Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-627-RC2, 2017

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.

Anonymous Referee #3

Received and published: 14 November 2017

In this work, the authors evaluate the GEM-MACH chemical transport model simulation of ammonia and other compounds in the Canadian oil sands region and assess the changes in model performance with the incorporation of ammonia bidirectional flux and wildfire ammonia emissions against ground-based, aircraft, and satellite data for the time period August 12 to September 7, 2013. They then use the model to assess the contributions of natural and anthropogenic emissions to ambient NH3 under the assumption that all reemitted NH3 was natural.

The manuscript is generally well written and easy to understand. Improving our ability to simulate NH3 and NH4 (NHx) is an important issue, and the incorporation of bidi-

rectional NH3 flux in chemical transport models is a needed and still emerging issue, which makes this work potentially important. However, I have a 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.

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. 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. 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.

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. 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.

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.

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. 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.

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. Also

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

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?

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.

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.

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.

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

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.

Figures 12 and 13 are missing panels.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-627, 2017.