Responses to the Manuscript ACP-2022-216: Estimating global ammonia (NH₃) emissions based on IASI observations from 2008 to 2018

Dear Editor-in-Chief:

We hereby submit the revised version of our manuscript (ACP-2022-216).

We greatly appreciate you and two referees for providing highly insightful and constructive comments, which have substantially improved the clarify of our manuscript. We have carefully addressed all these comments, please see below our point-to-point **responses in blue** and **red** text and refer to the **revised manuscript**.

In our attached documents, we have made the following major revisions:

- Add a section about the uncertainty evaluation and add two figures in this section.
- Move original Table S1 to the main text and add more explanations on the uncertainty and sensitivity analysis.
- Move original Figure 7 to the supplementary and add several figures in the supplementary.

We hope you find our manuscript suitable for publication and look forward to hearing from you

Yours sincerely, Zhenqi Luo, Yuzhong Zhang, Wei Chen, Martin van Damme, Pierre-François Coheur, Lieven Clarisse

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1. RESPONSES TO REFEREE, REFEREE #1

Comment #1: General comments

This manuscript showcases global NH_3 emissions estimated using a top-down approach constrained by IASI observations with comparison to bottom-up estimates. The approach used here is built upon a previous study with modifications in several aspects including NH_3 lifetime calculation and local mass balance approximation. The authors address the uncertainty of emissions by performing sensitivity tests on various parameters and discuss the limitations of current emission inventories. This work shows the promise of using satellite observations to constrain NH_3 emission inventories on the global scale, as well as the need to improve emission factors used in model simulations, particularly in developing regions. Overall, the manuscript is well-written and organized. The figures are clear, concise, and easy to follow. I recommend the publication of this manuscript in ACP with some minor comments/suggestions for the authors to address/consider.

We thank the referee for positive evaluation of the manuscript.

Comment #2: Specific comments

Line 80: You may want to emphasize this is the reanalyzed IASI dataset as opposed to the near real time dataset.

We add the text in **Line 79**.

Line 89-97: You may also want to state explicitly that you only used observations taken over land areas.

We add the text in **Line 92 and 136**.

Line 103 (Sect 2.2): One major distinction between this study and Evangeliou et al. (2021), besides modifications in the approach, is the CTM used for simulating NH_3. Can you elaborate a little on the differences between GEOS-Chem and LMDz-OR-INCA, and any outcomes they may have on the emission estimates?

The systematic comparison is out the scope of our study, and we do not find reference indicating that model differences are the major cause of discrepancies in emission inference.

Line 253-257: Are these speculations or do you have statistical evidence to support? Without seeing the inter-annual variabilities of emissions or some analyses on the NH_3/CO ratio, I am not completely sure if the positive trend in Canada can be explained by one particular wildfire season, likewise the negative trend in Russia and eastern Europe.

The fire emission inventory (Global Fire Emissions Database, GFED4, van der Werf et al., 2017) shows that large fires occurred in Canada are from 2008 to 2011 and in eastern Europe are from 2013 to 2016 and also 2017 (**Fig. S4**, now added in the Supplement). We attribute trends to fire events mainly based on this inventory. We now clarify in the text (**Line 253**).
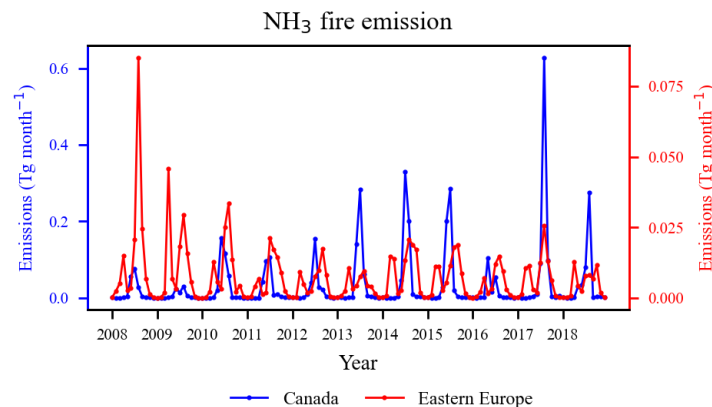
Figure S4. Monthly average of NH_3 fire emission over Canada (130°-50°W, 48°-84°N) and eastern Europe (10°-55°E, 36°-72°N) during 2008-2018. The emission data is from GFED4.

Line 282-285: I wonder how good the bottom-up estimates are in India and China, as you mentioned that emission factors in developing regions may not be as accurate. In Fig. 3, BUE1 in IP and EC is almost invariant throughout the whole period, which seems contradictory with the fertilizer and manure data in Fig. 4. The reason for asking this is even though the SO_2 correction largely closes the gap between BUE1 and TDE, if prior emissions are off in the first place do we have enough confidence to agree on the absolute magnitude of the emissions?

We now clarify here and elsewhere (e.g., caption of **Fig. 3**; **Sect. 2.2**) that the prior inventory implemented in our simulation has incomplete annual information on emissions (including NH_3 and SO_2) especially after 2013, and that's why it is inconsistent with fertilizer and manure data. We use CEDS as the default anthropogenic inventory replaced by MIX-Asia v1.1 in Asia. The objective of including both observed NH_3 and SO_2 in NH_3 emission quantification is to reduce dependence on prior emissions (of NH_3 and SO_2).

Line 332: What percentage of results or grid cells were determined as unreliable and removed?

Supplement: Table 2 should be renamed as Table S2. Also and again, I think showing the percentage of grids used may be more meaningful than just the number of grids.

We applied a monthly NH_x budget analysis based on the GEOS-Chem simulation and exclude grid cells from our analysis where transport dominates over local prior emissions or depositions in the monthly NH_3 budget. The total percentage of excluding grid cells range from 0 to 40 % for the seven selected regions. We now show this information in **Fig. S6** and **Table S1**.
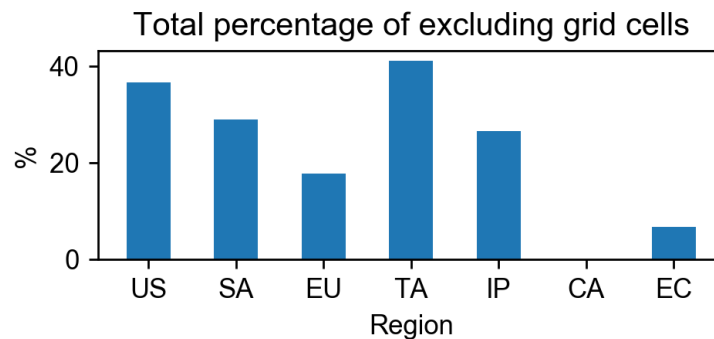
Figure S6. Total percentages of excluding grid cells for seven selected regions between 2008-2018.

Finally, the novelty of this study and why it is important should be highlighted more given the overlap with Evangeliou et al. (2021) in terms of topic, datasets, and methods. I was hoping to see a more conclusive statement on the implication of this

work to the scientific community interested in NH_3 emissions. You modified the fast top-down approach proposed by Evangeliou et al. (2021), and the resulting change in emission estimates is drastic (79 vs 180 Tg a^{-1}). My takeaway from this is the emission figures one will get from models are largely subject to the method they choose and assumptions they make. Do you think this approach is scientifically reasonable enough for the purpose of deriving global emissions, or is a full-fledged inversion still necessary to obtain more accurate numbers? And how might the results change if a different satellite product is used (CrIS, for example)?

Our method is particularly useful for long-term global analysis of emission trends (or changes). It is better than direct trend analysis of NH_3 column density (as often applied in current literature), because our method handles the effect of meteorology. In addition, including observed SO_2 accounts for the impact of SO_2 on NH_3/NH_4^+ partition, which is even conceptually better than a full-fledged inversion that only assimilate NH_3 observations. However, this is only applied in China and India in this study, as more investigation is needed to extend the idea globally because of variations in the regime of sulfate-nitrate-ammonium aerosol. We have modified the conclusion to include these points.

Comment #3: Technical corrections

Line 30: Emissions of ammonia (NH_3) to the atmosphere have…

Line 31: such as nitrogen oxides (NO_x) and sulfur dioxide (SO_2)

Line 276: an overall decreasing trend in NH_3 emissions

Line 316: driven by the prior emissions

Line 343: NH_3 emissions from eastern China are significantly decreasing

References: I see a few citations messed up due to subscripts in the titles (e.g., line 477, line 496 and 497). Please correct accordingly.

We have corrected them. Thank you!

2. RESPONSES TO REFEREE, REFEREE #2

Comment #1: General

Ammonia emissions estimates constructed from bottom-up inventories currently have large uncertainties. Top-down estimates of ammonia emissions using ammonia retrievals from satellite-borne instruments have the potential to greatly refine these bottom-up estimates. This paper uses ammonia retrievals from IASI to construct a global top-down estimate of ammonia emissions. The authors build on the work of Evangeliou et al., 2021, offering several improvements. These new emissions estimates yield much fewer emissions globally than derived in of Evangeliou et al., 2021, but significantly larger than the bottom-up estimates.

While a number of studies have recently been conducted that use similar methods to derive ammonia emissions regionally, currently few studies have provided top-down ammonia emission estimates globally. As such, this is a timely and scientifically relevant paper. Overall, the presentation of this paper is good, but some re-organization should be considered to improve the paper's readability. Additional analysis is also required before publication, as outlined below.

Thank you for reviewing our paper and for your helpful suggestions.

Comment #2: Major comments

I could not see any comparisons with an independent set of observations (such as surface observations). Validation with another set of observations needs be added. For this, calculations of FB, R^2, and RMSE should be examined (as done in Table S2).

We add the comparison of simulated concentrations with ground-based measurements, i.e., validation against the ground-based measurements (**Line 339-351**), though available observations are not sufficient to evaluate our major findings in regions like tropical Africa, South America, and South Asia.

Section 2.1 should contain some discussion of the uncertainties associated with the IASI NH_3 retrievals. There is a reference to using the relative errors that are reported with the retrievals in Section 2.4, so maybe part of line 183 could be moved to Section 2.1? What are typical uncertainties on the IASI retrievals?

We add the discussion of uncertainty on the IASI retrievals in terms of its vertical profile (**Line 128-131**).

The information related to the sensitivity analysis seems out of order, as this information is spread out over different sections. Also, by referring to Table S1 in Section 2.1 and 2.4, it seems to present results of the emissions inversion before the main results are presented. I would move the sentences starting with 'To reduce uncertainty' on line 94 to the end of line 97 to either Section 2.3 or 2.4. I would consider moving the sentence starting with 'We also test' on line 160 to Section 2.4 as well. Also, I think Table S1 should be moved from the Supplement to the main body of the paper. I also think it would be better to move the second paragraph in Section 2.4 that start on line 186 to the end of Section 2.3. I cannot see much discussion of the results of the sensitivity analysis in the 'Results and discussion' section. More discussion of the sensitivity analysis should be included. In addition to discussing the range of results of the global emissions from the sensitivity analysis, it would be good to add results/discussion/figures for the sensitivity analysis for emissions on regional scales. For example, would it be possible to add a plot like Fig. 2b, but for it to show the deviation from the TDE results instead (maybe as a percentage of the TDE emissions) when the parameters in Table S1 are varied?

We have reorganized the description on sensitivity analysis in **Sect. 2.4**. We move **Table S1** to the main text, which summarizes all sensitivity tests. We also add more discussion in **Sect. 3.5** and **Fig. 7** on uncertainty analysis (**Line 324-331**).
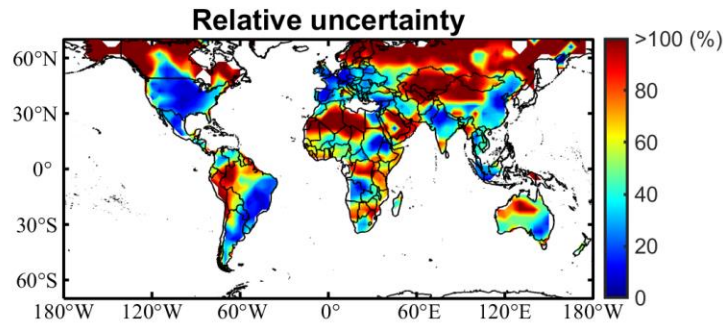
Figure 7. Spatial distribution of TDE relative uncertainty as the discrepancy of emission estimations in parameters perturbation (Table 1) divided by the TDE average during 2008-2018.

At the end of Section 2.2, you mention that averaging kernels are not provided in the retrieval product used. Including the averaging kernels in the calculation of the columns could potentially significantly change the column values. Is there reason to think the effect of the averaging kernel on the column is small? If so, could you provide some details on this? If not, is it possible to make a rough estimation of the averaging kernel and see how much this changes the results? Also, the two sentences starting with 'To compare' on line 129 until the reference to Van Damme et al. 2017 on line 131 should be moved elsewhere (maybe to Section 2.3 or a new subsection with the new information requested).

We add more clarification in the text (**Line 128-131**).

More discussion of the rational for using the formulation in Eq. (1) is necessary. Different mass balance methods use different methods to determine the proportionality constant between the columns and emissions. For instance, in the finite difference mass balance (FDMB) method, this proportionality is determined by comparing two different model runs: one run using the a priori emissions and one run with perturbed emissions. In the FDMB method, if you assume that you have a simplified model that assumes a steady state and no transport, the proportionality constant will be 1/tau, as in Eqn. (1). However, in general these two different methods will differ. So I'm curious what the rational in choosing this method over the FDMD method is. Do you expect that the two methods would give similar results? Alternatively, an inversion/assimilation method could be used instead, where the proportionality constant would instead be given by the Kalman gain, which takes into account the uncertainties of both the observations and the a priori emissions estimates. Could you describe the advantages and/or disadvantages of using the Kalman gain instead of a mass balance method? In this context, I'm assuming the Kalman gain would be a scalar just like tau, not a (large) matrix that would be employed in a Kalman Filter method such as an EnKF that would obviously be very computationally expensive.

Yes, our method is different from the FDMB. In FDMB, the proportionality constant β is calculated by perturbing emissions by a fixed amount and calculating the resulting change to the column abundance, which accounts for the sensitivity of

fractional changes in local columns to fractional changes in emissions if assumes a steady state and no transport. We suppose the difference of the emission estimation resulting from these two methods depend on the difference in β and τ applied in the equations. The ensemble Kalman filter (EnKF) update the state estimate with the Kalman gain. It is computationally expensive for CTMs with dozens of model simulations so that it may not be suitable for the long-term global analysis like this study. The comparison of different mass balance methods is out the scope of our study.

On line 143, you mention that you use the lifetime for NH_x instead of NH_3. The lifetimes of the two will differ, but I didn't quite follow why you would want to use the lifetime of NHx if the estimation is for the emissions of NH_3. Could you add more explanation why this makes sense conceptually?

We use lifetime of NH_3 (not NH_x) against the loss of the NH_x family. We now add more explanations on why we think this calculation is proper. See **Line 145-149**.

In regards to Eqn. (3), if the concern is that SO_2 emissions are underestimated in the bottom-up emissions, and you would like to make a correction for this, why not just increase the bottom-up emissions estimates by the same amount (i.e. omega)? Is the method used easier to implement? If the increase in SO_2 emissions are fed into GEOS-Chem, then ISORROPIA-II can work out the details of the NH_3 - NH_4^+ partitioning, i.e when NH_3 is in excess, etc...

Eq. (3) combines information from both NH_3 and SO_2 observations for NH_3 emission quantification, because the two are intrinsically connected. The method reduces our dependence on accurate prior emissions of either SO_2 or NH_3. It also allows to correct the SO_2 effect, without rerun the model with corrected SO_2 emissions. So it should be easier to implement than the approach described by the referee.

One line 186, you mention that 'we perform GEOS-Chem full chemistry simulations in selected years'. What was the GEOS-Chem mode run initially for the full 2008-2018 period? This should be moved to Section 2.2 and expanded on, i.e. give a brief description of the simulation modes and their difference, why you chose to use the full chemistry mode for only these three years, etc... Also, with the way the paper is currently organized, it is a bit confusing figuring out which simulation mode was used for what. I assume that the non-full-chemistry mode was used with Eqns. (1) and (3), but I can't see where this is specified in the paper. Please clarify in Section 2.2 exactly what the output of each simulation mode is used for. A table might make this clearer to the reader.

Sorry for the confused organization. All the GEOS-Chem simulations we run are in the full chemistry mode. We have corrected it as the 'GEOS-Chem simulation'.

In regards to the calculation of fractional bias of IASI as compared to GEOS-Chem, if the IASI observations were already used in the estimates of the emissions through comparisons to GEOS-Chem (Eqns. (1) and (3)), what is the goal of presenting these FB values? This comparison uses the full chemistry mode (I assumed that Eqns. (1)

and (3) where used in non-full chemistry mode, is that correct?), but I'm not clear on what this comparison is telling you. Add more explanation of what this is being used for. If comparisons with an independent observation data set are added, as suggested above, is this comparison still necessary?

We now add more clarification in the text (**Line 332-338**). This exercise is to check whether results from Eq. (1) and (3) (which are a simplified description of NH_3 chemistry and transport) indeed improve agreements with IASI.

On line 263, it says that the 'large post-2013 increase is inconsistent with flat or even declining fertilizer input and manure amount (Fig. 4).' Do the plots in Fig. 4 include emissions from livestock? If not, it may be hard to really tell if the trends found by using Eqn. (1) are really inconsistent with the data in Fig. 4.

We now clarify that livestock emissions are related to livestock manure amount (**Fig. 4 and Line 265**).

On line 275, it described that SO_2 trends from OMI and OMPS are used with Eqn (3). The estimates of SO_2 trends from OMI and OMPS will have uncertainties associated with them. Could these uncertainties be incorporated into your analysis? i.e. could you include another sensitivity test for the value of the SO_2 trend used?

We report the suggested sensitivity test in **Line171**. Yes, Wang and Wang (2020) reported the stand deviation of the yearly SO_2 trend values as 10-20 %. Thus, we perturb the ω in the Eq. (3) as 4/6 % and -4/-6 % over China and India in our uncertainty analysis (**Line 187-188**).

Comment #3: Minor comments

Line 31: 'particulate matters' to 'particulate matter'

Line 33: 'These particulate matters also affect' to 'Particulate matter also affects'
Line 35: '… and wet processes, and therefore are associated with …' remove the word 'therefore'

Line 50: 'depending' should be changed to 'dependent'

Line 136: Would be good to remind readers here that C_{NH3,obs} are the monthly mean observations, not an individual observation.

Line 180: Replace 'related to the number of IASI measurements (ð• ' ›) and their measurement errors:' by 'given by'

Line 187: 'top-down estimate (TDE) and prior emissions (BUE1)' the acronym TDE was already defined on line 134, while the acronym BUE was used prior to this line but not defined until this line. Change so that these acronyms are defined at their first appearance in the paper.

Section 3.2 starts by introducing Fig. 2 and then introduces Fig. 3 in the next sentence. Try to reorganize this section by first discussing Fig. 2 and then move on to discussing Fig. 3 instead of introducing them at the start of the section together.

We correct them, thank you for the careful read.

In regards to Fig. 2, I'm a bit confused about the colour bars and the colour scale. Fig 2c shows the difference between Fig 2a and 2b, so the units should be in g m^{-2} a^{-1}, but Fig 2c has blue in it, which isn't in the colour bar in the top row that has these units. The bottom row colour bar has blue in it, but it has the wrong units for 2c (g m^{-2} a^{-1} per decade). Could you clarify which colour bar goes with Fig 2c? Could the figure be rearrange or changed in some way to make this more clear?

The units for **Fig. 2c** are g m^{-2} a^{-1} and we add a color bar for **Fig. 2c.**
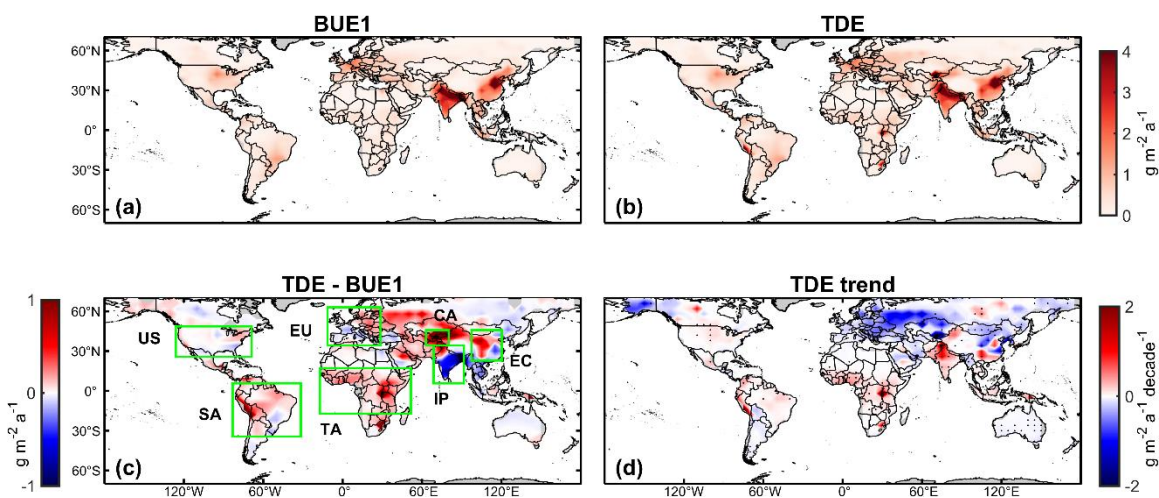
Figure 2. Spatial distribution of NH3 emission fluxes during 2008-2018. (a) Bottom-up emissions (BUE1), (b) top-down emissions (TDE) inferred from IASI observations, (c) difference between TDE and BUE1 estimates and (d) emission trends derived from TDE estimates. Green boxes denote seven regions analyzed in Sect. 3.2. Top-down emission fluxes are computed with Eq. (1) except for IP and EC where Eq. (3) is applied. Linear trends are computed from the time series of annual averages. Dots in (d) represent significant linear trends at the 95 % confidence level.

In the description of Fig 3, it says 'Shadings represent the range derived from uncertainty analyses' Table S1 describes a number of different sensitivity tests. Does the shading refer to the upper and lower bounds over all tests? Please specify in the main text.

We add the description of the uncertainty analysis as the referee suggested (**Line 185-195**)

Line 210: 'Both the satellite and model do not find significant trends in NH$_3$ concentrations over India (absolute value less than 1 % yr^{-1}).' Looking at Figs. 1(c) and (d), it looks like the trend over India are not insignificant. Could you confirm this?

Thank you for your suggestion. The overall observed NH_3 concentration trend over India are -0.8 % a^{-1} (p = 0.25) while trends in south-eastern part are significantly decreasing ($\sim$ -3.8 % a^{-1}, p < 0.05). The model does not find significant trends in NH_3 concentrations, with p > 0.1 in all grids. We revised the text accordingly (**Line 215-217**).
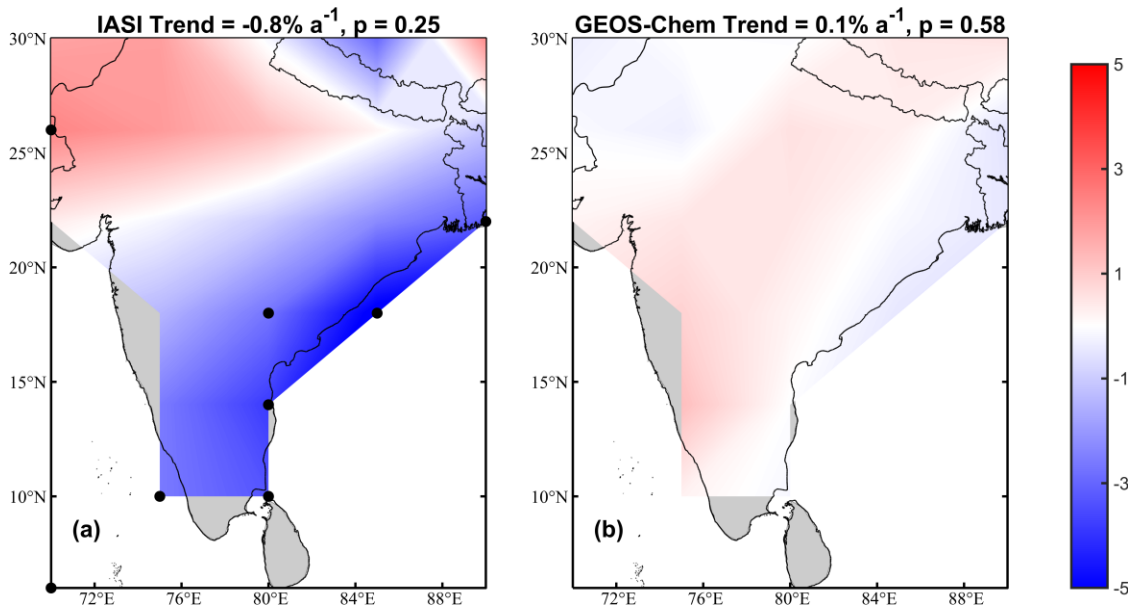
Figure A. Spatial distribution of relative linear trend of (a) IASI and (b) GEOS-Chem NH_3 column concentrations in India. Dots indicate that linear trends are significant at the 95 % confidence levels (p value < 0.05). Linear trends are computed from the time series of annual averages.

Line 261: Why is Eqn. (1) 'based only on NH3 column measurements' if Eqn. (1) blends information from the observations with a priori information of the emissions?

We correct following the suggestion (**Line 270**)

Line 295: Is the lifetime of 21.2 +/- 3.8 h the lifetime of NH3 (as stated) or is it the lifetime of NHx?

It is the lifetime of NH_3 as stated.

In Table S1, 'TDE' isn't really a 'parameter perturbed'. This line should probably be something like 'None' or 'None (TDE)'.

We correct **Table 1** following the suggestion.

REFERENCE

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