Response to Reviewer #1 comments:

Comment 1

This manuscript by Chen et al. used the recently developed multiphase CMAQ adjoint model and IASI satellite total NH_3 column observations to constrain the monthly NEI NH_3 emissions at 36 km spatial resolution in April, July, and October in 2011. A hybrid, two-step optimization scheme was applied. First the NEI inventory was nudged towards the posterior values by a mass-balance approach at a much coarser grid (216 km), and then 4D-Var inversion was performed using the updated inventory as the prior. The posterior emissions were then used to drive the CMAQ model, and the simulated NH_3 abundance, NH_4 deposition, and aerosol chemical composition were evaluated against independent observational datasets. Overall this work is solid, has applied state-of-the art satellite data and CTM tools, and could advance our limited understanding on the emission of NH_3 if its methodology can be fully justified. Hopefully the paper can be further improved after addressing my comments below.

Response

We thank the reviewer for providing insightful comments. In this revision, we addressed these comments carefully. In particular, the inversion was re-performed using daily IASI-NH_3 averages as constrain and revised error terms. The revisions help partly resolved the over-adjustment issue we encountered in Pennsylvania and surrounding regions. Please see our point-by-point responses for details. We hope that this new version of the manuscript has addressed all the concerns raised by the reviewer.

Comment 2

NEI 2011 covers the entire year continuously but this work only focused on three months, April, July, and October. Presumably the computing cost prohibited optimizing NEI for other months, but this should be discussed. Many CTM users would use multiple months or the entire year of NEI, and those three isolated months would hinder further application of the results of this work. Especially, the month of May will be a significant opportunity missed as a large fraction of fertilizer application happens in May, leading to abruptly different emission and column density dynamics relative to April and June.

Response

We thank the reviewer for pointing this out. Yes, we focused on three months because the computational cost to run full year simulation using adjoint model is too high. The CPU time required for one-day forward and adjoint simulation is 9.5 hours and 48 hours, respectively, which means that it takes over 20,000 CPU hours to perform a full year simulation. If the inversion takes 3~5 iterations to reach the converge criteria, the CPU time can reach 60,000 to 100,000 hours. A sentence is added to line 155 to clarify that the optimization only focused on three months due to the high computational cost as follows. "*Limited by the high computational cost of adjoint-model-based inversion, the optimization is only performed for the three months selected instead of a full year.*" In addition, as explained in the sentence in line 155 to 156, the optimization was not performed for the winter months (November, December and January) because the IASI-NH_3 observations are too noisy to serve as a reliable constrain.

The comparison between monthly average IASI NH_3 column density and CMAQ simulated values using the *a priori* NH_3 emission inventory for all twelve months in 2011 are provided in the revised SI (**Figure S9**). Simulated NH_3 column densities are biased low comparing to the IASI observed ones especially from April to August. For May, the simulated NH_3 column densities are much lower than the IASI observations, especially in southern states (Texas and Oklahoma). Although we only performed the inverse modeling in April to represent the spring months, we expect the emission and column density dynamics in May are similar to those in April. Sentences are added in line 287 to imply the potential low bias of NH_3 emission estimates in the NEI inventory in other months. "*Although the inversion is only applied for the three selected months, the simulated NH_3 column densities using the a priori inventory are consistently lower than the IASI-NH_3 observations in 2011 (**Figure S9**), suggesting that the NH_3 emission estimates in 2011 NEI may be biased low in other months, too.*"

Figure S9 was added to SI to provide the results of the comparison between monthly average IASI NH_3 column density and CMAQ simulated values using the *a priori* NH_3 emission inventory for all twelve months in 2011.

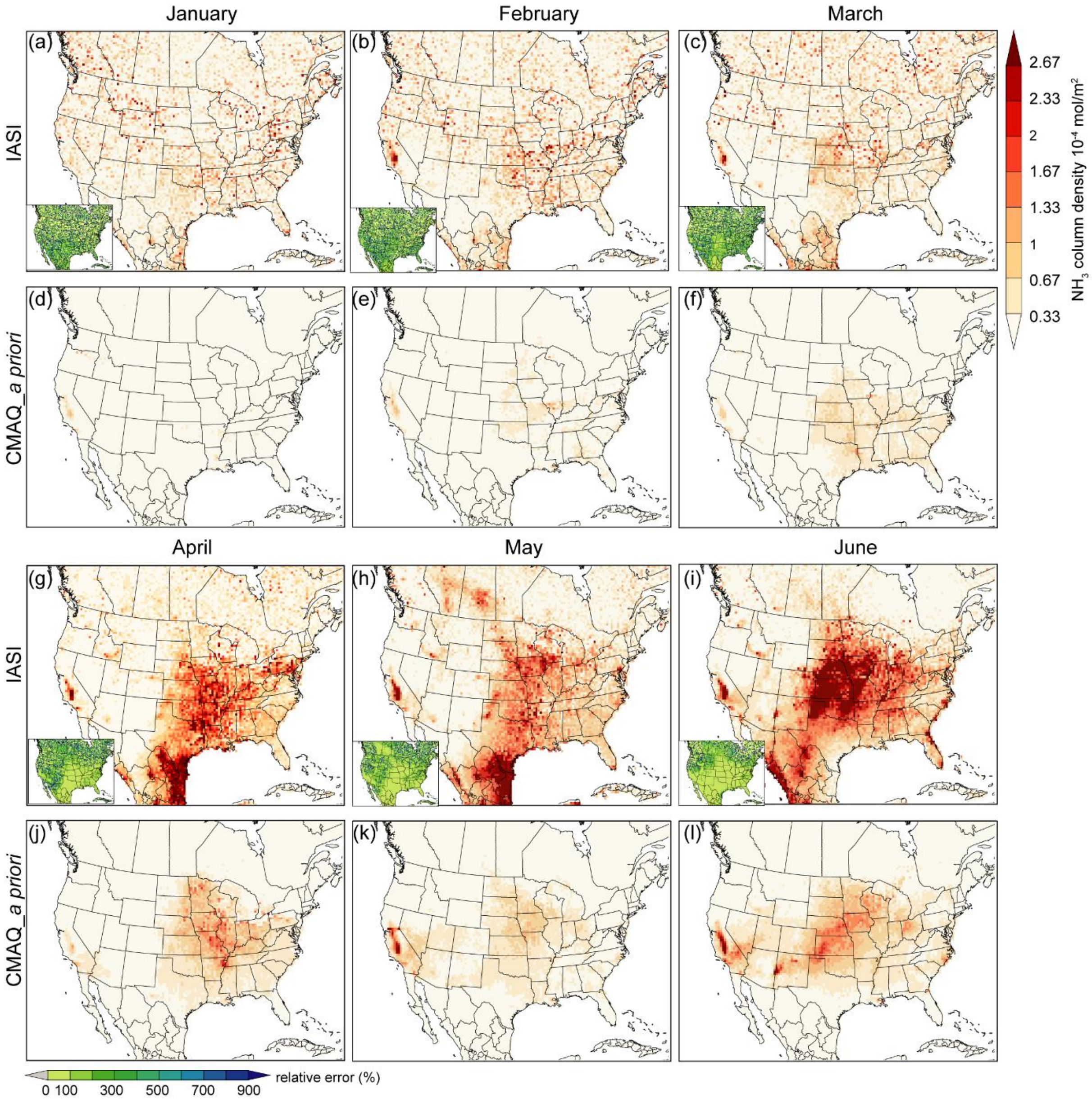

Figure S9 Comparison between monthly average IASI NH_3 column density (a-c, g-i, m-o, s-u) and CMAQ simulated values (d-f, j-l, p-r, v-x) based on the *a priori* NH_3 emission inventory in 2011. The monthly average relative error associated with the observed IASI NH_3 column density is shown in the corner of the corresponding plots.

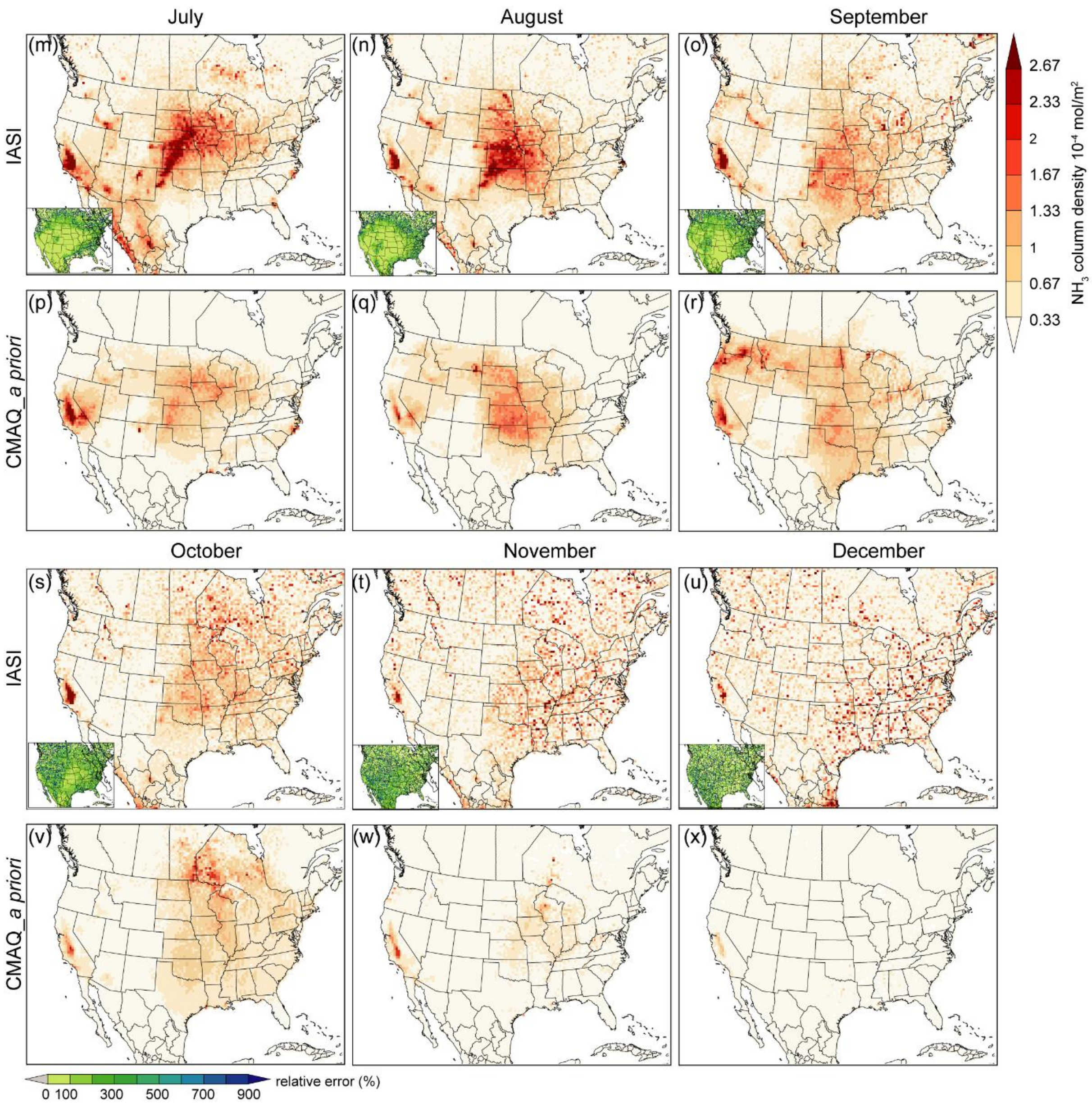

Figure S9 (continued) Comparison between monthly average IASI NH_3 column density (a-c, g-i, m-o, s-u) and CMAQ simulated values (d-f, j-l, p-r, v-x) based on the *a priori* NH_3 emission inventory in 2011. The monthly average relative error associated with the observed IASI NH_3 column density is shown in the corner of the corresponding plots.

Comment 3

The observation used in the inversion seems to be monthly averaged data over 36-km grid cells, and the grid average absolute error was used in the observational error covariance matrix. This may have led to the counterintuitively high values in Pennsylvania and southern Texas, as the monthly averaged grid value could have been driven by a few anomalously high observation dates, given the sparsity of IASI pixels. The error term (in Equation 1) does not include the scaling of the square root of N (the central limit theorem). As a result, if a grid cell contained only one day with extremely high values (the other days in the month were missing), it would be treated the same way as if all 30 days were those high values. Specifically, the high emissions in Pennsylvania, western New York, and east/south Texas (Fig. 3d) that were seemly driven by high IASI values in April (Fig. 1a) are hard for me to believe. It might be helpful to check IASI April data in other years, e.g., 2010 and 2012, to see if those high column abundance (and consequently high posterior emissions) are consistent.

Response

The reviewer's thought is well-taken. Indeed, using monthly averaged NH_3 column densities and averaged absolute error may lead to biased posterior emission estimates when the high averaged values are driven by high observations in several days. In response to this comment, we redid the inversion using daily observations as constraints. We also change the method to calculate the error term. A simple standard error of the mean column density in each grid was used. Please note that this was achieved by rerunning all the simulations, which was one of the main reasons we postponed the revision due date.

The specifics are described as follows.

The sentence in lines 146-147 is revised as "*The mean column density (Ω_o) is calculated as the arithmetic mean of all retrievals with their centroids falling in the same grid cell, following …*"

The sentence in line 148-153 is revised as "*The error (molec/cm^2) corresponding to the mean column density in each grid is calculated as:*

$$\bar{\sigma} = \sqrt{\frac{\sum(\sigma_i \times \Omega_i)^2}{n-1}}$$

where $\bar{\sigma}$ is the mean error (molec/cm^2), Ω_i is the NH_3 column density from IASI-NH_3 level 2 data, σ_i is the relative error associated with each Ω_i as reported, n is the number of retrievals within each grid cell during the defined time period. For 4D-Var inversion and IMB inversion, daily and monthly means and errors are calculated, respectively."

For the iterative mass balance optimization (IMB) step, the emission scaling factors are still derived at 216 km by 216 km resolution. However, in each day, only grid cells with satellite observations at 36 km by 36 km resolution are adjusted. Otherwise, the grid cells without observations at 36 km by 36 km resolution may be over-adjusted in the IMB step and there will not be enough constraint in the 4D-Var inversion to further adjust the emissions in these grid cells.

The sentences in line 178-185 are revised as "*The first step is to apply the IMB approach to adjust the a priori (2011 NEI) NH_3 emission at 216 km by 216 km resolution (referred to as the coarse grid cell hereafter) based on the ratio between the monthly-averaged observed and simulated NH_3 column density at the satellite overpassing time, iteratively. At each iteration, the emission in each 36 km by 36 km grid cell (referred to as the fine grid hereafter) is scaled by the ratio following the equation below,*

$$E_{t,i,j} = \begin{cases} \frac{\Omega_{o,m}}{\Omega_{a,m}} \times E_{a,i,j}, & IASI\ pixels\ available\ in\ grid\ cell\ i\ in\ day\ j \\ E_{a,i,j}, & no\ IASI\ pixels\ in\ grid\ cell\ i\ in\ day\ j \end{cases} \quad (2)$$

where $E_{t,i,j}$ and $E_{a,i,j}$ are the new and a priori emission estimates in fine grid cell i within the coarse grid cell on the jth day of the month, respectively. $\Omega_{o,m}$ and $\Omega_{a,m}$ are the monthly-averaged observed and simulated NH_3 column density in coarse grid cells, respectively. It is a modified version of IMB optimization performed in previous studies (Li et al., 2019; Cooper et al., 2017; Martin et al., 2003). The emissions in grid cells without IASI retrievals are kept unchanged to avoid over-adjustment."

The sentence in line 190 is revised as "*The final scaling factor (ε_0) for each grid cell is the multiplication of the scaling factors derived at each iteration.*"

For the 4D-Var inversion, daily mean column density from the IASI-NH_3 observations are used as constraints. Daily emission scaling factors are derived through optimization.

The sentences in lines 119-210 are revised as below.

"

$$J = \gamma(\varepsilon - \varepsilon_0)^T S_a^{-1}(\varepsilon - \varepsilon_0) + \left(\Omega_{o,d} - F(\varepsilon)\right)^T S_o^{-1}(\Omega_{o,d} - F(\varepsilon)) \quad (3)$$

*ε is the daily emission scaling factor to be optimized at each iteration where $\varepsilon = log\left({}^{E_t}/_{E_a}\right)$ on the 36 km by 36 km CMAQ grid, consisting of 6104 elements overland grid cells in CONUS. $\Omega_{o,d}$ is daily-averaged IASI-NH_3 column densities and $F(\varepsilon)$ is CMAQ simulated NH_3 column density sampled at the satellite passing time if there is at least one IASI-NH_3 retrieval in that grid cell. S_a and S_o are error covariance matrices for the a priori emission estimates and IASI-NH_3 retrievals, respectively. The two matrices are assumed to be diagonal. For S_o, the simple standard error corresponding to $\Omega_{o,d}$ is used to represent the observational error (Equation (1)). Our test shows that negative $\Omega_{o,d}$ will lead to a continuous decrease in the adjusted emission for the grid cell because modeled column density cannot become negative. To limit the influence of these negative $\Omega_{o,d}$, their original weights are multiplied by 0.01. For S_a, the uncertainty in each grid cell is assumed to be 100% of the a priori emissions. γ is the regularization factor balancing the relative contribution of the a priori emission inventory and IASI-NH_3 retrievals to the J value. γ is chosen to be 800 for April and 500 for July and October based on the L-curve criteria (Hansen, 1999) (**Figure S5**).*"

Using daily mean IASI-NH_3 column densities as constraints do help alleviate the over-adjustment in Pennsylvania in April. The *posterior* emission estimate in Pennsylvania is 127% higher than the *a priori* estimates using daily means as constraint, whereas 717% higher when using monthly means. For Texas, the difference is smaller (237% higher using daily means versus 335% higher using monthly means) because high IASI-NH_3 column densities were observed on many days, possibly because of the warmer weather condition and earlier fertilizer application activities in 2011. Please refer to the response to **Comment 11** for a detailed discussion. Again, we thank the reviewer for providing this insightful comment on the inversion method.

Comment 4

Page 2, line 49: clarify which NEI it is (prior or posterior) in "NEI-based" assessments.

Response

Thanks for the suggestion. The sentence is revised as "*The model results suggest that the estimated contribution of ammonium nitrate would be biased high in a priori NEI-based assessments.*"

Comment 5

Page 2, lines 61-65: this sentence might fit better at the last paragraph of the introduction.

Response

We thank the reviewer for this suggestion. The sentence in lines 61-65 is moved to the beginning of the last paragraph of the introduction. The last paragraph is revised as "*This work utilizes satellite observations from the IASI NH_3 column density measurements (IASI-NH_3) (Clarisse et al., 2009;Van Damme et al., 2017), to provide a high-resolution, optimized NH_3 emission inventory for the U.S. developed using an adjoint inverse modeling technique (Li et al., 2019), the robustness of which is demonstrated by evaluation against multiple independent in-situ measurements. The IASI-NH_3 dataset was applied to optimize NH_3 emission estimates from the 2011 National Emission Inventory (NEI 2011) using CMAQ and its adjoint model at a 36 km×36 km resolution. …*"

IASI is spelled out at its first appearance in line 70 as "*Several studies have utilized NH_3 column density retrieved from the Infrared Atmospheric Sounding Interferometer (IASI) (Clarisse et al., 2009; Van Damme et al., 2015b) …*"

Comment 6

Page 5, equation 1: this is a strange statistic to calculate. As indicated a few lines above, Ω_0 is the monthly arithmetic mean within a grid cell, but the $\sum(\sigma_i/\sigma_i^2)/\sum(1/\sigma_i^2)$ term is the variance-weighted mean of error. A simple standard error of the mean or standard error of the weighted mean (https://doi.org/10.1016/1352-2310(94)00210-C) might be better choices.

Response

In response to this comment, the error term is changed to a simple standard error of the daily mean in the revised manuscript, and the simulations are re-performed with the revised error covariance matrices. The results are updated throughout the text.

The sentence in line 148-153 is revised as "*The error (molec/cm^2) corresponding to mean column density in each grid cell is calculated as:*

$$\bar{\sigma} = \sqrt{\frac{\sum(\sigma_i \times \Omega_i)^2}{n-1}}$$

where $\bar{\sigma}$ is the mean error (molec/cm^2), Ω_i is the NH_3 column density from IASI-NH_3 level 2 data, σ_i is the relative error associated with each Ω_i as reported, n is the number of retrievals within each grid cell during the defined time period. For 4D-Var inversion and IMB inversion, daily and monthly means and errors are calculated, respectively."

Comment 7

Page 7, lines 201-202: how justified is it to assume that the a priori covariance matrix is diagonal? The error/bias in NEI often seem spatially correlated.

Response

Thank you for raising this concern. The error covariance matrix is assumed to be diagonal because there is no data available to estimate the spatial correlation of errors in NH_3 emission estimates. Including non-diagonal terms to the *a priori* covariance matrix, therefore, may further introduce uncertainties in the inverse modeling. The sentence in line 201-202 is revised to clarify the reason why the *a priori* covariance matrix is assumed to be diagonal as follow. "*With limited information on the spatial correlation of the error covariance, the two matrices are assumed to be diagonal (Paulot et al., 2014; Zhu et al., 2013).*"

References

Paulot, F., Jacob, D.J., Pinder, R.W., Bash, J.O., Travis, K., Henze, D.K.: Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE_NH_3). J. Geophys. Res. Atmos. 119, 4343-4364, https://doi.org/10.1002/2013JD021130, 2014.

Zhu, L., Henze, D. K., Cady-Pereira, K. E., Shephard, M. W., Luo, M., Pinder, R. W., Bash, J. O., and Jeong, G. R.: Constraining U.S. ammonia emissions using TES remote sensing observations and the GEOS-Chem adjoint model, J. Geophys. Res. Atmos., 118, 3355-3368, https://doi.org/10.1002/jgrd.50166, 2013.

Comment 8

Page 7, lines 203: it is important to let the readers understand if the observation vector used in the inversion is composed of single IASI pixels (level 2) or regridded maps (level 3). My impression is that the level 3 regridded IASI data were used. In that case, the single sounding detection limit of 4.8×10^{15} is not relevant as the averaging will reduce the noise level, and it is important to consider the number of averaging per grid cell.

Response

Yes, level 3 regrided IASI data is used in the inversion. In response to comment 3, the inversion was re-performed and daily means regrided at 36 km 36 km resolution were used as constraints in the 4D-Var inversion. The reviewer is right that the single sounding detection limit is higher than the actual noise level when pixels are averaged. We no longer add a detection limit to the error covariance S_o. The simulations are re-performed with the revised error covariance matrices, and the results are updated throughout the text.

This sentence in lines 203-205, "*To reduce the influence of retrievals close to or below the detection limit, an estimated detection limit of* 4.8×10^{15} *molecules/cm*^{2} *is added to the* S_o *(Dammers et al., 2019)*", is deleted.

Comment 9

Page 7, line 215: the convergence criterion that J decreases by less than 2% seems large and arbitrary.

Response

The convergence criterion was chosen following previous inverse modeling studies to optimize NH_3 emission estimates. Citations are added in the sentence in line 215 to clarify the choice of the convergence criterion. "*The iteration process is terminated when the decrease in J is less than 2% or the local minimum is reached (Li et al., 2019; Zhu et al., 2013).*"

References

Li, C., Martin, R. V., Shephard, M. W., Cady-Pereira, K., Cooper, M. J., Kaiser, J., Lee, C. J., Zhang, L., and Henze, D. K.: Assessing the Iterative Finite Difference Mass Balance and 4D-Var Methods to drive ammonia emissions over North America using synthetic observations, J. Geophys. Res. Atmos., 124, 4222-4236, https://doi.org/10.1029/2018jd030183, 2019.

Zhu, L., Henze, D. K., Cady-Pereira, K. E., Shephard, M. W., Luo, M., Pinder, R. W., Bash, J. O., and Jeong, G. R.: Constraining U.S. ammonia emissions using TES remote sensing observations and the GEOS-Chem adjoint model, J. Geophys. Res. Atmos., 118, 3355-3368, https://doi.org/10.1002/jgrd.50166, 2013.

Comment 10

Figure 2: please consider adding the residual map (IASI column-modeled column) as inserts, similar to Fig. 1.

Response

Residual maps are inserted as suggested by the reviewer. Figure 2 is revised as follows,

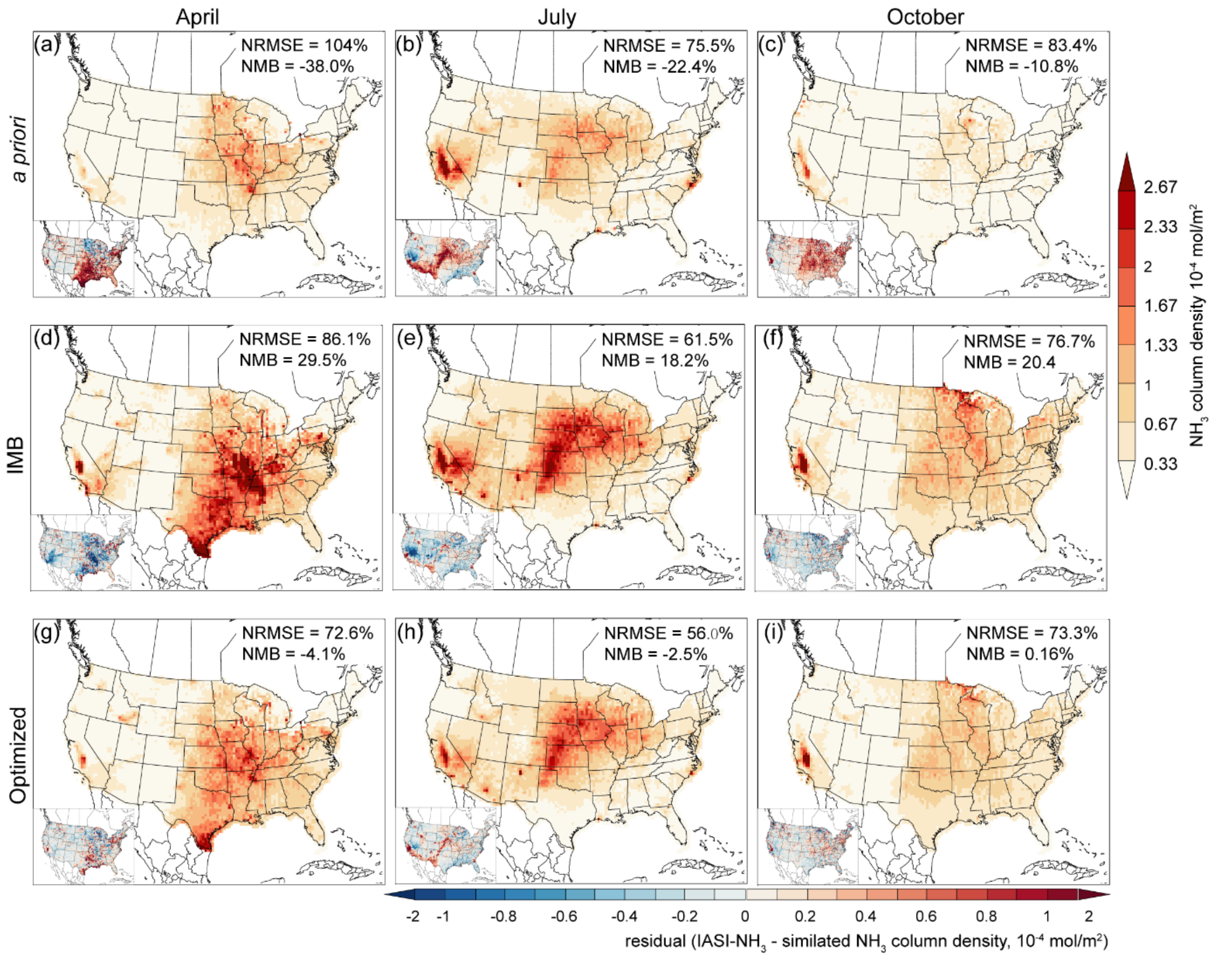

Figure 2 CMAQ simulated monthly average NH_3 column density for April, July, and October 2011 using the *a priori* emissions (a, b, c), the emissions adjusted by IMB (d,e,f), and the final optimized emissions using the hybrid approach (g,h,i). For comparison with the IASI-NH_3 retrievals, simulated NH_3 columns at the passing time are derived when there are observations in that grid cell. Normalized root mean square error (NRMSE) and normalized mean bias (NMB) between the simulated values and IASI-NH_3 are provided. Residue map (IASI-NH_3 – simulated NH_3 column densities) is shown in the corner of each plot.

Comment 11

Page 8, lines 234-235: please define the exact location of NRMSE that reduced by 98%. The high NH_3 observations in April in southern states seem curious and may warrant a closer investigation.

Response

By "southern states" we are referring to the states in the southern region defined by the USDA Farm Production region, which includes Texas and Oklahoma. In the revised simulation, the NRMSE in the southern states was reduced by 50% instead of 98% with the optimized NH_3 emission estimates. The sentence in lines 234-235 is revised as follows "*The optimized NH_3 emission successfully captures the high NH_3 column density in southern states (Texas and Oklahoma), reducing the NRMSE by half in that region.*"

The enhanced NH_3 emissions in the southern states in the optimized emission estimates are more consistent with the total NH_3 emission estimates when air-surface bidirectional exchange is considered (Shen et al., 2020). The ratio between NH_3 emission estimates in southern states and total NH_3 emission within CONUS is 20% and 18% in the optimized estimates and estimates including NH_3 bidirectional exchange in 2011, respectively. In comparison, the ratio is only 10% in the *a priori* NEI estimates.

The comparison of IASI-NH_3 in 2011 and adjacent years shows a substantial variation in the retrieved NH_3 column densities in the southern states. The NH_3 observations are the highest in 2011 and the lowest in 2010 in April and May. The difference coincides with the higher surface temperature in the southern states in these two months. NH_3 volatilization from agricultural lands will increase under warmer conditions (Shen et al., 2020).

The pieces of evidence mentioned above are incorporated in the discussion to support the increased NH_3 emission in southern states in the optimized estimates as follows. The sentences in line 261-263 are revised as "*The higher NH_3 emission estimates in the southern states are driven by the enhanced NH_3 column densities from IASI over that region. IASI-NH_3 column densities are higher in 2011 than those in adjacent years (**Figure S7**), which coincides with the higher surface temperature observed in 2011 (NOAA 2019)(**Figure S8**). NH_3 emission will increase due to enhanced NH_3 volatilization from agricultural lands under warmer conditions (Bash et al., 2013; Shen et al., 2020). In fact, the optimized NH_3 emission pattern in April is more consistent with the spatial pattern of inorganic nitrogen fertilizer estimated based on plant demand (Cooter et al., 2012). NH_3 emission in 2011 estimated by CMAQ with NH_3 bidirectional exchange model also predicted higher NH_3 emission in the southern states (Shen et al., 2020). The ratio between NH_3 emission estimates in southern states and that within CONUS is 26% and 18% in the optimized estimates and estimates including NH_3 bidirectional exchange, respectively. In comparison, the ratio is only 10% in the a priori NEI estimates, suggesting a potential low bias in 2011 NEI.*"

Two figures were added to SI as follows to provide the IASI-NH_3 column densities for 2010, 2011, and 2012 and surface temperature maps for these three years.

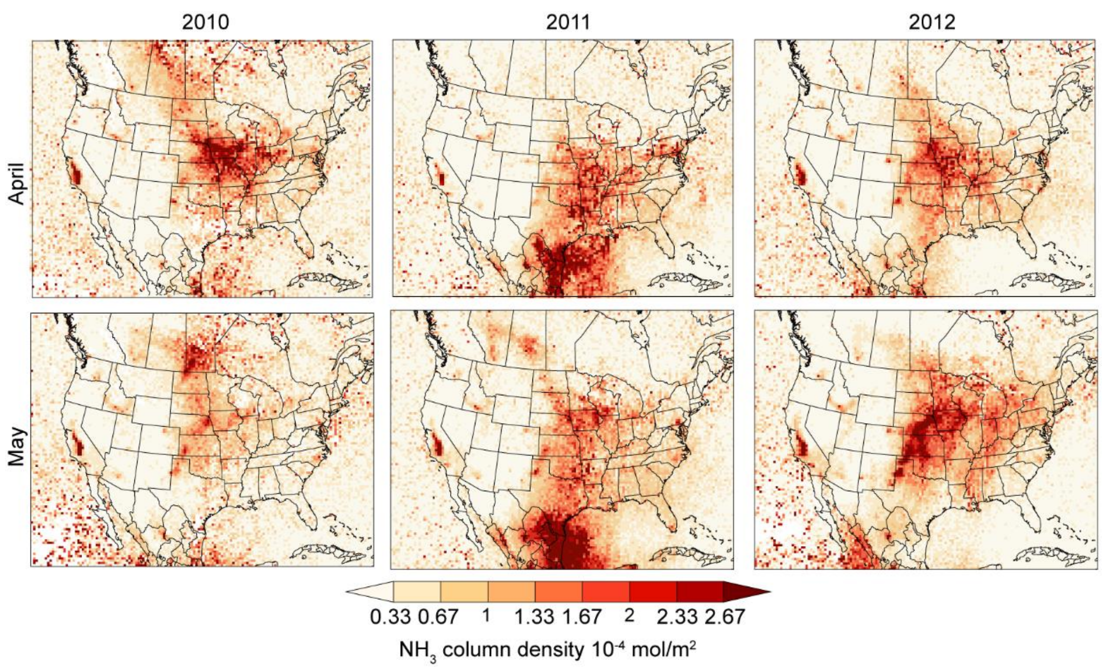

Figure S7 Monthly averaged IASI-NH3 column densities in April and May from 2010 to 2012. The satellite retrievals are regridded at 36 km by 36 km resolution.

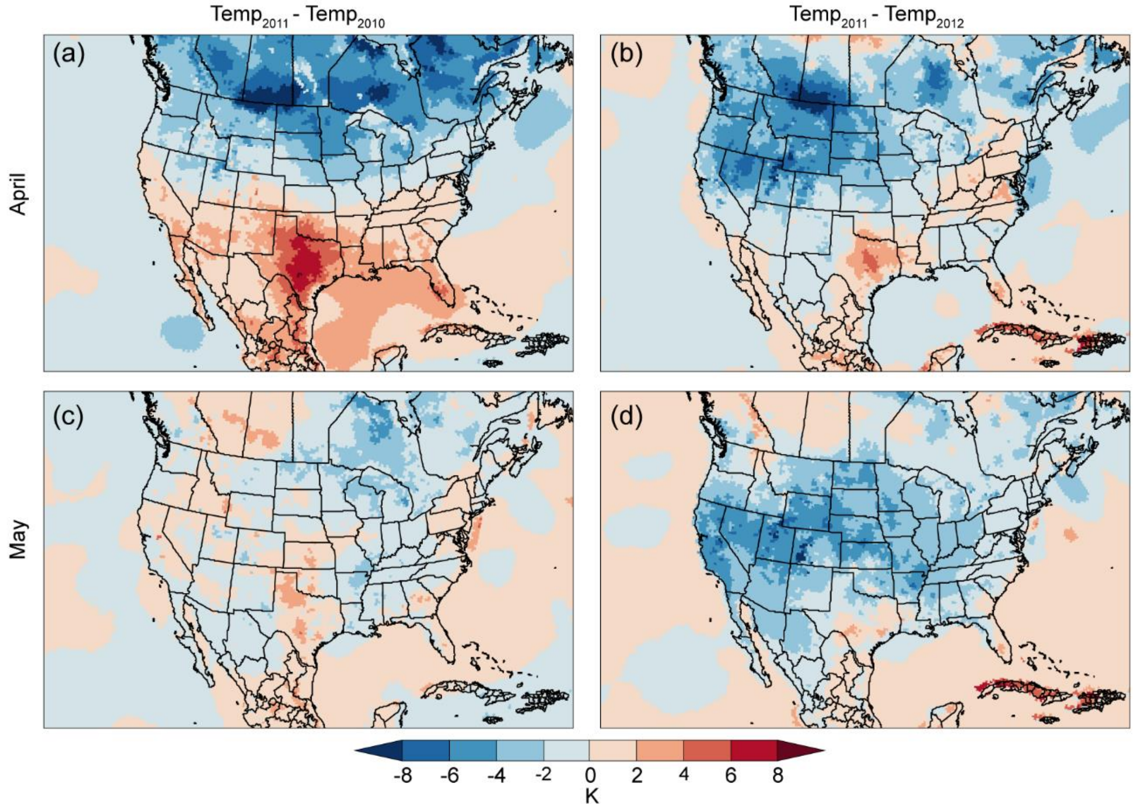

Figure S8 The monthly averaged surface temperature in April and May from 2010 to 2012.

References

Shen, H., Chen, Y., Hu, Y., Ran, L., Lam, S. K., Pavur, G. K., Zhou, F., Pleim, J. E., and Russell, A. G.: Intense Warming Will Significantly Increase Cropland Ammonia Volatilization Threatening Food Security and Ecosystem Health, One Earth, 3, 126-134, https://doi.org/10.1016/j.oneear.2020.06.015, 2020.

Bash, J.O., Cooter, E.J., Dennis, R.L., Walker, J.T., Pleim, J.E.: Evaluation of a regional air-quality model with bidirectional NH_3 exchange coupled to an agroecosystem model. Biogeosciences. 10, 1635-1645, https://doi.org/10.5194/bg-10-1635-2013, 2013.

Comment 12

Page 9, line 277: it may be helpful to also include a priori emission totals in those three months. The posterior emission indicates that the total NH_3 emission decreases linearly from April to July and to October. Then what would the seasonality look like?

Response

In response to this comment, a sentence is added in line 278 to include *a priori* emission totals, and the posterior emission estimates constrained by daily IASI-NH_3 averages are updated as follow: "*The total NH_3 emissions in the optimized estimates are 623 Gg, 564 Gg, and 320 Gg per month in April, July, and October, respectively. In comparison, the emission estimates in the 2011 NEI are 462 Gg, 475 Gg, and 304 Gg per month for the three months.*"

The updated *posterior* emission estimate in April is still the highest. But the difference between emission totals in April and July is much smaller comparing to that between the emission estimates constrained by monthly IASI-NH_3 averages. In comparison, the *a priori* emission estimate in July is slightly higher than that in April. Yet, we cannot draw a confident conclusion on the seasonality of NH_3 emissions due to high uncertainties in NH_3 emission estimates in April. As we suggested in the manuscript (lines 232 – 234, and lines 281 – 284), optimizing NH_3 emissions in April using the inverse modeling technique is more challenging than July and October because of the greater differences in the magnitude and the spatial distribution of the emissions. Better knowledge about agricultural activities and more independent ground and space observations are needed to better constrain the NH_3 emission inventory in the spring months.

Comment 13

Page 9, line 297 and page 12, line 384: it is contradictory to claim that the hybrid inversion "overcomes the over-adjusting problem for high emission rates" and meanwhile attribute the worsening RMSE against AMoN to the emission over-adjustment problem that has supposedly been overcome. Especially the comparison between posterior and AMoN in April (Fig. 4a) seems problematic.

Response

In response to this comment, the sentence in line 297 "*This is likely due to the tendency of satellite-based inversion to over-adjust emissions in high concentration areas (Zhu et al., 2013).*" is deleted. The simulated NH_3 concentration using optimized NH_3 emission estimates agrees better with AMoN observations when daily IASI-NH_3 means instead of monthly means are used as constraints in the 4D-Var inversion. In the updated results, only model evaluation in April shows an obvious increase in NRMSE and a decrease in R^2.

The worsening performance in April is caused by the over-adjustment of NH_3 emissions in Pennsylvania. Using daily means instead of monthly means as constraints help alleviate the over-adjustment. High NH_3 column densities were observed on April 14th and 15th. When daily means are used in the inversion, emissions in other days of the month won't be driven high by these two high observation days. In fact, the posterior emission estimate in Pennsylvania using daily means as constraint is 100% higher than the *a priori* estimates, whereas 700% higher when using monthly means as constraints in the inversion.

The over-adjustment still exists when comparing the simulated surface NH_3 and NH_4^+ concentrations with independent field observations. Although our hybrid method can overcome the over-adjusting problem for high emission areas in the direct 4D-Var method, it tends to over-adjust local emissions when long-range transport dominates the observed high NH_3 column densities. As we mentioned in lines 302 – 303, the hotspot in Pennsylvania on April 14th and 15th possibly came from a large transported plume at high altitude from the central U.S. (Figure S10 and Figure S11). If that was the case, the hybrid inverse modeling framework would have difficulties reproducing the long-range transport contribution for two reasons. First, local emissions in Pennsylvania would be enhanced in the IMB inversion and inter-grid transport were neglected at 216 km by 216 km resolution. Second, the results from such a statistical optimization method are always locally optimal rather than globally optimal. The 4D-Var inversion is more likely to adjust emissions from local and surrounding grid cells instead of grid cells at distance to achieve a local minimum of the cost function. Besides, the IASI-NH_3 column densities may be overestimated because vertical profiles with the highest concentrations near the surface have been assumed in the retrieval process.

The sentences in line 295 – 308 were revised to update the model evaluation results against AMoN observations and better explain the worsening model performance in April, as follow. "*In general, the optimized NH_3 emission reduces the negative NMB when comparing the CMAQ outputs with AMoN NH_3 concentration for all three months. There is a greater improvement at the high concentration end than the low concentration end because both IASI satellite and the passive samplers at the AMoN sites have higher uncertainties in areas with low NH_3 abundance (Van Damme et al., 2015a; Puchalski et al., 2011). Yet, the NRMSE gets higher and R^2 gets lower in April, indicating a higher spatial variation in the residuals. There is an over-adjustment for sites in Pennsylvania in April where there is a hotspot observed by IASI in April 14th and 15th. The hotspot possibly came from a large transported* *plume at a higher altitude from the central U.S. to Pennsylvania (**Figure S10 and Figure S11**), which is not measured by ground observations at AMoN sites at biweekly resolution. If that is the case, the hybrid inverse modeling framework would have difficulties in reproducing the long-range transport contribution for two reasons. First, local emissions in Pennsylvania would be enhanced in the IMB inversion and inter-grid transport were neglected at 216 km by 216 km resolution. Second, the following 4D-Var inversion very likely reached a local optimal by adjusting emissions from local and surrounding grid cells near the observed hotspot rather than grid cells at distance. Besides, the IASI-NH_3 column densities may be overestimated because vertical profiles with highest concentrations near the surface were assumed in the retrieval process (Whitburn et al., 2016).*"

The limitation is addressed by adding the following sentence in line 315: *"… in most of the CONUS, except in Pennsylvania and surrounding regions in April. The hybrid inverse modeling technique may over-adjust local emissions in hotspots dominated by long-range transport.*"

The sentence in line 385 is also revised as follow: "*The hybrid approach overcomes the over-adjusting problem for high emission areas in the direct 4D-Var method and reduces the computational cost, but it may introduce over-adjustment in special cases where the NH_3 abundance is dominated by transport instead of local emissions.*"

Comment 14

Table 1: the R^2 of 0.08 at other (also the majority of) sites between simulated NH_4^+ and observations in April is bothersome. The N is a reasonably large number (115), so such a low R^2 indicates that the model essentially lost all explanation power after the inversion. The authors are suggested to take a closer look at the April data (for other years than 2011 as well) and make sure they are representative.

Response

When checking the data of Table 1 multiple calculation errors are found. We sincerely apologize for the mistakes. The R^2 at other sites between simulated NH_4^+ and observations in April is 0.26 instead of 0.08.

Both corrected Table 1 for the initial submission version and revised Table 1 based on new optimizing scaling factors are provided below for comparison. The optimized NH_3 emission estimates still exacerbate the high bias in the Pennsylvania state and surrounding areas, but the magnitude is significantly reduced comparing to the initial version. The high IASI-NH_3 observations in April in Pennsylvania state was driven by high retrievals in a few days and using daily means instead of monthly means as constraints helped avoid the artificial high bias in the days without observations. We thank the reviewer again for the critical suggestion.

By comparing the satellite data in different years, we find that IASI-NH_3 column densities in April are higher in 2011 than in 2010 and 2012, however, it is common to have high variations in the column densities in adjacent years and months (Figure S7). We believe the IASI-NH_3 observations in 2011 show a reasonable pattern of NH_3 column densities considering the variations in meteorological conditions and emission activities. The over-adjustment in Pennsylvania and the surrounding region is possibly due to the tendency of this hybrid inverse modeling technique to over-adjust local emissions when long-range transport contributed to the high abundance of NH_3 in that region. Please refer to the response to **Comment 13** for a detailed explanation.

Table 1 (corrected version for initial submission) Statistical summary of the correlation between simulated monthly average NH_4^+ and NO_3^- concentrations and observations in April[a]

NH_4^+	Midwest		Penn		Other	
	a priori	optimized	*a priori*	optimized	*a priori*	optimized
N	47		37		115	
NMB	0.27	0.07	0.00	0.48	-0.35	-0.36
NRMSE	0.40	0.14	0.28	0.42	0.45	0.32

slope	0.52	0.58	0.41	0.32	0.60	0.56
R^2	0.57	0.62	0.24	0.36	0.25	0.26
NO_3^-	Midwest		Penn		Other	
	a priori	optimized	*a priori*	optimized	*a priori*	optimized
N	69		38		240	
NMB	0.64	0.29	0.25	1.40	-0.39	-0.41
NRMSE	0.96	0.66	0.66	1.73	0.63	0.80
slope	0.44	0.50	0.29	0.48	0.62	0.33
R^2	0.76	0.73	0.33	0.67	0.28	0.13

[a] The correlation between observed concentrations and simulated ones based on *a priori* and optimized NH_3 emission estimates are compared. The sites are grouped as the Midwest region, Pennsylvania state and surrounding areas, and other areas.

Table 1 (revised version) Statistical summary of the correlation between simulated monthly average NH_4^+ and NO_3^- concentrations and observations in April[a]

NH_4^+	Midwest		Penn		Other	
	a priori	optimized	*a priori*	optimized	*a priori*	optimized
N	47		37		115	
NMB	0.27	0.22	0.00	0.07	-0.35	-0.35
NRMSE	0.40	0.35	0.28	0.30	0.45	0.44
slope	0.52	0.54	0.41	0.39	0.60	0.65
R^2	0.57	0.65	0.24	0.18	0.25	0.28
NO_3^-	Midwest		Penn		Other	
	a priori	optimized	*a priori*	optimized	*a priori*	optimized
N	69		38		240	
NMB	0.64	0.55	0.25	0.43	-0.39	-0.38
NRMSE	0.96	0.88	0.66	0.73	0.63	0.65
slope	0.44	0.46	0.29	0.29	0.62	0.55
R^2	0.76	0.78	0.33	0.31	0.28	0.25

[a] The correlation between observed concentrations and simulated ones based on *a priori* and optimized NH_3 emission estimates are compared. The sites are grouped as the Midwest region, Pennsylvania state and surrounding areas, and other areas.

Comment 15

Page 10, line 302-303 and page 11, lines 345-346: as CMAQ is a full 3D CTM driven by real WRF meteorology and hourly emissions, those transport should have been captured. Why not?

Response

The hybrid inverse modeling technique is a statistical optimization technique that takes into account the chemistry and physics of the CTM. The system is underdetermined because the model freedom far exceeds the number of satellite observations available. The forward CMAQ model can indeed capture long-range transport with real WRF meteorology and hourly emissions. However, instead of solving for the global optimal, the inversion can adjust emissions from local and surrounding grids instead of grids at distance to achieve a local minimum of the cost function. Besides, in our case of over-adjustment in Pennsylvania, local emissions were enhanced in the IMB inversion and inter-grid transport was neglected at 216 km by 216 km resolution.

It is a limitation of this hybrid inverse modeling method that local emissions may be over-adjusted when the satellite observed hotspots were dominated by long-range transport. The limitation is clarified and addressed in the revised manuscript as follows.

The sentences in lines 300 – 308 are revised as "*There is a greater improvement at the high concentration end than the low concentration end because both IASI satellite and the passive samplers at the AMoN sites have higher uncertainties in areas with low NH_3 abundance (Van Damme et al., 2015a; Puchalski et al., 2011). Yet, the NRMSE gets higher and R^2 gets lower in April, indicating a higher spatial variation in the residuals. There is an over-adjustment for sites in Pennsylvania in April where there is a hotspot observed by IASI in April 14th and 15th. The hotspot possibly came from a large transported plume at a higher altitude from the central U.S. to Pennsylvania (**Figure S10 and Figure S11**), which is not measured by ground observations at AMoN sites at biweekly resolution. If that is the case, the hybrid inverse modeling framework would have difficulties in reproducing the long-range transport contribution for two reasons. First, local emissions in Pennsylvania would be enhanced in the IMB inversion and inter-grid transport were neglected at 216 km by 216 km resolution. Second, the following 4D-Var inversion very likely reached a local optimal by adjusting emissions from local and surrounding grid cells near the observed hotspot rather than grid cells at distance. Besides, the IASI-NH_3 column densities may be overestimated because vertical profiles with highest concentrations near the surface were assumed in the retrieval process (Whitburn et al., 2016).*"

A sentence is added in line 315: *"... in most of the CONUS, except in Pennsylvania and surrounding regions in April. The hybrid inverse modeling technique possibly over-adjusts local emissions in hotspots dominated by long-range transport.*"

We thank the reviewer for providing the thoughtful comments and suggestions.