Response to Reviewer #2 comments:

Comment 1

This manuscript applied a hybrid inversion approach, which combines a coarse resolution mass balance inversion and a fine-resolution 4D-VAR inversion, to optimize NH_3 emission estimates from the 2011 National emission inventory (2011 NEI) for the U.S. based on the satellite observations of the Infrared Atmospheric Sounding Interferometer NH_3 column density (IASI-NH_3) and the numerical simulations using the CMAQ v5.0 and its multiphase adjoint model. The optimized NH_3 emission inventory suggests the underestimation in the 2011 NEI, especially the NH_3 emission amount in April. The study demonstrated the robustness of the inversed NH_3 emission inventory by evaluating the CMAQ modeling performance of ambient NH_3 concentrations and NH_4^+ wet deposition, analyzed the potential factors accounting to the differences between the NH_3 emissions in 2011 NEI and the optimized estimates, and assessed the influences of the optimized NH_3 emissions to the simulations of ambient aerosol concentrations as well as to the nitrogen deposition exceedances in the U.S. The results are presented in a clear way and the manuscript stands in a good structure. I would recommend publication in Atmospheric Chemistry and Physics after consideration of the following comments.

Response

We thank the reviewer for the comments and valuable suggestions. The detailed responses can be seen below.

Comment 2

Specific comments

1. The adjustment to the a priori emissions of NH_3 is driven by the difference between the observed NH_3 column density and the simulated one, which requires that the uncertainty in the a priori emissions is the dominant explanatory factor for the bias in the simulated NH_3 column density. As we know, several factors other than NH_3 emissions might affect the uncertainty of the simulated NH_3 column density, such as the meteorological fields, the simulated concentrations of other related species, and even other primary emissions. The performance of the WRF model and the CMAQ model in the study are suggested to be introduced in the section 2.3. The influences of these factors on the inversion of NH_3 emissions are also suggested to be discussed in the evaluation of the optimized emission estimates.

Response

We agree with the reviewer that the performance of the inversion will also be influenced by uncertainties and biases in the WRF and the CMAQ model. The model performance of the two models are added in the manuscript as suggested by the reviewer.

The WRF model performance is evaluated by comparing simulated wind speed, temperature, and humidity against surface observations. In general, the WRF simulated meteorological fields agree well with the observations, except for a slight overestimation of wind speed. The CMAQ model performance for simulating gas-particle partitioning of semi-volatile species and reactive nitrogen deposition has been evaluated in detailed in our previous papers using the same input data and model configuration (Chen et al., 2019; Chen et al., 2020). There is a consistent low bias in simulated NH_3 and NH_4^+ concentrations indicating that the NH_3 emission estimates are biased low. Most of the observation-simulation data pairs for $\varepsilon(NH_4^+)$ scatter within the 0.5 to 2 range, and there is no significant systematic bias found in $\varepsilon(NH_4^+)$. Larger biases were found for locations with low relative humidity, low NH_3 and NO_x emissions, or significant dust emissions (Chen et al., 2019). For deposition evaluation, both dry and wet deposition amount are biased low, further indicating a possible low bias in NH_3 emission estimates. Besides, the biases in gas-particle partitioning ratio and precipitation amounts also affect the model performance (Chen et al., 2020). The most relevant evaluations including the gas-particle partitioning of NH_3 and NH_4^+ ($\varepsilon(NH_4^+)$, defined as the molar ratio of NH_4^+ to the sum of NH_3 and NH_4^+), as well as deposition of NH_4^+ are provided in the supporting information.

A sentence describing the WRF model performance is added in line 170 as follows. "*The simulated meteorological fields show good agreement with surface observations (**Figure S2**) (NOAA, 2020).*"

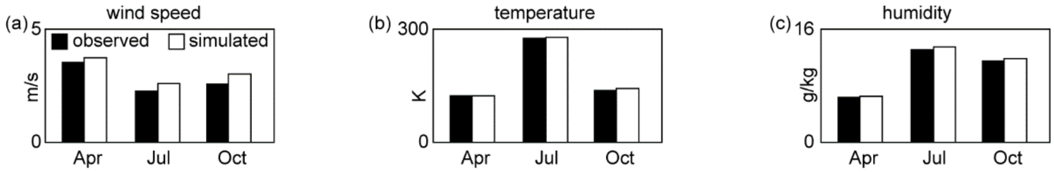
Sentences describing CMAQ model evaluation results are added in line 174, section 2.3, as follows. "*To evaluation CMAQ model performance, the simulated gas-particle partitioning ratio of* NH_3*-*NH_4^+ *and* NH_4^+ *deposition is compared with observations from AMoN, Clean Air Status and Trends Network (CASTNET), and National Atmospheric Deposition Program (NADP) (**Figure S3 and Figure S4**). CMAQ captures the overall spatial pattern of these governing processes for atmospheric* NH_3 *abundance, considering the uncertainties in emissions, model parameters, and meteorological fields. Expanded evaluation of CMAQ model performance in simulating gas-particle partitioning and nitrogen deposition has been conducted in previous studies (Chen et al, 2019; Chen et al., 2020).*"

Sentences are added in the discussion to address the impacts of uncertainties from the WRF and the CMAQ model as follows.

Sentences are added in line 284 as follows. "*Besides the a priori emission inventory and observational constraints, the inversion performance will also be affected by other processes (e. g., gas-particle partition, transport, cloud and precipitation, and dry and wet deposition) governing the atmospheric abundance of* NH_3*. Future works refining the pertinent processes will also help improve the optimized* NH_3 *emission estimates.*"

A sentence is added in line 313 as follows. "*A better representation of the cloud, precipitation, and deposition processes in the WRF and the CMAQ model is needed to close the gap between simulated and observed* NH_4^+ *deposition amount.*"

Figures showing the WRF and CMAQ performance were added to SI as follows,



Bias (m/s)	0.24	0.40	0.55
RMSE (m/s)	2.09	1.86	1.90

Bias (K)	0.02	0.19	0.34
RMSE (K)	2.22	2.04	2.09

Bias (g/kg)	0.11	0.41	0.20
RMSE (g/kg)	1.19	1.88	1.13

Figure S2 Model evaluation for WRF simulated meteorological fields against TDL hourly observations for April, July, and October. The bias and RMSE are listed below each plot.

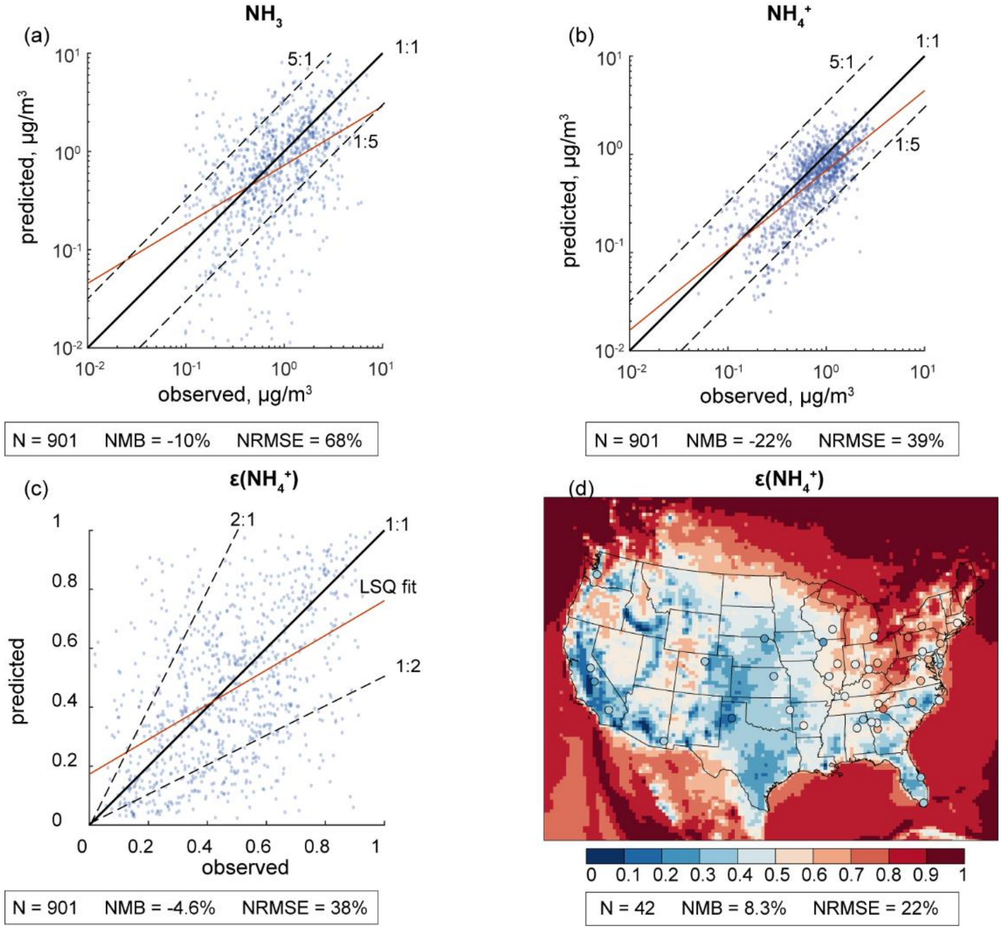


Figure S3 Model evaluation for CMAQ simulated bi-weekly average surface concentrations of NH_3 (a), NH_4^+ (b), and the gas-particle partitioning ratios, ε(NH_4^+) (c) against observations from collocated AMoN (Ammonia Monitoring Network) and CASTNET (Clean Air Status and Trends Network) sites. Overlay of annual mean ε(NH_4^+) based on simulated (color map) and observed (colored dots) concentrations are also plotted (d). The 1:1 line (solid black line), data range line (dashed back line with ratio labeled) and regression line (red) is also plotted. Number of data points (N), NMB, and NRMSE are provided along each plot.

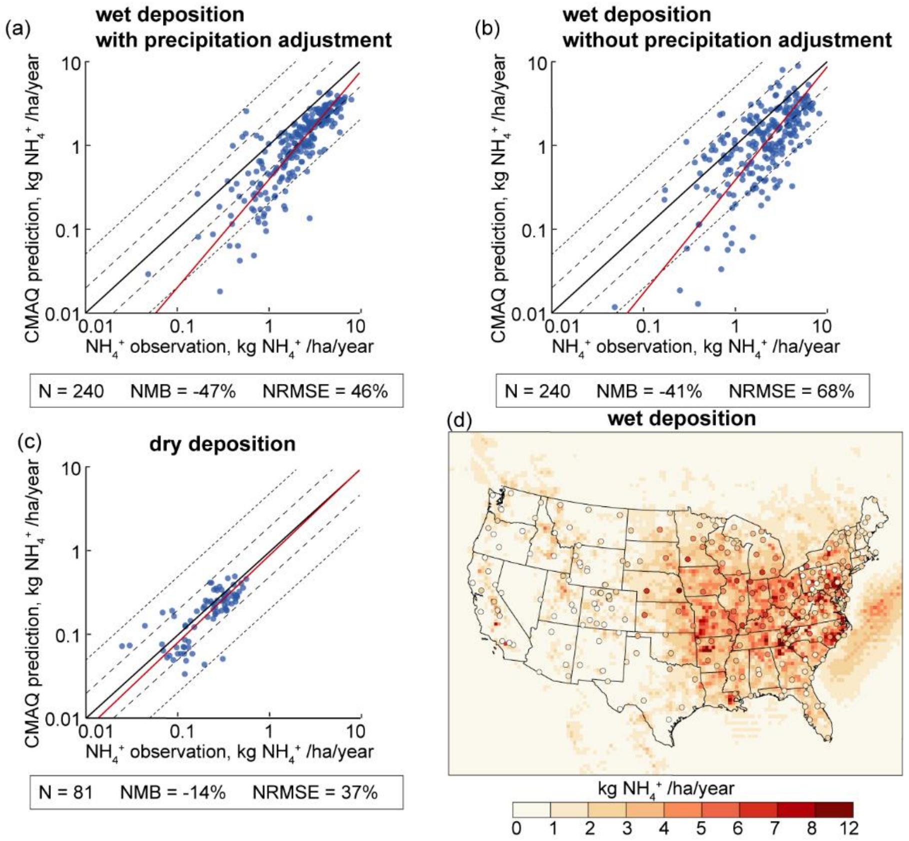


Figure S4 Model evaluation for CMAQ simulated wet (a and b) and dry (c) deposition of NH_4^+ against observations from the NADP (National Atmospheric Deposition Program) and the CASTNET (Clean Air Status and Trends) Network. Overlay of annual NH_4^+ wet deposition based on simulated (color map) and observed (colored dots) amount are also plotted (d). The scatter plots show the comparison between CMAQ predicted and observed annual dry, wet, and total deposition amounts, with the blue line showing the linear regression line. The 1:1 line (solid black line), data range line (dashed back line with ratio labeled) and regression line (red) is also plotted. Number of data points (N), NMB, and NRMSE are provided along each plot. For wet deposition, the CMAQ model performance with (a) and without (b) precipitation adjustment are evaluated.

References

NOAA (2020). Meteorological Development Laboratory/Office of Science and Technology/National Weather Service/NOAA/U.S. Department of Commerce: TDL U.S. and Canada Surface Hourly Observations, Research Data Archive at the National Center for Atmospheric Research, Computational and Information Systems Laboratory, https://rda.ucar.edu/datasets/ds472.0/, 1987. Accessed 24 Dec 2020.

Chen, Y.; Shen, H.; Shih, J.-S.; Russell, A. G.; Shao, S.; Hu, Y.; Odman, M. T.; Nenes, A.; Pavur, G. K.; Zou, Y.; Chen, Z.; Smith, R. A.; Burtraw, D.; Driscoll, C. T.: Greater contribution from agricultural sources to future reactive nitrogen deposition in the United States. Earth's Future, doi: 10.1029/2019EF001453, 2020.

Comment 3

2. In section 3.3, lines 301-306: Do the outputs of the WRF/CMAQ model present the large transported plume from the central U.S. to Pennsylvania on April 14th and 15th? Do other data or analysis (such as wind observations at high altitude, trajectory analysis) support the possibility of this transport?

Response

The spatial pattern of CMAQ simulated NH_3 column density does not present similar patterns observed by the IASI satellite on April 14th and 15th, even using optimized NH_3 emissions as input. This is probably because the optimized results failed to capture long-range transport contribution and over-adjusted local emissions in Pennsylvania.

Although the Atmospheric Infrared Sounder (AIRS) and the Tropospheric Emission Spectrometer (TES) also measures NH_3 column densities in 2011, it is hard to derive daily spatial pattern in the CONUS. For AIRS, only monthly level 3 data has been developed at this moment and the coverage is poor in northeastern U.S. For TES, the satellite swath is too narrow to provide complete daily coverage for CONUS.

In the revision, we performed a trajectory analysis using NOAA HYSPLIT model driven by meteorological fields forecasted by the North American Mesoscale Forecast System (NAM) at 12 km by 12 km resolution. Forward trajectory simulation was performed for April 13th to 15th with a source located in Oklahoma at surface level (37.0 N, 94.7 W). Backward trajectory simulation was performed for April 15th with a receptor located in Pennsylvania (40.9 N, 77.6 W) at both surface level and elevated level (5 km). The forward air parcel trajectories show that long-range transport toward northern and northeastern regions occurred on April 14th and 15th. The backward air parcel trajectories also show that NH_3 in elevated height may came in from the central U.S.

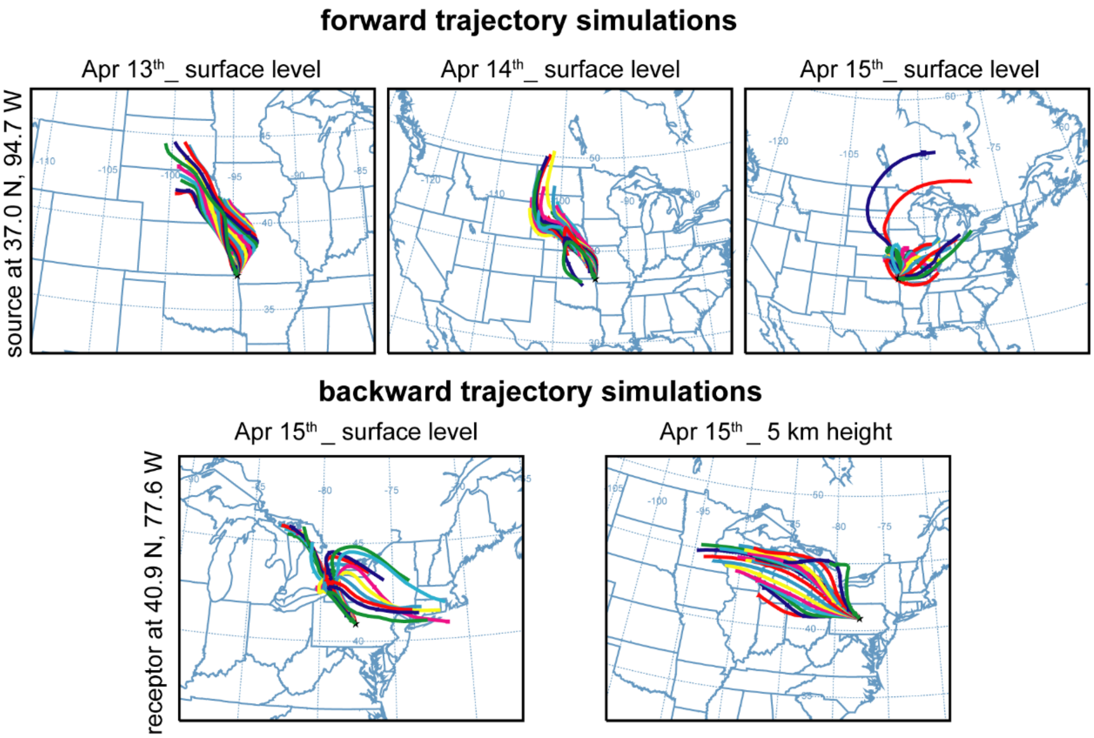


Figure S11 Forward and backward trajectory analysis generated from the NOAA HYSPLIT model. The location of the source (forward) and receptor (backward) are shown as stars in the figures. The starting time of each trajectory is 1 hour apart, from 00:00 to 24:00 local time on each day.

Again, the long-range transport contribution is our speculation based on the IASI-NH_3 spatial distribution. Although the trajectory analysis partially supports our speculation, the high IASI-NH_3 column densities on April 14th and 15th warrants further investigation. In the revised manuscript, we further clarified that the long-range transport is our hypothesis to explain the discrepancy between IASI-NH_3 and surface observations in Pennsylvania for April 2011.

The sentences in lines 300 – 308 is revised as follows. "*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).*"

Figure S11 showing the trajectory analysis results is added to the SI.

Comment 4

3. As shown in Figure 4, the optimized NH_3 emission reduces the negative NMB when comparing the CMAQ outputs with AMoN NH_3 concentrations, but increases the NRMSE and decreases the correlation. In my opinion, the optimized NH_3 inventory does not greatly improve the agreement between CMAQ simulated NH_3 concentrations and the observations. The near ground ambient NH_3 concentrations might reflect more direct signal of the NH_3 emissions than the NH_3 column density. If the ambient NH_3 measurements together with the satellite observations are used to inverse the NH_3 emissions, we would obtain more reasonable optimized emission estimates.

Response

We agree with the reviewer that near ground ambient NH_3 concentration observations might better constrain NH_3 emissions than the satellite NH_3 column densities. However, only 110 active sites are measuring bi-weekly average NH_3 concentration from the AMoN network in the U.S. The ground observations are too sparse to provide useful constraints in the inversion because of the high spatiotemporal heterogeneity of NH_3. Therefore, we decide to leave out the AMoN observations as an independent set of observations to evaluate the robustness of the inversion outcomes. It would be ideal if the two sets of observations can be used together in the inversion if more ground NH_3 observations become available in the future.

The sentence in line 395 is revised as follows: "*…shows that the optimized NH_3 emission estimates reduce the NMB between model outputs and independent observations, especially in April. The NRMSE remains high, indicating 1) the potential to further optimize NH_3 emission estimates when more representative observations of ambient NH_3 abundance becomes available; 2) the need to address the uncertainties in other processes affecting the NH_3 abundance, such as gas-particle partitioning, dry and wet deposition, and in cloud processes.*"

Comment 5

Technical comments

1. In lines 434-436 and lines 541-542: Please add the journals which the references are submitted to.

Response

The two references are updated as follows.

lines 434 – 436:

Cao, H., Henze, D. K., Shephard, M. W., Dammers, E., Cady-Pereira, K., Alvarado, M., Lonsdale, C., Luo, G., Yu, F., Zhu, L., Danielson, C. G., and Edgerton, E. S.: Inverse modeling of NH_3 sources using CrIS remote sensing measurements, Environ Res Lett, 15, 104082, 10.1088/1748-9326/abb5cc, 2020.

lines 541 – 542:

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.

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