Response to Referee #2

We thank the reviewer very much for the detailed and valuable comments. We believe that addressing the issues raised by the reviewer will considerably improve the quality of our manuscript. Please see our response to each comment below (in blue).

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This is a useful, but also rather coarse and preliminary, study using IASI satellite retrievals to provide information about surface NH_3 concentrations and trends. The study uses coarse resolution GEOS-Chem vertical profile information with column information retrieved from IASI. Overall there is convincing correspondence of the IASI retrievals with surface concentrations, although more robust statistical analysis beyond showing correlation and bias is precluding understanding how good (or bad) the correspondence really is. How many observations were within a factor of two of the satellite derived values, is there a difference between rural, semi-urban, urban values, etc.

Thanks very much for this comment. We have added the following text for clarifications in the section of "Validation of satellite-derived surface NH_3 concentrations":

"Overall, 72.85% of observations (including China, the US and Europe) were within a factor of two of the satellite-derived surface NH_3 concentrations. In China, there is approximately 71.43% and 77.27% of observations were within a factor of two of the satellite-derived surface NH_3 concentrations in urban and rural land uses, respectively. There is no big difference in the accuracy of satellite-derived surface NH_3 concentrations between urban and rural land uses. In the US, the monitoring sites were generally distributed at rural sites (http://www.radiello.com) (Li et al. 2016), and, in Europe, there is no information to indicate the land use of each site (https://projects.nilu.no//ccc/) (Tørseth et al. 2012)."

One of the issues that have always remained a bit of mystery to me with regard to the satellite retrievals is the importance of using a-priori profile information for the retrievals, given the lack of sensitivity close to the surface and possibly also saturation effects where concentrations are high. This paper adds another question mark: when on the one hand the retrieval uses profile information, and in a second step the method uses the same model to calculate surface information is there a potential for using twice the same information?

We have added the following text for more clarifications (the purposes of using the profiles twice were different) in Sect. “IASI NH_3 measurements”:

“The ANNI-NH3-v2.2R-I datasets used the ANNI algorithm and took account of the influence of the NH_3 vertical profiles, pressure, humidity and temperature profiles, which was to make the columns accurate. There is no information on NH_3 vertical profiles in the ANNI-NH3-v2.2R-I datasets. The NH_3 vertical profiles used in this paper was to convert the columns to surface concentrations and to make the surface NH_3 estimates accurate.”.

Also unclear to me how the vertical resolution of GEOSCHEM can resolve the strong vertical gradients that are likely to exist in source regions. The authors should indicate 1) the vertical structure of the model, 2) the measurement characteristics of the surface observation (including height), 3) how this information is used to calculate surface concentrations. Even if the authors will not resolve all issues, a thorough discussion and way-forward discussion are needed about this.

Thanks very much for this good comment. We have added the following text for clarifications:

“The IASI NH_3 data we gained are column data, and there is no information on the vertical information. To convert this columns to surface concentrations, we used the widely used modelled vertical profiles from GEOS-Chem. The GEOS-Chem outputs include 47 layers, which are not continuous in the vertical direction. To gain the continuous vertical NH_3 profile, we used the Gaussian function to fit the 47 layers’ NH_3 concentrations. The main advantage to simulate the vertical profiles is that the NH_3 concentration at any height indicated by satellite can be obtained. On the other hand, the simulated profile function has a general rule, which can convert the columns indicated by satellite to surface concentration simply and quickly.”

The GEOS-Chem can simulate the NH_3 vertical profiles at 47 layers, and can simulate NH_3 concentrations at each layer (from approximately 50 m to 20000 m). Most of all the sites in China, US and Europe were set a height of 1-50 m above the ground (Li et al. 2016; Xu et al. 2015). Please note that the height that we mean here is the height to the ground rather than the height above sea level.

For these reasons I recommend major revisions to his paper.

I would ask the authors to already put on-line the vertical model information for use by other readers.

Thanks very much for this good suggestion. We added the NH_3 vertical model information (Matlab code) as the supporting materials in this revision.

Detailed comments

l. 24 Not only for dry deposition, also for modelling of the formation of ammonium nitrate.

We have added it as suggested.

l. 32: I am wondering what a high correlation of satellite/surface obs taken all regions together is really telling? I think it mostly depends on getting the levels of the 'high' concentrations correct, which is confirmed by the numbers given later. Consider removing this statement.

This indicates the overall accuracy assessment of satellite-based estimates compared with all observations, which include not only "high" concentrations but also "low" concentrations.

l. 65. They have not been established to measure NH_3 by itself, but as one of the parameters of a larger range of pollutants.

We have changed it as suggested.

l. 110 -116. It seems a selling point to suggest that vertical profile information for NO_2 and SO_2 have been useful for modelling, and therefore also for NH_3. The issues is more complex for NH_3, with sources almost entirely close to the surface, and a complex mix of source and sinks, which will make the model profile more dependent on the mixing characteristics of the CTM. For NO_2 and SO_2 the sources and locations are better known, most of SO_2 is nowadays emitted also well above the surface, which makes interference with the dry deposition process less sensitivity to errors.

We agree with you that there are different sources and sinks between NH_3, NO_2 and SO_2. There is no causal relationship of using vertical profile information for NO_2, SO_2 as well as for NH_3. IASI-derived surface NH_3 concentrations combining NH_3 vertical profiles from CTMs in China and Europe were evaluated previously (Graaf et al. 2018; Liu et al. 2017). Following these studies, the aim of this paper is to determine for the applicability and the assessment of using IASI retrievals and the vertical profile for global surface NH_3 concentrations. Our results shows that the satellite-based approach achieved a high predictive power for annual surface NH_3 concentrations compared with the measurements of all sites in China, US and Europe (R^2=0.76 and RMSE=1.50 μg N m^{-3}).

l. 134: GEOSCHEM vertical profiles were used in the retrieval and subsequently used to derive surface concentrations=>explain

We have added the following text for more clarifications in Sect. “IASI NH_3 measurements”:

“The ANNI-NH3-v2.2R-I datasets used the ANNI algorithm and took account of the influence of the NH_3 vertical profiles, pressure, humidity and temperature profiles, which was just to make the columns accurate. There is no information on NH_3 vertical profiles in the ANNI-NH3-v2.2R-I datasets. The NH_3 vertical profiles used in this paper was to convert the columns to surface concentrations and to make the surface NH_3 estimates accurate.”.

l. 147. Please summarize some characteristics. E.g. error statistics, characteristic of sites (urban, rural, vicinity to direct sources) height of observations.

We have added the following text for clarifications in the section of “Surface NH_3 measurements”:

“In China, we used the national measurements from the Chinese Nationwide Nitrogen Deposition Monitoring Network (NNDMN) including 10 urban sites, 22 rural sites, and 11 background sites.

The precision for monthly measurements at a site using DELTA systems is as below approximately 10% (Sutton et al. 2001), the correlation between the ALPHA and DELTA measurements was highly significant (R^2=0.919, p<0.001) (Xu et al. 2015). Surface NH_3 concentrations in the AMoN-US were measured by the radiello diffusive sampler (http://www.radiello.com) as a simple diffusion-type sampler collected every 2 weeks, and these sites were generally distributed at rural sites (Li et al. 2016). The overall bias of the different instruments in EMEP varied from -30 to 10% for all sites (Bobrutzki et al. 2010). Most of all the sites in China, US and Europe were set a height of 1-50 m above the ground (Li et al. 2016; Puchalski et al. 2011; Xu et al. 2015).".

l. 153 Need to explain why temporal averaging to 2 weeks is done.

We have added the following text for clarification:

"Surface NH_3 concentrations in the AMoN-US were measured by the radiello diffusive sampler (http://www.radiello.com) as a simple diffusion-type sampler collected every 2 weeks (Li et al. 2016). We calculated annual surface NH_3 concentrations by averaging all the measurements since we compared the measured surface NH_3 concentrations with satellite-derived surface NH_3 concentrations on a yearly scale.".

l. 157 measured systems=>measurement systems

We have replaced "measured systems" with "measurement systems".

l. 164 Please give the characteristic heights of the layers in the boundary (mixing) layer.

We have added the following text in the caption of Fig. S4 to show more information:

"The middle height of 1, 10, 20, 30 and 40 layer was approximately 60, 700, 2000, 6000 and 10000 m, respectively.".

l. 160 Any spin-up considered?

Yes, we have added the following text for clarifications:

"We have done the spin up for 5 months, which well exceed the typical lifetime of atmospheric NH_3 (typically within 24 hours) and aerosol ammonium ions (typically within a week) (Pye et al. 2009).".

l. 174: how does this compare to the widely used HTAP2 emissions for 2010? What changes to EDGAR result from substituting with regional inventories. Any seasonality applied and what would be the reference for it?

HTAP v2.2 is constructed by harmonizing regional emission inventories from USA, Canada, Europe and Asia, and gap-filling the rest of the world by EDGAR v4.3 (Janssens-Maenhout et al., 2015), which is methodologically consistent with our emission configuration. We compared the emissions from EDGAR v4.2 with HTAP v2.2 at 2008, which have differences in global total NH_3 within 10% (Crippa et al., 2018). The main difference between the regional inventories and EDGAR is that seasonality of emissions is included in regional inventories,. The seasonality of the regional emissions inventories is embedded as integral part of the inventory except EMEP (Crippa et al. 2018; Janssens-Maenhout et al. 2015; Lenhart and Friedrich 1995). We have added the above explanations in the section of “GEOS-Chem model”.

l. 186 some clarification is need as regards the use of ‘local’ times, which I think are not considering any shift in legal times (i.e. winter/summertime).

We have added the following text for more clarification, and there is no need to consider shift in legal times:

“The local time is the time in a particular region or area expressed with reference to the meridian passing through it.”.

l. 206. It is not clear why this more complex fitting procedure is needed. What was the problem, and how is solved by this new fitting. In figure S2 vertical profiles are shown but I do not have the information to understand if GEOSCHEMs vertical resolution would be able to resolve such profiles.

Please refer to the first paragraph in the section of “Estimation of surface NH_3 concentrations. The IASI NH_3 data we gained are column data, and there is no information on the vertical information. To convert the columns to surface concentrations, we used the widely used modelled vertical profiles from GEOS-Chem. The GEOS-Chem outputs include 47 layers, which are not continuous in the vertical direction. To gain the continuous vertical NH_3 profile, we used the Gaussian function to fit the 47 layers’ NH_3 concentrations. The main advantage to simulate the vertical profiles is that the NH_3 concentration at any height indicated by satellite can be obtained. On the other hand, the simulated profile function has a general rule, which can convert the columns indicated by satellite to surface concentration simply and quickly.

l. 223 like mentioned earlier, the correlation is merely due to the fact of having very high concentrations in one region, versus low in other regions. If one would compare the low concentration range a factor of 5 or so difference in concentrations belong to a single column value would be found. And maybe in reality even more, depending on a whole lot of things.

We agree with you that, on a local scale, the relationship of surface NH_3 concentrations and NH_3 columns may be affected by many factors. Here we show the overall accuracy assessment on a global scale between the surface NH_3 concentrations and NH_3 columns based on the GEOS-Chem outputs, which include not only “high” concentrations but also “low” concentrations.

l. 234 also this seems to be a rather error sensitive approach. I am mostly concerned about possible co-variance between the intra-day emission variations and the limited sampling at 9 O’clock. Are there observations that can be used to explore this issue?

No, we donot have observations to validate the intra-day emission variations.

L 242 Something wrong with reference E et al. And Van et al. And maybe other references as well.

We have corrected all these references.

l. 241-249 I am confused about the Figure S1 (with typical maxima of about 20-40 meter) and the statement that models and aircraft measurements can be used to verify them. I think that high towers like the one at Cabouw (NL), and observations at several levels, are probably the more reliable verification, but unfortunately there are not many of these.

Fig. S1 just show an example of a possible NH_3 vertical profile, and the typical maxima can be any height such as 20 m, 200 m or other values. In the future we hope to have more aircraft measurements to validate the simulations.

L 250 I have no idea what heights the first and fifth layer are corresponding to.

We have added the following text in the caption of Fig. S3 to show more information: "The middle height of first and fifth layer was approximately 60 m and 340 m, respectively.".

l. 284 It is true that NH_3 can be more accurately be retrieved in one region than another depending on the thermal contrast. But it is not clear to me why this would be so much better in China than e.g. in the US? I guess it is also just a matter of detection limits? It could also be related to more reliable simulation of mixing, depending on sufficient observational input into the parent weather model.

We agree with you that the accuracy of IASI-retrieved surface NH_3 concentrations in different regions is highly linked with the thermal contrast (TC) and the simulation of NH_3 mixing from GEOS-Chem. We have added the following text to discuss the potential reasons.

"The accuracy of IASI-retrieved surface NH_3 concentrations in different regions is highly linked with the thermal contrast (TC) and atmosphere NH_3 abundance (Whitburn et al. 2016). The lowest uncertainties occurred when high columns and high TC coincide. In case either of them decrease, the uncertainty will gradually increase. In case both the TC and column are low, all sensitivity to NH_3 is lost. When high TC and high NH_3 columns (high HRI) occurs, the major contribution to the uncertainty results from the thickness of the NH_3 layer, the surface temperature as well as the temperature profile (Whitburn et al. 2016). In addition, the simulation of NH_3 mixing from GEOS-Chem may have different accuracy in different regions, and thus can cause uncertainty to the different accuracy of IASI-retrieved surface NH_3 concentrations in different regions.".

l. 296 the fixed profiles=>fixed profiles (language)

We have corrected it as suggested.

l. 304-312 I believe that there can be a large difference between 40-60 meters, but as the authors explain this is all in the same geos-chem layer. I fail to understand how this information is then used to interpret geos-chem profiles.

We used the equation (2) to fit NH_3 vertical profiles at each grid box by the following equation (Liu et al. 2017):

$\rho = \sum_{i=1}^{n} \rho_{max,i} e^{-(\frac{z-z_{0,i}}{\sigma_i})^2}$ (2)

Once the NH_3 vertical profiles were determined at each grid box, we can extrapolate NH_3 concentrations at any height from the GEOS-Chem ($G_{GEOS-Chem}$).

Then we can calculate the IASI-derived NH_3 concentrations any height using the NH_3 vertical profiles and IASI NH_3 columns:

$\overline{G_{IASI_{9-10}}} = \frac{G_{GEOS-Chem}}{\Omega_{GEOS-Chem}} \times \overline{\Omega_{IASI_{9-10}}}$ (3)

where $\overline{G_{IASI_{9-10}}}$ is the satellite-derived surface NH_3 concentrations at a GEOS-Chem grid size at 9-10am; $\frac{G_{GEOS-Chem}}{\Omega_{GEOS-Chem}}$ is the ratio of surface NH_3 concentrations to NH_3 columns calculated from GEOS-Chem; $\overline{\Omega_{IASI_{9-10}}}$ is the average IASI NH_3 columns at a GEOS-Chem grid at 9-10am.

All the information has been described in detail in the method section.

l. 323 this is mostly a confirmation that crop mask used by the regional and global emission inventories correspond to the MODIS one. And that the fertilizers used in those countries indeed end up on these fields.

Yes, it is.

l. 355 According to inventories, in Europe about 20 % of NH_3 emissions is related to the use of mineral fertilizer, and 80 % to manure managements. So it would be more relevant to determine the correspondence of those emissions (mineral is often used to top up what wasn’t provided by manure).

Thank you very much for this suggestion. We have carefully checked the NH_3 emissions in Europe. According to Emissions Database for Global Atmospheric Research (EDGAR), in western Europe, manure management accounts for 53% and the share of emissions from agricultural soils for 43% of the ammonia emissions. So we have added the N manure into our analysis in Fig. 4 and Fig. 5 and revised related text in the discussion.

364 Van et al. Please check this reference. It seems to be a problem of your reference manager.

We have checked this reference, and revised it.

370 It is probably opportune to refer to the paper by Pozzer et al, a 1x1 model study that has more extensively studied the role of NH_3 emission for aerosol. It is also important to critically assess ammonium nitrate measurements, which are notoriously difficult at higher concentrations. Would it be an option to use the model to estimate (equilibrium) ammonium sulfate and nitrate concentrations associated with the 'retrieved' surface ammonia?

We have carefully read the suggested paper on the the role of NH_3 emission for aerosol (Pozzer et al. 2012). We agree with the reviewer that it is important to assess ammonium nitrate measurements associated with the retrieved surface NH_3 concentrations. However, this has been out of the scope of this paper, and this paper focuses on the estimates of surface NH_3 concentrations inferred from satellite retrievals. It is more appropriate to estimate ammonium sulfate and nitrate concentrations in another paper in the future.

421-430 Biomass burning can be an important source of NH_3, especially in the smoldering phase. Therefore, I have some doubts that active fire products are the best proxy for NH_3 emission. Did you consider burnt area products instead?

We here compared the monthly variations of surface NH_3 concentrations and biomass burning. The MODIS active fires are considered to be more accurate than the burnt area products on the timing of burning. Please see the temporal intercomparison of burned area products with Active Fire data set (Humber et al. 2019).

activity leaded=>led?

We have replaced "leaded" with "led".

504: why inconsistent? It could be rather consistent, as you explain in the following sentences.

We have added the following text to explain this inconsistency:

"This inconsistency between NH_3 and NO_x trends in the US was mainly due to different emission control policies. Over the past two decades, due to the implementation of effective regulations and emission reduction measures for NO_x, the NO_x emission in the US decreased by nearly 41% between 1990 and 2010 (Hand et al. 2014). However, this NH_3 increase in eastern US is likely due to the lack of NH_3

emission control policy as well as the decreased NH_3 removal due to the decline in acidic gases (NO_2 and SO_2) (Li et al. 2016; Warner et al. 2017).".

Supplementary

Figure S3: Please indicate what heights approximate correspond with the first and fifth layer boundaries.

We have added the following text in the figure caption:

"The middle height of first and fifth layer was approximately 60 m and 340 m, respectively.".

Figure S4: no idea what heights these layer correspond to.

We have added the following text in the figure caption:

"The middle height of 1, 10, 20, 30 and 40 layer was approximately 60, 700, 2000, 6000 and 10000 m, respectively.".

Figure S5: the figure caption is not self-explaining.

We have revised the figure caption by the following text to better describe the figure:

"Difference of surface NH_3 concentrations between 40m and 60m.".

Figure S6: first PM2.5 and then NO_2 in caption.

We have corrected it in the caption to match it with the figure.

Figure S9: describe upper panel as well.

We have added the following text to describe the panel:

"The upper panel is the annual raw fire counts in 2014.".

Figure S10: trends of what (annual concentrations?) and for what period

Yes, it is annual concentration during 2008-2016. We have changed the original descriptions by the following text:

"…trends of annual surface NH_3 concentrations during 2008-2016".

Reference

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