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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Contributions of natural and anthropogenic sources to ambient ammonia in the Athabasca Oil Sands and north-western Canada" *by* Cynthia Whaley et al.

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[CW] 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 (responses start with "[CW]"). Please see our response to the other reviewer for the attached supplement, which is the revised paper, to which the line #s refer to.

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 NHx in the boundary layer versus NH4+ in the soil pool to assess whether surface-to-air fluxes were sustainable. They found that soil NH4+ » boundary layer NHx (by over two orders of magnitude), further supporting the assumption in our bidirectional flux scheme. In addition, the turnover time for soil NH4+ is on the order of 1 day, and the majority of soil NH4+ comes from org-N decomposition (Booth et al., 2005, Ecol. Monogr.), hence it is unlikely that NH3 bi-directional fluxes would significantly deplete/enhance soil NH4+ 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:

(see attached Fig_R1) 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 during our study's time period, 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).

(see attached Fig_R2) 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, R2 = 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_numbe %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_numbe %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.

Specific comments 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 N2-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.

(see attached Fig_R3) 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).

(see attached Fig_R4) 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.

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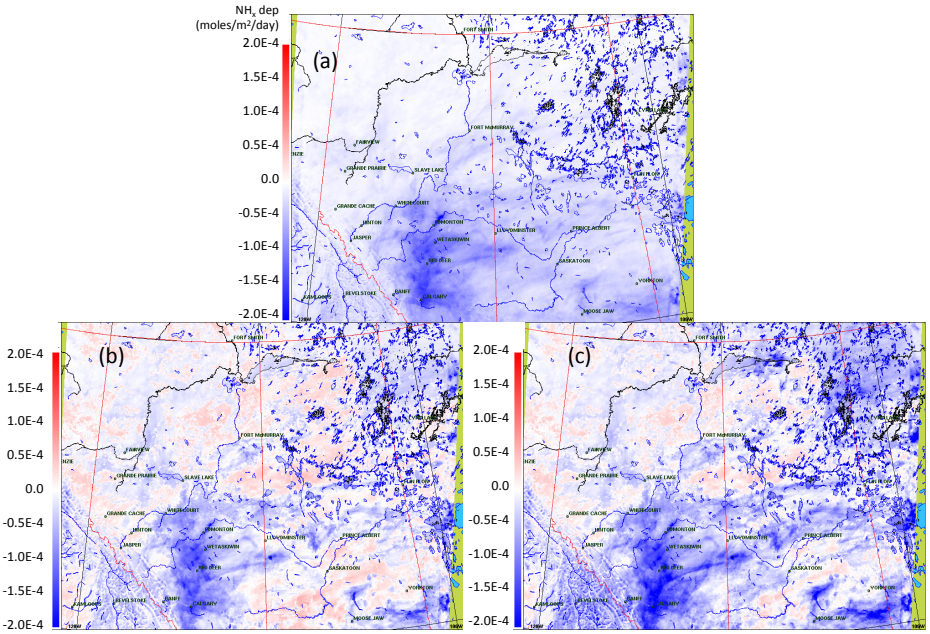

Fig. 1. Total deposited NHx (dry NH3 + wet NH4+) in (a) base, (b) bidi, and (c) fire+bidi. Red regions indicate net NHx emissions; and blue regions indicate net deposition.

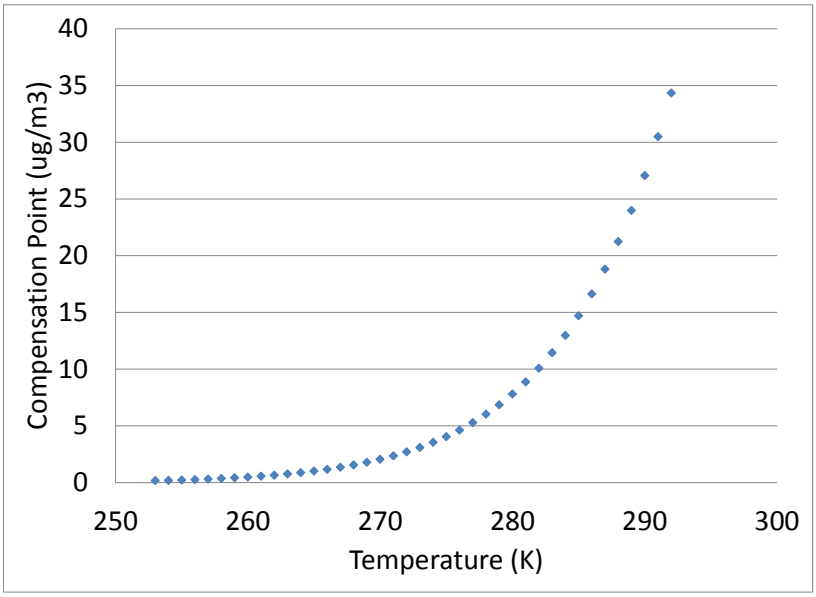

Fig. 2. Compensation point (Cg) relationship to temperature; Cg for evergreen needleleaf LUC shown as example.

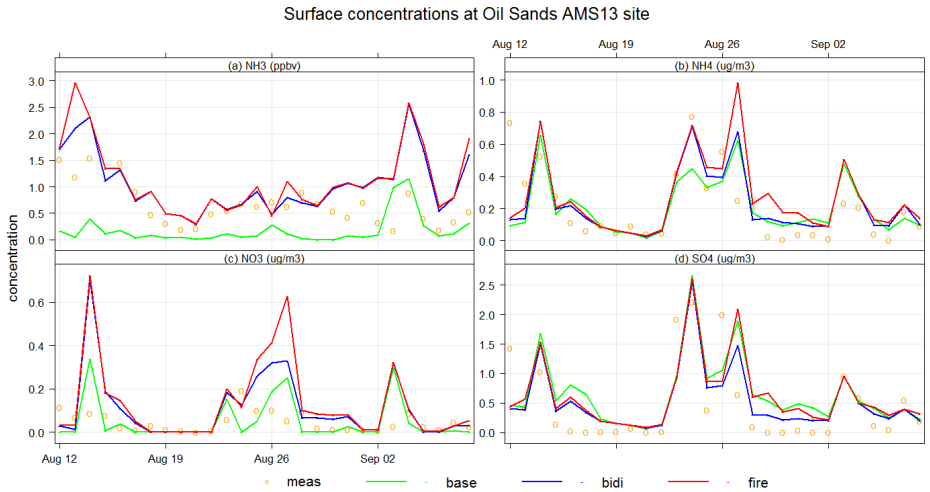

Fig. 3. daily average times series at the AMS13 ground site.

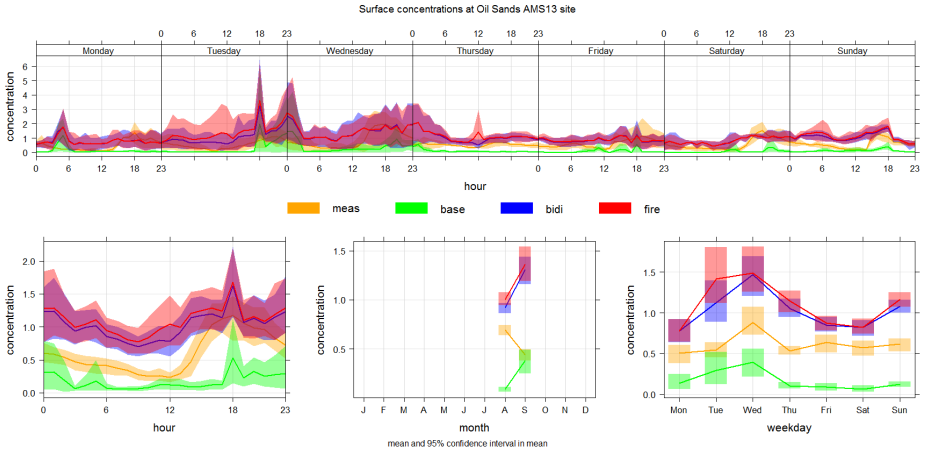

Fig. 4. time series analysis for NH3 at the AMS13 ground station. Hours are in UTC (subtract 6 to get local time).