map is 4.5 ppbv in the lower right corner (an agricultural region with high NH$_3$ emissions), and the minimum is 0 ppbv (Fig. 12~~,~~b). This means that nowhere in the domain, did the bidirectional flux formula result in ~~*more*~~ more net deposition than the base model calculated via the Welesley/Robichaud/Zhang scheme. The maximum fire contribution to surface NH_3 is 27.9 ppbv where large fires occurred in northern Saskatchewan (Fig. 12~~,~~c).

5.2 Effect on Deposition

Similar to our analysis from the previous section, we can use the model to determine how bidirectional flux and fires impact daily NH~~$_3$ dry deposition~~$_x$ deposition (which equals the dry deposition of NH_3 + the wet deposition of NH_4^+). Figure 13 shows the average daily net ~~dry~~ deposition (or net flux) of NH~~$_3$~~$_x$ from the base, bidi, and fire+bidi models. Negative (or blue) indicates net deposition (downward flux), and positive (or red), net emission (upward flux). The base model (Fig. 13a) had no re-emission (upward flux) option, thus NH_3 was always net dry deposited in that scenario~~, and was 9.85×10^{-6} moles/m^2/day on average~~. The bidi (Fig. 13b) and fire+bidi (Fig. 13c) maps show that ~~over much~~ most of the Alberta and Saskatchewan area ~~, there is net emission of NH_3, and net deposition only occurs where concentrations are highest (~~has net deposition (e.g., near the cities, agriculture, and forest fires)~~. Average flux has changed to~~, but that some regions (with low atmospheric NH_3 concentrations) have net emission of NH_x. The dry NH_3 flux is net positive over the domain, ~~with averages of $+2.44\times10^{-5}$ moles/m^2/day and $+2.10\times10^{-5}$ moles/m^2/day for~~however, when the increase in wet NH_4^+ is accounted for, the net flux of NH_x is still negative (downward). This is very similar to what Wichink Kruit et al. (2010) found in a 2007 study in Europe; a reduction in dry NH_3, compensated by an increase wet NH_4^+ deposition.

Note that the ~~bidi and fire+bidi cases, respectively. Note that this result is partly due to our~~ assumption of an infinite soil pool of NH_4^+ ~~. Following the~~ in our bidirectional flux scheme has not caused an overwhelming upward flux of NH_x. In fact, the average results across the domain actually have more deposition in the fire+bidi scenario than in our base scenario. Table 4 shows the mean and median net NH_x flux for each scenario (presented as deposition, so negative signs removed). That said, following the soil pool approach (Pleim et al., 2013; Zhu et al., 2015), the soil pool of NH_4^+ ~~would~~ may eventually get depleted~~, thus the average net flux may not be as largely positive as we calculated in this study.~~. However, that is very unlikely for the following reasons: (1) Deposition of NH_x throughout the year continually replenishes the soil pool – especially when temperatures are cooler in winter, spring, and fall, since the compensation point is exponentially dependent on temperature. (2) The short time frame of this study would not be long enough to deplete the soil pool. For example, Zhu et al. (2015) needed to spin up their model for three months in order to get the NH_4 soil pool stable.

In the AOSR near Fort McMurray, we can compare our NH_3 dry deposition results to those calculated in Hsu and Clair (2015). Their values range from 0.7 to 1.25 kg-N/ha/year (or 1.13 to 2.01 × 10^{-5} ~~mol~~moles/m^2/day), and ours are 10 ~~×~~ times lower at around 0.13 kg-N/ha/year (or 2.12 × 10^{-6} ~~mol~~moles/m^2/day) near Fort McMurray, and do not vary much among our three model scenarios. Our deposition underestimate may be partially due to the fact that our modelled ambient NH_3

concentrations are also low compared to those measured in Hsu and Clair (2016) near Fort McMurray. They measured an average of 1.55 ± 0.6 ppbv (1.9 μg/m~~^{2}~~^{3}) at Fort McMurray, whereas our fire+bidi model has an average of 1.01 ppbv there (0.73 ppbv in bidi, and 0.39 in base). There may also be differences in that our model has more of the NH$_x$ deposition coming down as NH$_4^+$, rather than as NH$_3$.

~~Figure ?? (a) shows the difference in deposition between the bidi and base cases – essentially the contribution of bidi to the total flux. The bidi model has increased flux in the positive direction everywhere by an average of +3.43~~Our fire+bidi NH$_x$ deposition values (Table 4 are well in line with reported NH$_3$ deposition in Kharol et al. (2017), who report satellite-derived NH$_3$ deposition of about 2.1-7.0$\times 10^{-5}$ ~~μ~~moles/m^2~~across the domain. Figure ?? (b)shows the~~ /day in Alberta), and are at the low end of NH$_3$ deposition values reported within Behera et al. (2013).

The difference in deposition between the fire+bidi and bidi cases ~~–~~– which is the contribution of fires to the total ~~flux. The fires have decreased flux (in other words~~ NH$_x$ flux – showed that the fires increased downward flux~~, or deposition)~~ /deposition over large swaths of the domain ~~.~~ (e.g., difference between Figure 13c and b). The fires contributed an average of ~~-3.47~~1.954 $\times 10$~~$^{-6}$ μ~~$^{-5}$ moles/m^2~~of~~ /day of NH$_x$ deposition across the domain.

~~The wet deposition of NH$_4^+$ was also modelled and analysed in a similar way (Fig. ??). Unlike NH$_3$, since there is no re-emissions of NH$_4^+$ in the model, all flux is negative.~~ While the particulate NH$_4^+$ concentrations did not change much in our three simulations (see Sections 4.1 and 4.2), the wet deposition of NH$_4^+$ increased significantly going from the base to bidi to fire+bidi models~~(Fig. ?? from a to b to c).~~. This is in contrast to what Zhu et al. (2015) found, which was little change to NH$_4^+$ due to bidirectional flux. However that could be due other parameters, such as the meterological conditions, scavenging parameters, and/or gas-particle partitioning of NH$_x$. It would seem that in GEM-MACH-Bidi, the increased NH$_3$ concentrations were scavenged by precipitation. The average NH$_4^+$ deposition from the three simulations ~~was: -2.04$\times 10^{-5}$ μmoles/m^2 for base, -4.25$\times 10^{-5}$ μmoles/m^2 for bidi, and -5.86$\times 10^{-5}$ μmoles/m^2 for fire+bidi. That is nearly a~~ had a nearly threefold increase in the NH$_4^+$ deposition due to the increased NH$_3$ concentrations that the fire+bidi simulation yields. ~~Note that in the soil pool approach of Pleim et al. (2013); Zhu et al. (2015), this deposited NH~~The average NH$_4^+$ ~~would contribute towards the soil pool, which could be re-emitted as NH$_3$. In our case, once deposited, the NH$_4^+$ is not re-emitted~~wet deposition for our fire+bidi simulation is 5.86$\times 10^{-5}$ moles/m^2/day, which is in between values reported in the United States in Stensland et al. (2000) (where they found an average of 1.9$\times 10^{-5}$ moles/m^2/day over the country), and in Japan in Murano et al. (1998) (where they found an average of 10.3 $\times 10^{-5}$ moles/m^2/day over the country).

In the three scenarios, the average daily relative ratio of dry/wet deposition was: 0.43 for base, -0.77 for bidi, and -0.51 for fire+bidi (the negative value for the bidi and fire+bidi cases are because of the average upward direction of NH$_3$). Since all average ratios are less than 1, this means that most of the removal process is from wet deposition, rather than dry deposition (even for the base case that had no re-emission of NH_3). Therefore, increased monitoring of wet deposition in the region would be useful. These results may also be useful for AEP terrestrial/aquatic scientists interested in nitrogen eutrophication. ~~The negative value for the bidi and fire+bidi cases are because of the average upward direction of NH_3.~~ Maps of these ratios can be found in the supplemental material.

6 Conclusions

The GEM-MACHv2 air quality forecasting model was altered to include both the Zhang et al. (2010) bidirectional flux scheme for NH_3 and forest fire emissions of all species. This new "fire+bidi" model greatly improves the simulated NH_3 in the modelled Oil Sands domain at 2.5-km resolution when compared to independent *in situ* measurements at the ground (at the AMS13 oil sands monitoring site) and aloft (aircraft measurements), as well as at 10-km resolution when compared to ~~remote sensing~~ cutting-edge satellite measurements from the CrIS instrument. ~~We have also shown that for further improvements in the Alberta/Saskatchewan region, the NH3 emission factors for fires, and the NH3 emissions from agriculture likely need to be reduced~~Almost all comparison statistics are best with our fire+bidi simulation. This suggests that the fire+bidi model shows promise for improving NH_3 model predictions elsewhere and during other time periods. However, more work is required to validate the model in other regions of the continent (e.g., with the Wood Buffalo Environmental Association (WBEA) and the U.S. Ammonia Monitoring Network (AMoN) surface networks, and further CrIS satellite measurements), and for different time periods (e.g., springtime fertilizer season, cooler conditions, etc.). We ~~'ve~~ have also shown that for further improvements in the Alberta/Saskatchewan region, the NH_3 emission factors for fires, and the NH_3 emissions from agriculture likely need to be reduced.

Despite the significant increase in NH_3 concentrations with these additional sources, the impact on its byproduct, NH_4^+, was miniscule - as was the change to SO_4^{2-} concentrations (0.02 μg/m^3 for each). The model bias for those species was not significantly changed in either direction. This is probably because of the extra NH_4^+ wet scavenging by precipitation, and the NH_3 concentrations were already high enough (before adding the extra sources) to charge balance the SO_4^{2-} and NO_3^- in the aerosols. Thus, any additional NH_3 would remain in the gas phase. That said, the model bias for NO_3^- at the AMS13 ground station was essentially removed with the fire+bidi model.

By running the base, bidi, and fire+bidi model scenarios, and taking the fire+bidi results as "true", we were able to calculate their differences and determine the average contributions from each source. We found that, on average, during the 12 August to 7 September 2013 time period in the Alberta/Saskatchewan model domain, 23.1% of surface NH_3 comes from ~~anthropogenic sources~~direct anthropogenic emissions, 56.6% of surface NH_3 comes from bidirectional flux (re-emission from soils and plants), and 20.3% of NH_3 comes from forest fires. Possible sources of error that remain in the bidi and fire+bidi simulations are the agricultural and fire emissions of NH_3, as well as the emission potentials for different land-use categories. The fraction of NH_3 from fires is highly variable depending on the time periods and spatial domain analysed: on average from 12 August to 7 September 2013, the largest impact was in northern Saskatchewan. We expect the re-emission source to be near the highest at this time of year because of the high temperatures, and this source should be much lower during the cold season, when deposition is expected to dominate the bidirectional flux process.

The bidirectional flux process has decreased NH~~$_3$~~$_x$ deposition on average ~~, resulting in~~ across the domain, with some areas having a net emission of NH_3~~across the domain. This increase~~. However, that upward flux is due to the ~~bidirectional flux, coupled with the increase driven by fires , enhances wet deposition of NH_4^+ by a factor of three~~low atmospheric concentrations and high temperatures, and does not exceed the amount of NH_x deposition that occurs during the cooler winter and spring times. When fires are also taken into account, the net NH_x deposition is greater, on average across the domain, compared to the base model.

Acknowledgements. The project was supported by Environment and Climate Change Canada's Oil Sands Monitoring program (OSM), and the Climate Change and Air Quality Program (CCAP). We would also like to acknowledge the University of Wisconsin-Madison Space Science and Engineering Center Atmosphere SIPS team sponsored under NASA contract NNG15HZ38C for providing us with the CrIS level 1 and 2 input data, in particular Keven Hrpcek and Liam Gumley.

Data availability: The CrIS-FRP-NH3 science data products used in this study can be made available on request (M. W. Shephard, Environment and Climate Change Canada, Toronto, Ontario, Canada). Similarly, the AMS13 observations can be made available on request from Greg Wentworth (AEP), and the model output or code from Cynthia Whaley (ECCC). The aircraft observations are on the ECCC data portal (http://donnees.ec.gc.ca/data/air/monitor/ambient-air-quali

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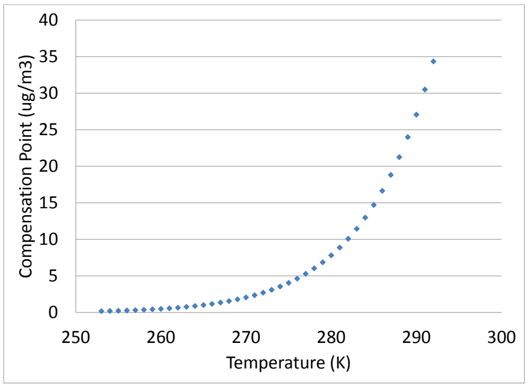

Figure 1. Compensation point (C_g) relationship to temperature; C_g for evergreen needleleaf LUC shown as example.

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~~Maps modelled daily average (a) bidi and (b) fire components to dry deposition. In all maps, red/positive represents upward flux, and blue/negative represents downward flux. These are daily amounts, averaged over 12 August to 7 September, 2013.~~

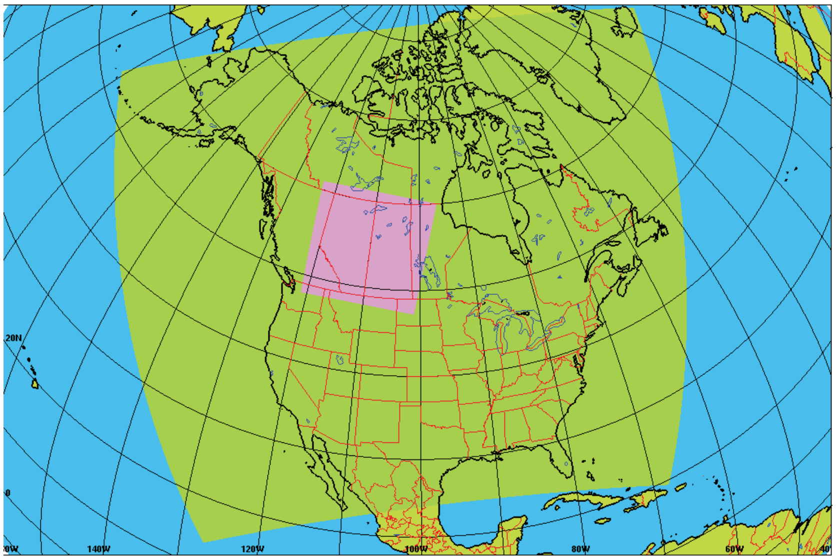


Figure 2. Map of 10-km resolution continental piloting model domain (green), and 2.5-km resolution nested model domain (purple).

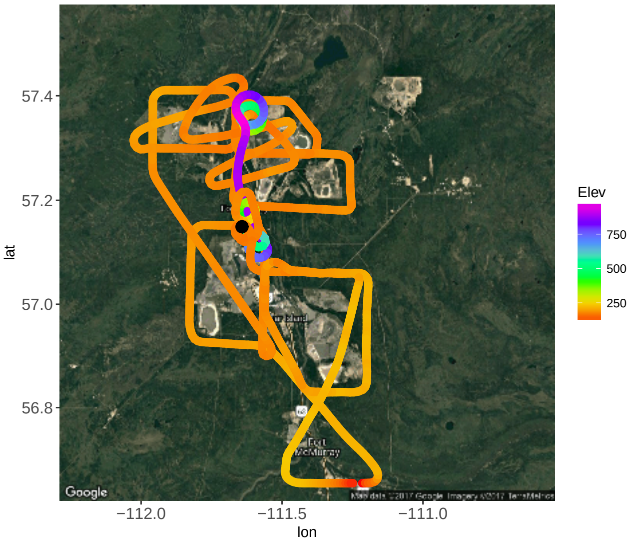


Figure 3. Flight path on 13 August 2013, where elevation (in meters) is denoted by the colour scale, and the AMS13 site is indicated by a black circle.

~~Maps of the modelled average NH_4^+ wet deposition for (a) base (b) bidi, and (c) fire+bidi models. Negative represents downward flux. These are daily amounts, averaged over 12 August to 7 September, 2013.~~

~~(Top panels) Images of the Alberta/Saskatchewan region with clouds and fire hotspots from MODIS. (Bottom panels) Map of CrIS-measured surface NH_3 concentrations, with coloured boxes showing the regions where model and satellite measurements were sampled. These three examples are for (a) northern bidi case study (cyan), (b) southern bidi case study (black), and (c) fire case study (magenta), discussed in Section 4.3), and the blue box is the region of our overall comparison.~~

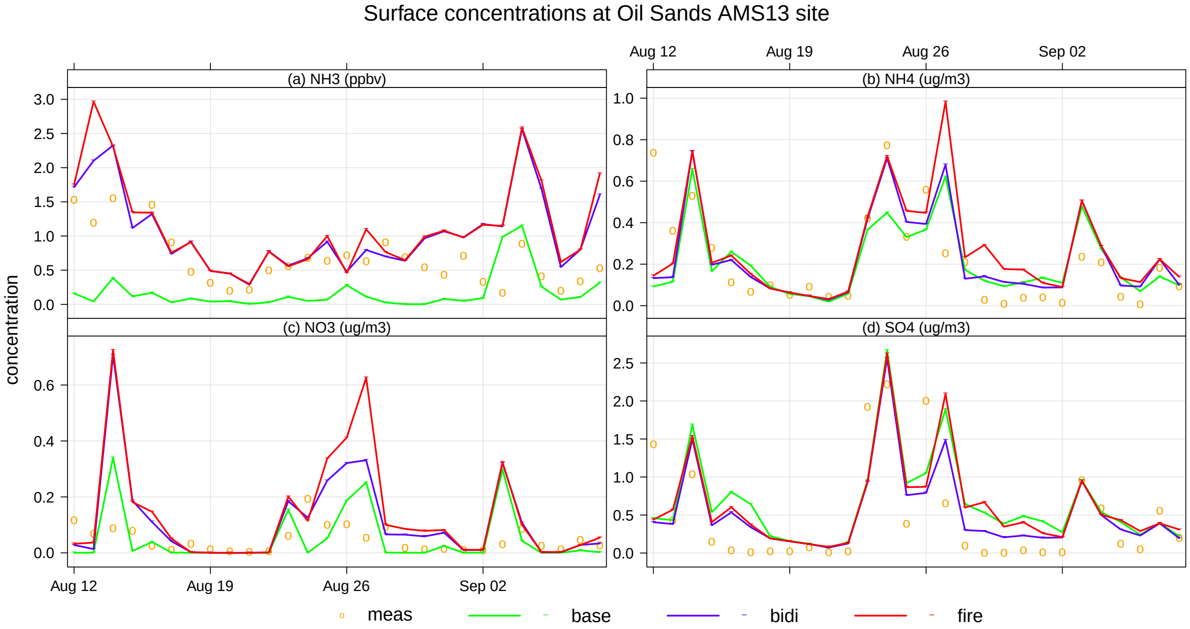


Figure 4. Surface daily average (a) NH_3, (b) fine particulate NH_4^+, (c) NO_3^-, and (d) SO_4^{2-} concentrations at the AMS13 ground site in the AOSR. Measurements in orange, base model in green, bidirectional flux model in blue, and fire+bidi model in red.~~Y-scale is logarithmic.~~

Table 1. Latitude and longitude ranges that the model was evaluated over with the CrIS satellite measurements

domain	date (in 2013)	lat range (°)	lon range (°)
AB/SK large domain	12 Aug to 7 Sept	48 to 60 N	-122.0 to -100.0 W
northern, no-fire case study	3 Sept	55 to 60 N	-120.0 to -110.0 W
southern, no-fire case study	1 Sept	49 to 53.5 N	-117.0 to -106.0 W
northern, fire case study	12 Aug	56.5 to 60 N	-110.0 to -104.4 W

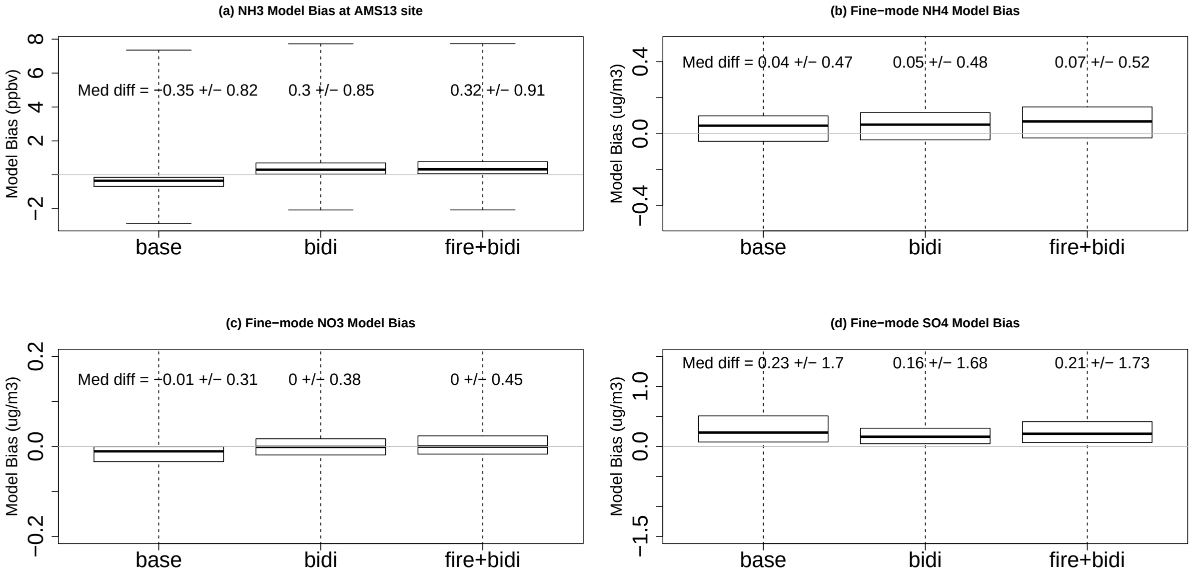
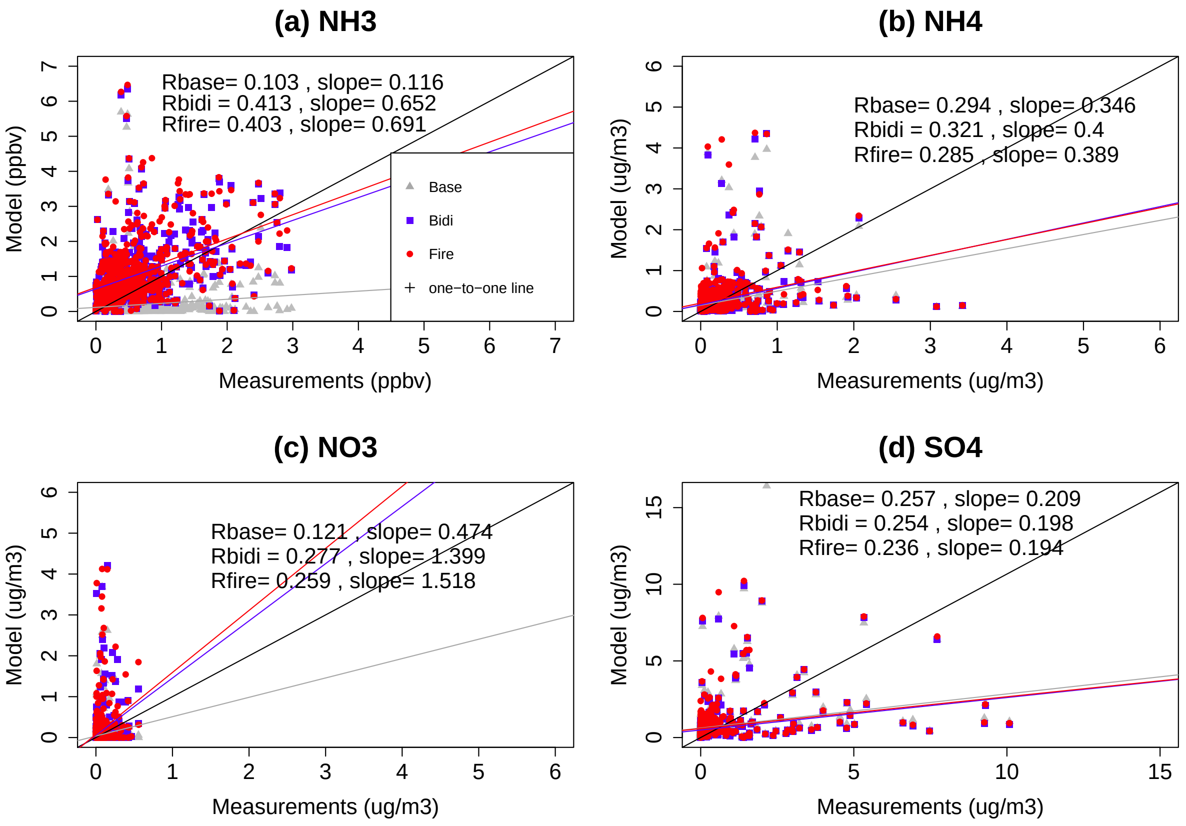


Figure 5. ~~Model-measurement~~ Hourly model-measurement bias in surface (a) NH_3, (b) NH_4^+, (c) NO_3^- and (d) SO_4^{2-} concentrations at the AMS13 ground site in the AOSR.



(a) NH3

(b) NH4

(c) NO3

(d) SO4

Figure 6. ~~Modelled~~ Hourly modelled vs measured surface (a) NH_3, (b) NH_4^+, (c) NO_3^- and (d) SO_4^{2-} concentrations at the AMS13 ground site in the AOSR. Base model in grey, bidirectional flux model in blue, and fire+bidi model in red.

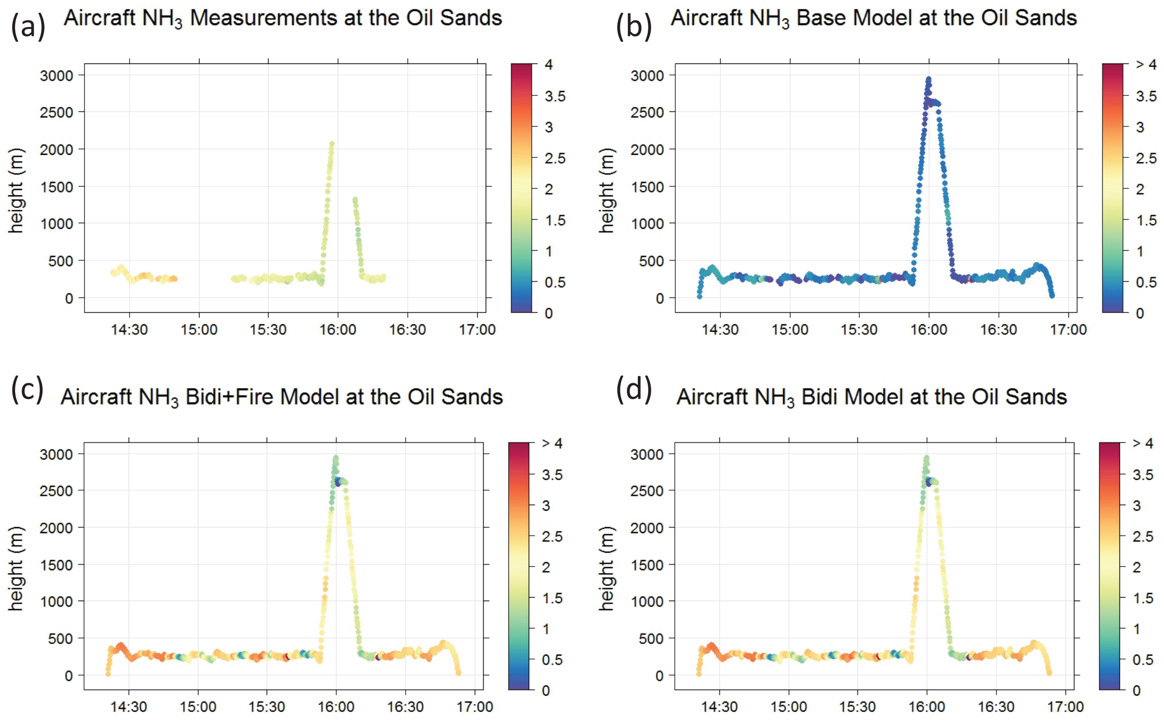


Figure 7. NH_3 concentrations aloft (colour scale) over the OS region during the 13 August 2013 flight. (a) measurements, (b) base model, (c) fire+bidi model, and (d) bidi model.

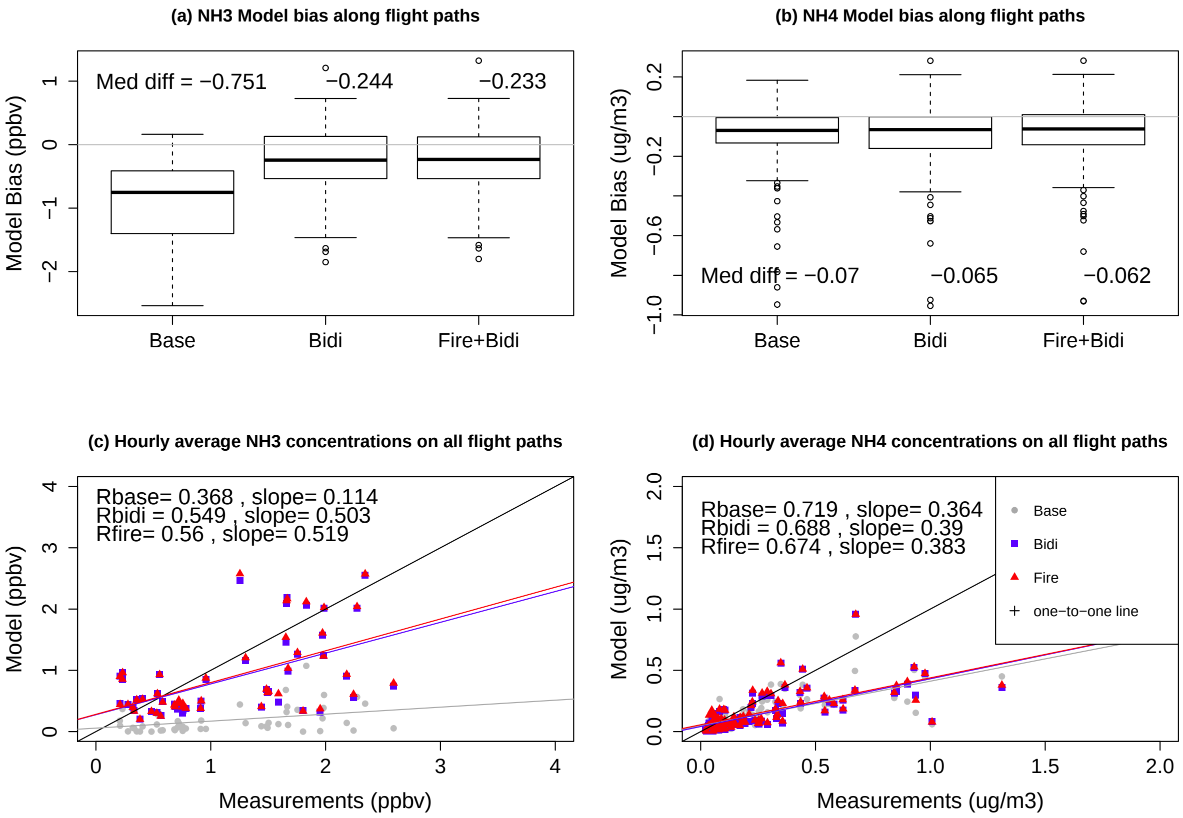


Figure 8. Hourly averages along all flight paths over the OS region during the summer 2013 campaign: Model-measurement bias in (a) NH_3 and (b) NH_4^+. Modelled vs measured (c) NH_3 and (d) NH_4^+ concentrations aloft. Base model in grey, bidirectional flux model in blue, and fire+bidi model in red.

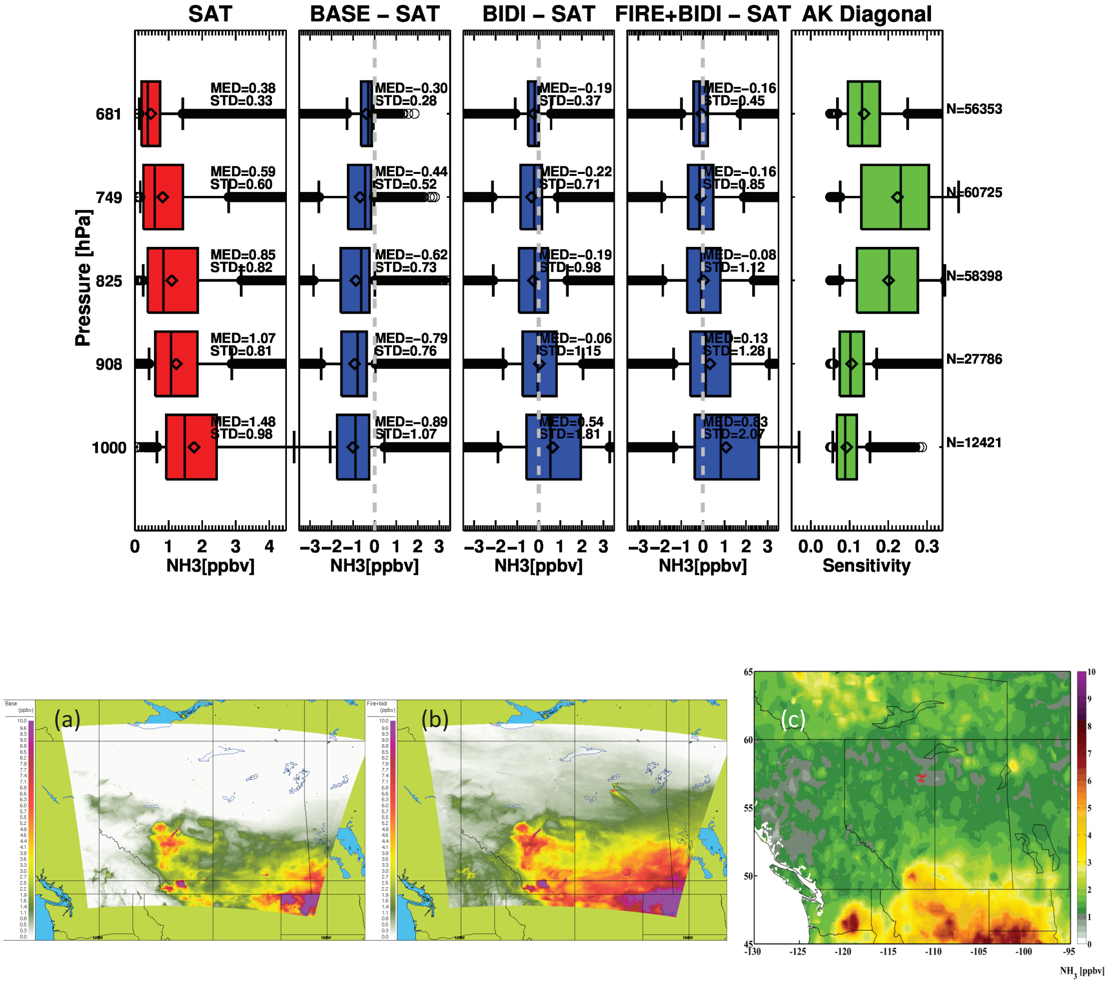


Figure 9. Top panel: (a) NH_3 vertical profile as measured by CrIS satellite, difference between measurement and (b) base model, (c) bidi model, and (d) fire+bidi model, and (e) averaging kernel of CrIS satellite for NH_3 retrieval. Bottom panel: average (12 Aug - 7 Sep 2013) surface NH_3 concentrations given by the (a) base model, (b) fire+bidi model, and (c) CrIS satellite.

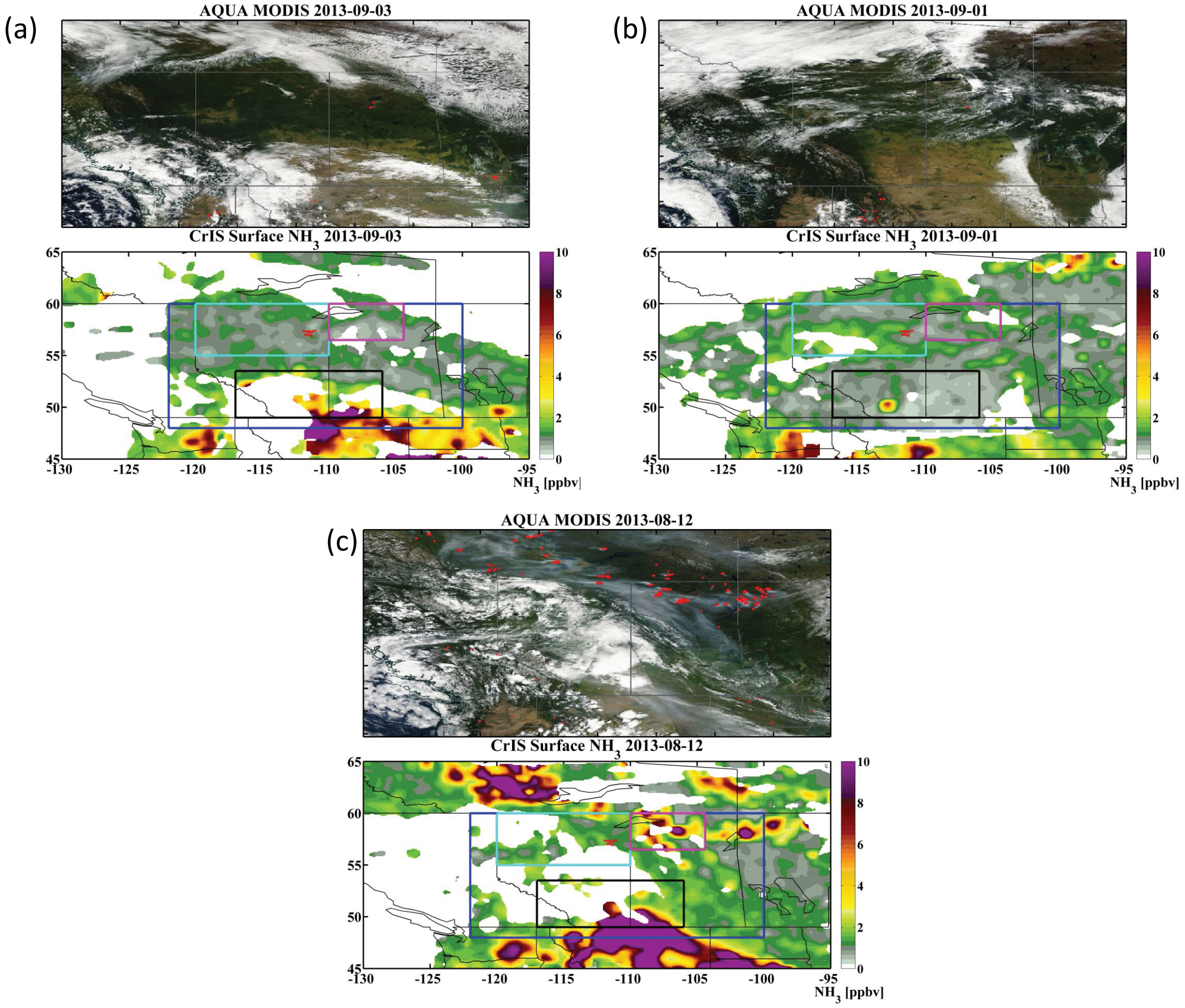


Figure 10. (Top panels) Images of the Alberta/Saskatchewan region with clouds and fire hotspots from MODIS. (Bottom panels) Map of CrIS-measured surface NH_3 concentrations, with coloured boxes showing the regions where model and satellite measurements were sampled. These three examples are for (a) northern bidi case study (cyan), (b) southern bidi case study (black), and (c) fire case study (magenta), discussed in Section 4.3), and the blue box is the region of our overall comparison.

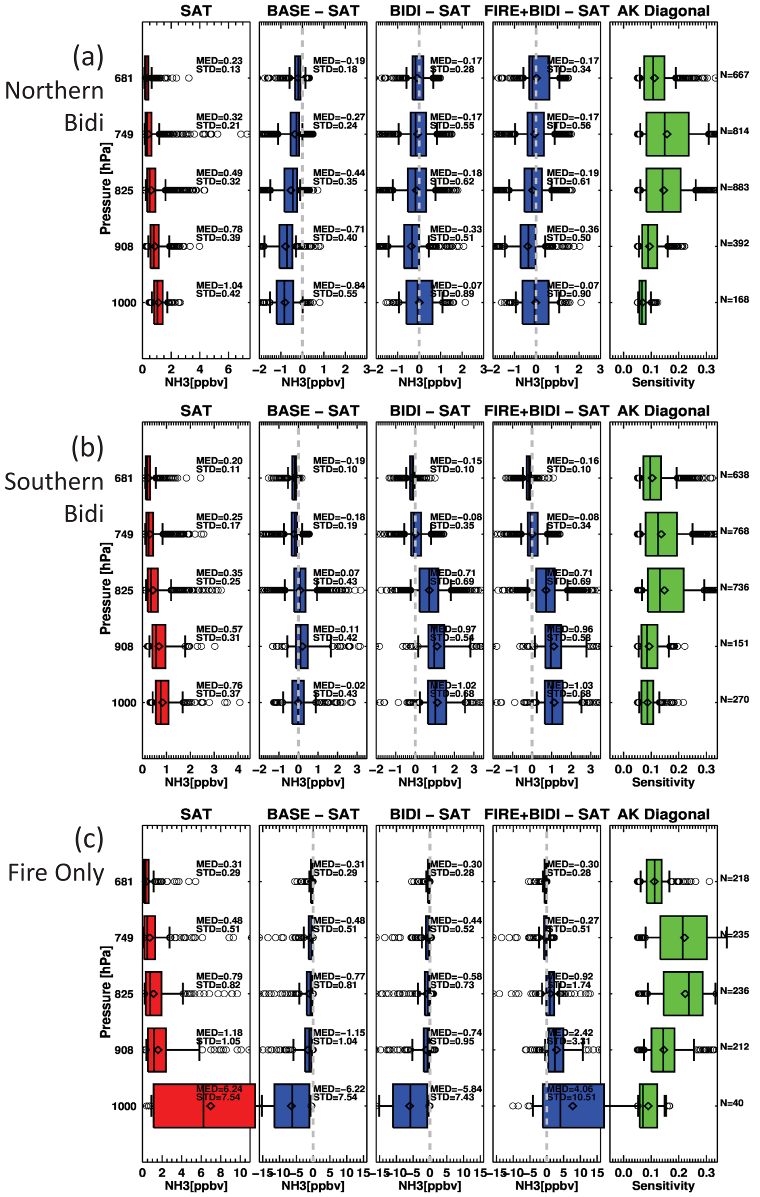


Figure 11. As in Fig. 9, but for our (a) northern “bidi-only" case study (3 Sept 2013), (b) southern “bidi-only" case study (1 Sept 2013), and (c) northern “fire-only" case study (12 Aug 2013). Regions are shown in Figure 10a (cyan), 10b (black), and 10c (magenta) boxes, respectively).

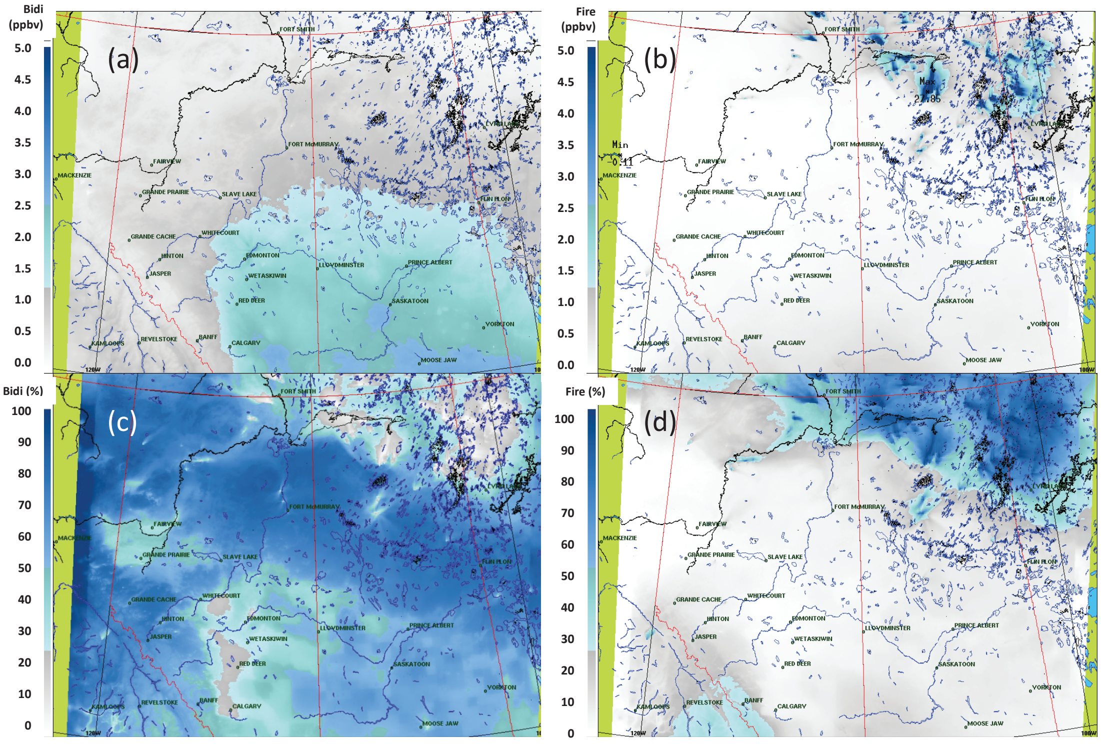


Figure 12. Maps of the modelled ~~average~~ (a) ~~surface NH_3 concentrations (b)~~ absolute bidirectional flux contribution, (~~c~~b) absolute fire contribution, (~~d~~c) percent bidirectional flux contribution, and (~~e~~d) percent fire contribution to surface NH_3. These are ~~averaged~~ averages over 12 August to 7 September, 2013.

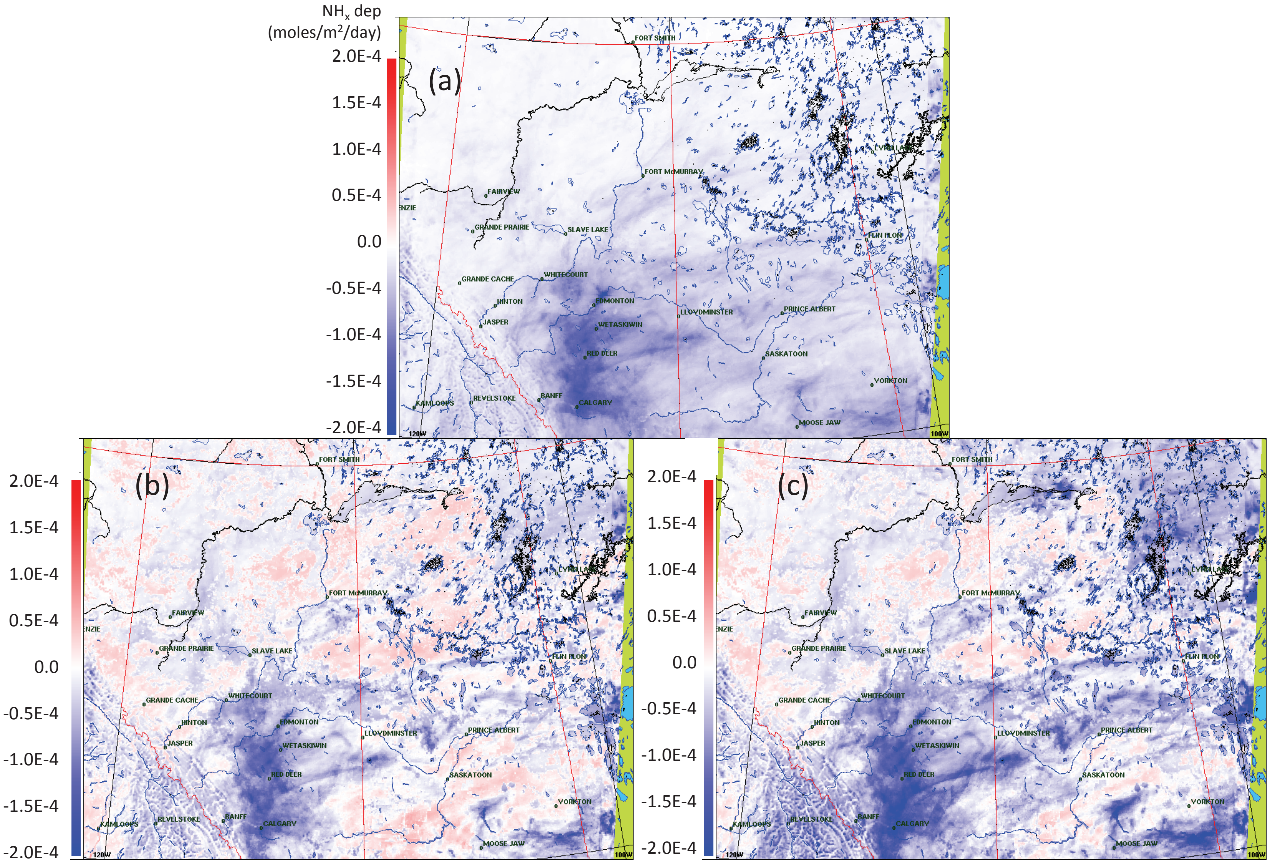


Figure 13. Maps of the modelled average NH~~$_3$ dry~~$_x$ deposition for (a) base (b) bidi, and (c) fire+bidi models. In all maps, red/positive represents upward flux, and blue/negative represents downward flux. These are daily amounts, averaged over 12 August to 7 September, 2013.

Table 2. Model-measurement NH_3 comparison statistics from 12 August to 7 September 2013: R=correlation coefficient; slope is of the line-of-best fit between model vs. measurement; p and t are from a paired t-test between model and measurement data pairs ($p>0.05$ and $|t|<1$ means that the model is statistically indistinguishable from measurements); the median model bias; RMSE=root-mean-square error; and FE=fractional error of the models. CrIS (troposphere) results are for the entire model domain at all tropospheric levels shown in Figure 9(top), and CrIS (surface) results are for the lowest retrieval level (both are during mid-day satellite overpass times); aircraft results are from the 12 flight paths over the oil sands facilities, hourly averages during the daytime; and AMS13 results are from hourly data (day and night) at the one ground station.

	R	slope	p	t	bias (ppbv)	RMSE (ppbv)	FE
CrIS (troposphere)							
base	0.248	0.076	<2E-16	-247.5	-0.430	2.02	-5.3E-6
bidi	0.302	0.205	<2E-16	-77.4	-0.176	1.93	-1.2E-6
fire+bidi	0.338	0.425	<2E-16	36.2	-0.126	2.45	5.9E-7
CrIS (surface)							
base	0.272	0.118	<2E-16	-19.0	-1.11	5.72	-1.6E-3
bidi	0.289	0.162	<2E-16	-12.8	-0.66	5.32	-8.9E-4
fire+bidi	0.566	1.195	1.4E-06	4.9	-0.19	8.67	3.7E-4
aircraft (hourly)							
base	0.368	0.114	8.5E-14	-10.3	-0.751	1.14	-2.5E-3
bidi	0.549	0.503	0.0026	-3.2	-0.244	0.69	-5.0E-4
fire+bidi	0.560	0.519	0.0052	-2.9	-0.233	0.68	-4.5E-4
AMS13 (hourly)							
base	0.103	0.116	<2E-16	-12.4	-0.35	0.92	-1.6E-3
bidi	0.413	0.652	<2E-16	12.1	-0.30	0.95	8.0E-4
fire+bidi	0.403	0.691	<2E-16	13.1	0.32	1.04	9.0E-4

Table 3. Average source contributions to ambient NH_3 concentrations over the AB/SK model domain during 12 Aug to 7 Sep 2013.

source	median (ppbv)	median (%)	average (ppbv)	average (%)
total surface NH_3	1.60	100	2.53	100
from fires to surface	0.25	10.4	0.42	20.3
from bidi to surface	0.97	56.3	1.24	56.6
from anthro to surface	0.38	33.3	0.87	23.1
total column NH_3	18.8	100	25.6	100
from fires to total column	6.1	27.7	8.1	30.5
from bidi to total column	8.8	48.1	11.15	50.0
from anthro to total column	3.9	24.2	6.35	19.5

Table 4. Average NH_x deposition (downward flux) over the AB/SK model domain during 12 Aug to 7 Sep 2013.

Net Flux (moles/m^2/day)	base	bidi	fire+bidi
mean	3.025×10^{-5}	1.811×10^{-5}	3.765×10^{-5}
median	2.061×10^{-5}	1.299×10^{-5}	2.843×10^{-5}