Interactive comment on "Global evaluation of ammonia bi-directional exchange" by L. Zhu et al.

Anonymous Referee #3

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The manuscript reports an ambitious attempt to evaluate improvements in the representation of ammonia surface-atmosphere exchange in chemical transport models. A significant portion of the manuscript is devoted to discussing the implementation of a new representation of diurnal variability for agricultural emissions (referencing an in prep publication) and a new bottom-up agricultural inventory (MASAGE_NH3). However, the title of the manuscript only reflects the second aspect of the paper, which examines the implementation of a bidirectional exchange scheme.

Thanks. Our revised title is now:

"Global evaluation of ammonia bi-directional exchange and livestock diurnal variation schemes"

In the description of GEOS-Chem in 2.1, the authors should emphasize that the description of the NH3 emissions is the base case and that the variants will be explained in the following sections.

Thanks. We updated the text as below and we also added a new table (Table 1) to summarize all the inventories used in this study.

"The anthropogenic emissions inventories described here are only used for base case nested grid model runs over the US. Variants will be explained in the following sections. Table 1 is a summary of the different emission inventories used in different sections of the work." See line 103-105.

A pervasive problem with the manuscript is that the comparisons between different model runs and between model runs and observations are difficult to digest. Partly this is because the figures are so small and the information is all over the continents, and partly it is because the text reports the extremes of differences, rather than more general metrics. Below I provide general and detailed comments for the two portions of the manuscript separately:

Sections 3 and 4

The evaluation of the updated dynamic emissions scheme is quite haphazard. It is challenging to extract quantitative information from Figures 2, 3, and 4 and the related text which describes comparisons with ground sites and remotely sensed representative volumetric mixing ratios reports biases or improvements in a handful of regions, but the approach lacks consistency. While the cases reported may be representative, the reader *is left wondering about regions and times that aren't mentioned.*

We have added a new figure (Figure 2) showing the modeled and measured timeseries at SEARCH sites. We hope the differences here are more apparent, as well as their significance as compared to the observations.

In our analysis, we chose to make regional evaluations as we are not expecting the diurnal variability, which only affects livestock emissions, to impact the model NH3 everywhere. It is reasonable that some regions with large fertilizer application would change less. The impact on all regions, even those not discussed, are evident from the global figures, which are indeed small but at least comprehensive.

Section 3.1 Surface measurements – what is the impact of having observational constraints at such differing time resolutions?

The fine time resolution observations from SEARCH allow us to evaluate the improvement in diurnal variations, which lets us know, mechanistically, how the model is behaving. The coarsely resolved measurements from AMoN (e.g., two-week) observations are used to evaluate the broader impacts of such changes. The networks are also positioned in different parts of the country.

What is the impact of including urban and rural sites in some regions, and only rural sites in others?

The source types would be different between urban and rural sites, and the model (particularly the global scale simulations) would likely more reliably estimate background concentrations. We thus indeed exclude the urban sites of EANET in comparison of ammonium wet deposition, as we found that the wet deposition observed by surface monitoring sites are much higher in some urban sites than in the model (e.g., 50 vs 1.3 kg/ha/yr), likely outside of what we expect to be able to simulate at the global model resolution. We updated the text to clarify this, see line 146.

P4828, L22-25 This sentence reads as though soil pH and fertilizer application influence livestock emissions. Is that correct?

No, we apologize for the confusion. This sentence means that soil pH and fertilizer would influence the NH3 in the model; we made new development to the model, which are NH3 bi-directional exchange and a diurnal variation to NH3 livestock emissions.

We updated the text as below:

"In this paper, we develop the adjoint of bi-directional exchange and we use this adjoint model to investigate the sensitivity of modeled NH3 with respect to soil pH and fertilizer application rate."

P4829, L11-10, This paragraph is hard to follow. How many SEARCH sites are used, and do they all provide observations of NH3 and wet deposited NH4+? Are the three sites with high time resolution data combined because they fall in the same model grid *cell?*

Three SEARCH sites are used because only three sites have 5 min samples. We average the 5 min observations to hourly values for each site. Two of the three are in the same grid cell, and the other one is two grid cells away. We compared to the corresponding modeled values for each site location. We only average them when we calculate the mean differences between model and observations. We now updated the text. See line 124-127.

We were not using NH4+ from SEARCH.

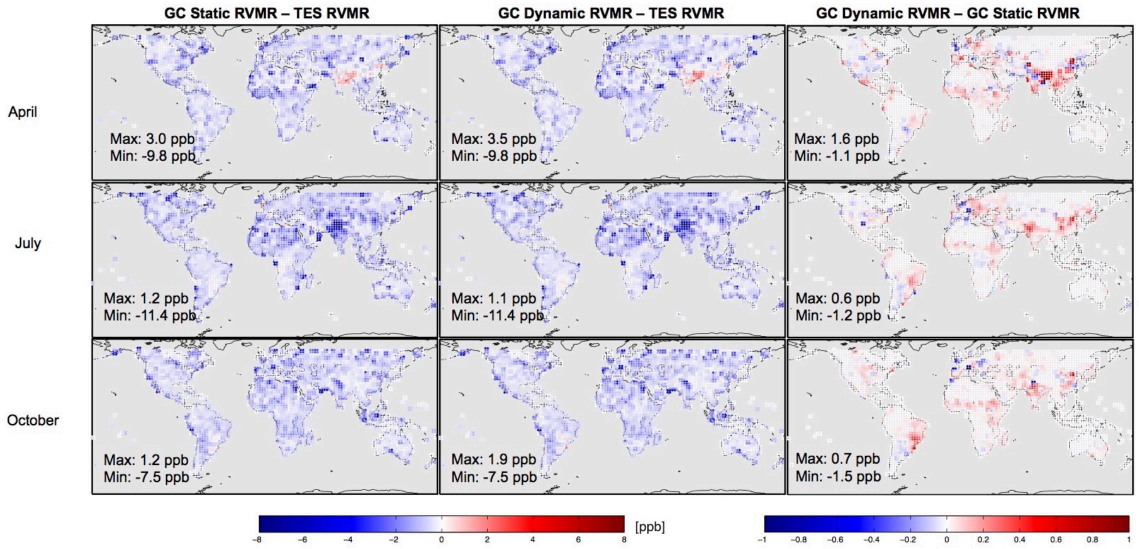
We think it is better to make a separate paragraph for the first sentence of this section. We updated the text. See line 119-120.

P4831 – L10-14 If I understand correctly, the fraction of anthropogenic emissions that are due to livestock are estimated for all regions of the world based on the NEI for the U.S. Is this fraction likely to be the same in other parts of the world?

No, we will try to be more clear. The fraction calculated based on the NEI was only used for the U.S., not for the world. There was another emission inventory used for world and it has the livestock and fertilizer sectors separated. So we didn't need to calculate this fraction based on the NEW. We apologize for the misunderstanding. We have now added a table to summarize all the inventories used in this study. See Table 1.

P4832, L6-23 This section describes a comparison with modelled RVMR and those retrieved from TES, but is very hard to follow. Why not include a figure, or a table of statistics, rather than quoting differences from a few regions?

We have considered such a figure (shown below), but because the magnitude of dynamic RVMR changes (-1.5 – 1.6 ppb) is much smaller than the differences (-11.4 – 3 ppb) between the static RVMR and TES RVMR, the differences between "GC Static RVMR – TES RVMR" and "GC Dynamic RVMR – TES RVMR" are not particularly obvious. The ability of low-earth-observations to detect such differences is not that great, as demonstrated further in another recent article (Zhu et al., in press, 2015).



A larger question from this section is: If the total livestock emissions are staying constant, how can the deposition be decreasing?

Gross deposition is based on the NH3 concentrations in atmosphere, not the total mass of NH3. The NH3 concentrations are quite different at night. Perhaps this is now more clear with the inclusion of the new Figure 2.

Sections 5-7

The manuscript provides significant detail on the representation of the soil ammonium pool, which responds to atmospheric deposition. On the other hand, there is no mention of the ammonium pool in the vegetation, which one assumes would influence the stomatal compensation point. Is there a reason this is not addressed in a similar online manner?

The reviewer is correct that the vegetation plays a role. However, the soil ammonium pool is also a reservoir of ammonium from fertilizers, which is much larger source than that from deposition. Based on sensitivity tests, the influence of the ammonium potential in the soil is much larger than that in the stomata. Thus, we don't think the stomatal pool is necessary.

What is the rationale for looking at the adjoint sensitivity with respect to soil pH rather than soil [H+]? It seems like the log scale might skew the perception of the emission potential.

Pragmatically, soil pH is the actual input we provide to the model, and thus for which adjoint sensitivities are directly calculated. It is also more constant than soil [H+], which may be adjusted in regional models that include a detail soil model. Although we don't have a detail soil model in GEOS-Chem yet, this may be a future development. The emissions potential wouldn't be impact by whether we use soil pH or soil [H+].

A more general question is whether the adjoint of GEOS-Chem been sufficiently validated for a species like NH3 with signficiant non-linearities in its behavior? Presumably, one would need to have met fields very accurate and also abundance of SO4, HNO3. As stated by the authors, the HNO3 in the model is likely biased, and one would assume that the sensitivity of NH3 concentrations to emissions depends on the model HNO3.

The adjoint has been verified to be accurate, see Figure 7, i.e. sensitivities calculated by the adjoint are accurate compared to those in the forward model. A different and more challenging question is whether the GEOS-Chem model itself contains correct sensitivities, which as the author points out are related to meteorology and the concentrations of sulfate and nitrate. For this reason we feel it is important to evaluate the model relative to NH3, NH4+ and nitrate, rather than just NH3 or NHx.

An issue with many of the comparisons between models runs in Section 6 is that the value that is typically quoted in the text is the largest difference, which may not provide much insight on typical behaviour. I recommend quoting the median difference, as well as the maximum.

We only expect large changes in regions with large fertilizer applications. The global mean or median value will wash out these changes and would be close to zero in some cases given the positive and negative differences. While we agree that ranges, by themselves, are not that informative, the inclusion of the global maps allows for visual analysis of what the typical behavior is in different parts of the world.

In section 6.1, it would be interesting to know if the annual gross emissions are lower or higher across the US in the base vs BIDI cases.

We haven’t done the annual simulations. We only did simulations for three months. We do however now present the gross emissions in each month in Table 1.

In section 6.1.1, the AMoN comparison suggests that the BIDI parameterization degrades the ability of the model to represent the variability in two-week integrated measurements in the spring and fall. Can the authors speculate if this would also be the case for higher time resolution? Additionally, what fraction of the gross emissions are from bidirectional exchange as a function of space and time?

We should first emphasize that the underestimation of NH_3 primary emissions in the model is the largest reason. We are more worried about the spatial resolution rather than the time resolution (point vs ~ 3000 km^2). It is challenge for the model to match observations, especially for the sites with large sources near by. We thus think it is useful to show the fraction of the gross emissions from bi-directional exchange in space. Accordingly, we added a spatial plot of these fractions over the global. See new Figure 15 and additional text on line 464-467.

“Figure 15 shows the percentage of emissions from fertilizers in BIDI case in the global simulations. BIDI fertilizers contribute more to gross emissions in July than in other months in the Northern Hemisphere, which again demonstrates the delayed effect of fertilizer NH_3 (mostly applied in the springtime) in the BIDI model."

But, to speculate as requested, the limited set of higher-time resolution measurements are not more help for evaluations of NH3 from BIDI at this stage since the emission biases in the current emission inventory are much larger than the BIDI could fix. BIDI changes are consistent (either increase or decreases) in one location during the whole month when we look at results in finer time resolution (hourly).

In Section 6.1.3, it is not really clear what the authors are trying to demonstrate with this comparison. Are the 'uni-directional' emissions from Zhu et al., 2013, replacing the MASAGE inventory? I think the hybrid, piecemeal nature of the comparison makes it difficult to interpret the results.

We didn't use the MASAGE inventory in the nested simulations over the US, which we hope is now clarified with the addition of Table 1. The purpose of this section is to evaluate the BIDI ability of reducing the high bias, which is found in Zhu et al. (2013).

Section 6.2 – again, it would be interesting to know how the annual emissions change for each model run.

This information is now included in Table 1.

P4845, L17-23 I find this section confusing. On some spatial scale, there ought to be mass balance between the changes in emission and deposition. Obviously, there could be some change to the amount of dry deposition, so one cannot expect the emissions and wet deposition to change in exactly the same way, but they should be close. In comparing the changes in wet deposition to the changes in emissions, why quote one change in absolute terms and the other as a percent. It makes in challenging to compare them.

We added the absolute values of emissions in the text. See line 517-518.

Section 6.4.3 – I think this spot sensitivity analysis is one of the more interesting parts of the manuscript, as it provides one of the more robust and digestible results of implement bi-directional flux.

Thanks.

Technical corrections:

Figure 3 is missing a colour scale.

Thanks. Corrected.

P4826, L26-27 – missing word in sentence

Thanks. Corrected.

P 4836, L8 Gaussian is misspelled

Thanks. Corrected.

Fig 9 shows R2 whereas Fig 10 shows R, it would be better to be consistent

Thanks. We changed the R to R^2 in Figure 10.