10.5194/amt-2020-319 Revisions: Response to Reviewer 2

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General Revisions:

We thank the two reviewers for their helpful comments, which have enabled us to improve the manuscript. The reviewers' comments are in regular font below and our responses are in bold font. Line numbers in the responses refer to the revised manuscript with changes tracked. Also of note is that there was a minor bug in the trend analysis code; this was revised, and affected values were corrected (this only affected the 2σ confidence intervals from bootstrap resampling).

Reviewer 2

General Comments:

Why was the nested version of GEOS-Chem over North America not used? It includes Toronto in the domain and is at finer resolution (0.25°′ 0.3125°) than the global domain.

The nested model would be very computationally expensive to run given the long time series. In addition, the amount of storage space required to archive all of the meteorological fields at high resolution for the whole observational record is also a limiting factor. Given that the focus of the paper is the long time series of NH_3 observations, we believe that using a model that could be run over the entire time series was more appropriate.

There is quite a lot of information relevant to model representation of NH3 that is missing in the model description section. These include the following: The inventories used in the model to represent US and Canadian SO2 and NO_X sources that form sulfate and nitrate that influence NH3 uptake to aerosols. The version of EDGAR and whether this is the inventory that represents anthropogenic NH3 emissions over the domain of interest or whether it is a combination of EDGAR and GEIA (now quite outdated and only really used in the model to represent natural NH3 emissions). The base year of each inventory. Whether annual scaling factors are applied to any of the emissions that would have declined due to emission regulations (typically NO_X and SO2). Whether seasonal scaling factors are applied to NH3 emissions in the model.

EDGAR v4.2 and GEIA were used as global inventories, with GEIA providing the natural source of NH_3. The global inventories were replaced with the US EPA National Emission Inventory for 2011 (NEI11) in the United

States, and by the Criteria Air Contaminants (CAC) from the National Pollutant Release Inventory in Canada. The NEI11 emissions were scaled between the years 2006–2013, whereas the CAC NH_3 emissions used 2008 as the base year, with no scaling applied. The NEI11 emissions were hourly, whereas the CAC emissions are monthly.

The information above was added to the manuscript in Section 2.4.

The model also seems to be underutilised to provide context for the study region. The inventories could, for example, be used to assess the relative proportion of vehicular, agricultural, and natural emissions to total NH3 emissions and to determine the role of changes in sulfate and nitrate (due to emission regulations of SO2 and NO_X sources) on observed trends in NH3.

We agree that this would be a good use of the model. However, to effectively attribute the observed change in $NH_3$to vehicular, agricultural, or other emission sources would require use of the nested model, and as we noted in our previous response it is not computationally feasible to run the nested model over the whole observational record. This suggestion would be a valuable follow-up study, focusing on a limited period of the record (e.g., one or two years). Our focus in this manuscript is on the long time series of the FTIR measurements.

What is the fit that is applied to the data to obtain the trends? And what is the determination of significance? It is stated in the text that "The number of years of measurements needed for the trend to be statistically (2s) significant was found to be 33.8 years and 29.3 years" (p. 6, lines 177-178), but it is not clear why this is the case given that the 2s uncertainty is much less than the trend value. An explicit statement of what the authors use as a significance criterion might help avoid confusion.

The fit used in this study was a trended Fourier series of order 3. This is discussed in Section 2.6. Two different statistical analysis methods were used in this study. The uncertainties given for each values were obtained using bootstrapping, and the "number of years of measurements needed for the trend to be statistically significant" was estimated using a method outlined by Weatherhead et al., (1998). This method has several drawbacks when used with data with irregular measurement intervals, as is the case for FTIR. This is discussed in the Section 2.6.

The FTIR instrument and measurements are referred to in figures/tables/text as FTIR, TAO, or TAO FTIR. To avoid confusion, stick with one of these throughout.

Most of the references to the ground-based FTIR were consolidated to simply "FTIR." However, in some sections (especially sections where IASI is mentioned, e.g., Sections 2.3, 2.5, 3.3, 4), the term "TAO FTIR" was used to avoid confusion, as IASI is also an FTIR spectrometer instrument. "TAO FTIR" was also used in places where NDACC, and/or other FTIRs were mentioned. It should also be mentioned that TAO is home to several instruments, including the FTIR. Additionally, in places where the *location* of the FTIR is mentioned (e.g., Figure 7 caption), term TAO was used.

Specific Comments:

p1, line 14: There is no context for the use of "resampling" in the abstract to be able to follow what this implies for the results obtained. What is being resampled? And why does it alter the correlation?

"Resampling" was changed to "averaging" to avoid confusion (Line 14).

p2, line 38: Briefly elaborate on the link between NH_3 concentrations and SO_2 and NO_X emissions.

Sentence clarifying this was added (Line 42-44).

p2, line 39: "...as well as by reactions with acids in the atmosphere" sounds like it is happening in the gas phase. Make clear that this is a heterogeneous process.

"[H]eterogeneous" was added to make this clear (Line 43).

p3, line 59: What is the NH_3 source from greenery? Application of fertiliser to gardens and public spaces?

Chemical fertilizers are "commonly applied" to green spaces in Southern Ontario during spring time (Hu et al., 2018). A statement clarifying this was added (Line 66).

p4, line 97: What is the shape of the a priori profile used for the retrieval? How does it compare to that from GEOS-Chem?

The a priori used at TAO is based on the a priori used at Bremen, which is based on balloon-based measurements (Toon et al., 1999). The a priori is comparable to the model profile scaled by a factor of 7. Further details of NH_3 retrieval at TAO is described in Lutsch et al. (2016).

p4, line 121: Odd to express the swath like this. Standard is as 2200 km.

2×1100 was changed to 2200 (Line 131).

p5, line 137-138: Say what model years are sampled after the one year spin up.

Fixed (Line 157).

p5, line 145-147: This approach is reasonable and widespread, but what if the spatial extent is less than the spatial resolution of IASI (at best 12 km at nadir), as seems to be the case in this work?

As suggested later in the paper, the NH_3 column from the FTIR likely has a representative scale of about ~50 km. Also, as discussed in Section 3.3, another FTIR study (Tournadre et al., 2020) found that an FTIR in Paris was capable of providing information about NH_3 variability at a ~120 km scales. For these reasons, we believe this methodology is appropriate.

Figure 2: Does the seasonality differ if the median is calculated for each month?

There are minor differences, but the general seasonality remains the same; the peak still occurs in May, and minima in January, as was the case when looking at the mean.

Figure 2: Consider showing the y-axis as 1e16 rather than 1e17.

This was fixed.

p7, line 189: Why is the seasonality solely attributed to emissions? What about partitioning of NH3 to acidic aerosols? Is there any seasonality to this process?

The sentence was revised to "… largely due to agricultural and soil emissions increasing…". A statement about lower NH_3 columns during winter, and lower temperatures favoring NH_4SO_3 was also added (Line 209-211).

Table 1: Is there a reason that this table is included if this information is already illustrated in Figure 2?

This was included for completeness, and because while the mean column value of May was given in text, other months were not.

Table 2: The layout of the table is confusing, as the row labels correspond to specific time periods, but then the final column is labelled "during the same timeframe". What is this timeframe then? Why is the FTIR TAO trend for this same timeframe not given?

The final column gives the trends of TAO when examining data from the observational periods of NAPS and IASI. The TAO trend for "the same time period" is not given, as it would simply be itself. This was included in the table because this information is given and discussed in text. The label for this

column has been changed to " TAO trends during the same timeframe as either the NAPS or IASI data".

Figure 4: The lines in (a) are not easy to see. Consider making these thicker.

Fixed.

p12, line 248: Tournadre et al. (2020) is not cited correctly.

Fixed (Line 283).

p12, line 254: What is "simple linear regression"? Ordinary least squares?

Yes, this was clarified in text (Line 288).

p12, line 259-260: It's not clear what this means: "Without temporal resampling, no significant correlation was found (r £ 0.27) for any spatial coincidence criteria". What is this temporal resampling and why does it impact the correlation?

As with the p.1 line 14 comment, the word "resampling" was changed to "averaging" to better describe what was done (Line 294).

Table 3: The information as presented in this table is okay, but would have been more visually interesting and easier to identify patterns in the data if each variable (r, slope etc.) was illustrated on 2D colored grids.

This would certainly be visually interesting, but we believe including the numbers is ultimately more important, and we have kept the table as is.

p13, line 267: What does this gridbox include other than Toronto that might dilute or increase NH3 concentrations and affect the comparison?

The gridbox contains areas near Toronto that may increase NH_3 due to agricultural emissions, as well as a significant portion of Lake Ontario, which may dilute it.

Figure 7: It would be helpful to say in the caption or text what this is showing from Table 3.

This is mentioned in text (line 287-288).

Figure 8: It is not easy to discern the red and black points in panel (b).

Figure 8b was replotted to make the points easier to discern. Due to the large number of data points, it is difficult to plot them clearly.

Figure 9: Are units for GEOS-Chem in panel (b) correct?

Yes, they are correct; the GEOS-Chem output was converted to total column values (in molecules/cm^2) to allow comparison with IASI measurements.