"Atmospheric ammonia variability and link with PM formation: a case study over the Paris area" by Camille Viatte et al.

Anonymous Referee #1

Authors: We would like to thank the referee for his/her insightful comments. We have made changes to the manuscript to address those comments.

Referee: This manuscript uses observations from two independent satellites to assess the role of NH_3 in springtime particle pollution episodes in the Paris region by examining the seasonal and interannual variability (IAV) in NH_3 columns over northwestern Europe.

The observations are compared to simulations from the CHIMERE chemical transport model. In general, the authors do a good job of reviewing the existing literature to provide context for their results, but it would be useful if they could include a comparison with the study of Schiferl et al. (2016), which examines seasonal cycles and IAV of NH_3 over the US.

Authors: We have added sentences in the revised manuscript to compare with the interesting study of Schiferl et al., (2016):

In section 3.1.2: "In addition, inter-annual variabilities of NH_3 concentrations over the United-States are dominated by meteorological conditions [Schiferl et al., 2016]."

In section 3.2.1: "This is a different finding than in Schiferl et al. (2016) since they restricted IASI high relative errors when comparing to the GEOS-Chem model over the United-States, which inherently favors larger columns and thus lead to weaken the observed seasonal cycle."

Referee: In Section 2.2, it is important that the authors report what proportion of the column observations from each satellite were below the limit of detection and how those data were incorporated into the monthly means used throughout the paper. If observations below the limit of detection were discarded, then the resulting monthly means will be biased high. It would then be important to filter the model output in a similar way to ensure that the observation-model comparison is more appropriate.

Authors: As mentioned in the manuscript, IASI's detection limit is 4-6 10^{15} molecules/cm^2. Observations below this detection limits represent about 60% of the 2014-2015 dataset. Those were not discarded when computing monthly means. CrIS's detection limit is 1-2 10^{15} molecules/cm^2 but no observations in the current product are reported (Shephard et al., 2019). This is a potential reason why CrIS is high compared to IASI in absolute values (See figure R1). However, when comparing to the model data, we selected CHIMERE outputs located within the same 0.15°x0.15° grid box than the satellite and within 1 hour from its measurement to ensure that the comparisons are appropriate.

We now have added a sentence about this difference in averaging IASI and CrIS when comparing monthly means to the model outputs in section 3.2.1: "Note that values below detection limits have not been filtered out from the IASI dataset whereas the quality flag was used to discard CrIS's retrievals associated with DOFS<=0.1 (Section 2.2.2) favors larger observed columns. Consequently, the normalized seasonal cycle amplitude derived from CrIS is weaker than the IASI one."

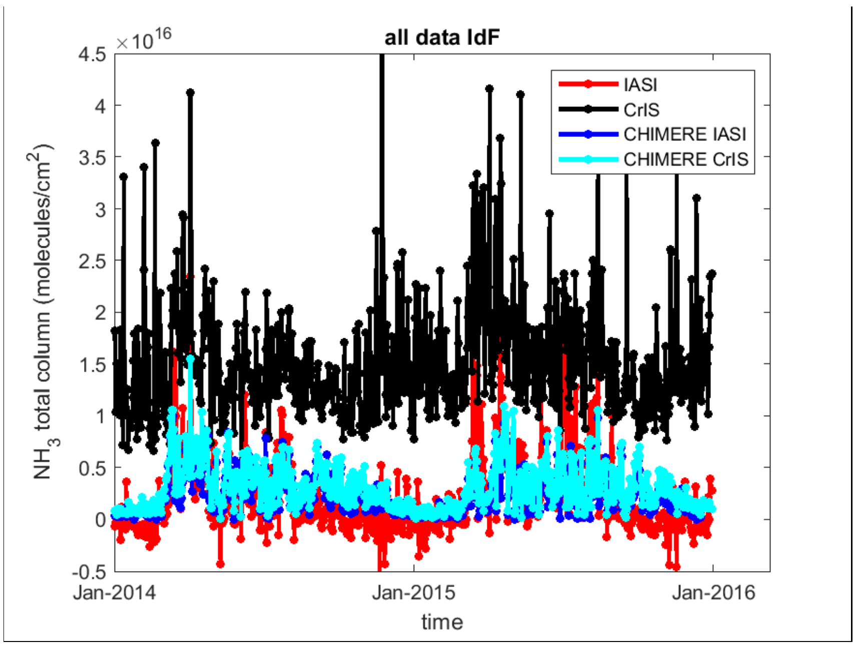

Figure R1: Time series of daily mean NH_3 concentrations (in molecules/cm^2) derived from IASI and CrIS satellite measurements (red and black, respectively), and from the CHIMERE model outputs coincident in space and time with IASI (in blue) and CrIS (in cyan).

Referee: A general concern in Section 3.1 is the confidence with which the authors interpret the causes contributing to the seasonality and IAV of the ammonia columns. In many cases, the explanations provided by the authors seem reasonable, but unless there is conclusive proof, the language should be toned down to indicate that these are possible/likely explanations rather than the only ones:

Referee: Lines 282-301, a handful of data are provided to describe farming practices in different regions, but not in a consistent way. What evidence is there that the factors described are the most important in causing the spatial and temporal patterns observed?

Authors: We have changed the tone of the text, it is now: "The observed seasonality is mainly related to agricultural practices (fertilizer application period varying as function of the crop types and type of livestock) and changes in temperatures, with higher temperatures favoring volatilization. This likely explains the high concentration in July and August."

Referee: Lines 313-314 How do crop type and phenological stage impact ammonia concentrations leading to interannual variability?

Authors: The phenological stage controls the fertilizer spreading dates, driving NH_3 emissions, and consequently, is likely to regulate NH_3 Inter-annual variability observed in a specific region.

We have added details in the manuscript: "It has been recently shown that spatial variability of NH_3 emissions in France is due to fertilizer use and type and pedoclimatic conditions, and that temporal variability depends on seasonal timing of fertilizer applications [Ramanantenasoa et al., 2018]. In addition, inter-annual variabilities of NH_3 concentrations over the United-States are dominated by meteorological conditions [Schiferl et al., 2016]. Thus, inter-annual variability of observed NH_3 total columns is likely to be driven by meteorological conditions and specific agricultural constrains (crop type and phenological stage for instance)."

Referee: Lines 330-333 These seem like plausible explanation for the impact of precipitation amount of ammonia columns, but is there direct evidence that they are the only (most) important factors?

Authors: We added likely and toned down our language throughout this section and in the conclusion.

Referee: Lines 334-335 The relationship between gas phase ammonia and temperature should be exponential based on the temperature dependence of its volatilization (either vapor pressure or effective solubility). Does the correlation coefficient change if a non-linear fit is tried?

Authors: We have checked and found a correlation of $R = 0.30$ instead of 0.33 when using a linear fit. We have rectified the manuscript accordingly. The residuals of the fit, however are similar when trying linear and exponential based fitting.

Referee: In Section 3.2, the authors compare 'standardized' monthly means for the years 2014 and 2015 between the two satellite products and the model. More explanation should be provided about how these standardized means were calculated. Do the emissions used in the model differ between the two years? This would be useful to know to help in interpreting the variability produced by the model.

Authors: We have included the computation equations regarding the standardization in the 2.4 section: "The standardized columns have been computed following equation 1:

$X_{stand}^{data} = \frac{(X^{data} - \mu(X^{data}))}{S(X^{data})}$ (1)

Where $(X^{data}) = \frac{1}{N}\sum_{i=1}^{N} X_i^{data}$, $S(X^{data}) = \sqrt{\frac{1}{N-1}\sum_{N=1}^{N}(X_i - \mu)^2}$, X^{data} corresponds to NH_3 columns derived from a dataset (IASI, CrIS, or CHIMERE), and X_{stand}^{data} is the corresponding standardized dataset. ”

The emissions of the model are the same for the 2 years of simulations; the interannual variability of the model is therefore likely to be attributed to meteorological conditions changes. We have clarified in the text that the emissions were the same for the two years and have added a sentence: “In addition, year-to-year variability can be seen in the model with lower concentrations in March 2015 compared to 2014 for instance, despite constant emissions in the 2-years simulation. This interannual variability is likely to be attributed to meteorological conditions changes.”

Referee: Lines 371-382 This discussion is a bit confusing because initially the values quoted from the correlation plots of are the coefficients of determination, and then the comparison is restricted to select months and the values quoted are the slopes. I would recommend quoting the r2 values for both, to make it more clear that the coefficients of determination did not increase significantly when the months were restricted. Also, the fact that the slope is close to 1 is not that meaningful since each dataset has already been standardized.

Authors: We have changed the text accordingly by removing the slope values and adding p-value instead:

“Over the whole period, the coefficient of determination (r^2) between the standardized monthly mean NH_3 columns derived from IASI (CrIS), and the CHIMERE model is 0.58 (0.18) for the annual cycles of 2014 and 2015 with low associated p-values of 1.5 10^{-5} (0.06) reflecting the significance level of the fits (not shown here). If we only consider months of high NH_3 in the domain from March to August, the correlation between the observational datasets and the model is rather good with r^2 values between IASI (CrIS) and CHIMERE of 0.29 (0.14) with associated p-values of 0.07 (0.24), as shown in Figure 7. Since annual total emissions are the same for the two years and simply disaggregated with a monthly profile in the model, the correlations reveal that the seasonal cycle is likely to be reproduced by the model. In addition, year-to-year variability can be seen in the model with lower concentrations in March 2015 compared to 2014 for instance, despite constant emissions in the 2-years simulation. This interannual variability is likely to be attributed to meteorological conditions changes. However, the values of the r^2 lower than 0.5 indicate that the CHIMERE model only reproduces at most half of the observed monthly temporal NH_3 variabilities in the domain. Similar variabilities are found between the observations and the model outputs since the coefficients of correlation of the standard deviations are 0.4 and 0.6 between CHIMERE and IASI and CrIS, respectively.”

We have also changed the abstract accordingly:

“A detailed analysis of the seasonal cycle is performed using both IASI and the CrIS instrument data, together with outputs from the CHIMERE atmospheric model. For 2014 and 2015 the CHIMERE model shows coefficient of determination of 0.58 and 0.18 when comparing with IASI and CrIS, respectively.”

Referee: In Section 3.3, which focuses on the role of NH_3 in producing $PM_{2.5}$ in the Ile de France region, the analysis is overly simplistic. Why have the $PM_{2.5}$ observations included in the analysis been restricted the measurements between 9 and 11 am? This time interval is particularly challenging to interpret because of the impacts of primary emissions and the role of the rapidly changing boundary layer height. It seems like a poor choice of time window to focus on a phenomenon that is influenced by long-range/ regional transport of a precursor species like NH3. The role of temperature and relative humidity on the formation of ammonium salts is well-described by thermodynamic relationships. Statements like those on Lines 504-509 are not fully accurate.

Authors: Over the studied area, Metop-A and Metop-B have an overpass time difference ranging from only a few seconds to 67 minutes depending on the viewing geometry of the satellite scans; the average difference is of 26 minutes for the 1325 days of common measurements. Over the whole time period IASI (MetopA and B) overpass time is about 9.50am on average. Therefore we have selected $PM_{2.5}$ data between 9 and 11 am to study cases in which $PM_{2.5}$ and NH_3 (observations averaged with MetopA and B) concentrations are enhanced simultaneously (or within a one-hour interval) over the IdF region. We also tried a similar analysis considering $PM_{2.5}$ measured at 10am only and averaged all day (between 8am and 6pm), and this did not change our results regarding the number of events detected for case A and B.

Concerning the statements concerning the role of temperature and humidity on the formation of ammonium salts, we have added ‘mainly’ and ‘in particular’ to be more accurate: “Our observations are in agreement with previous studies [Bessagnet et al., 2016; Wang et al., 2015], which have shown that the formation of ammonium salt needs a specific humidity of 60 - 70%, mainly because it corresponds to the deliquescence point of NH_4NO_3 in ambient air. This is in agreement with our results since the mean of relative humidity in case A is 70%. Our results also support the idea that a relatively low atmospheric temperature favor $PM_{2.5}$ formation in particular since the phase equilibrium leads to NH_4NO_3 decomposition above 30 °C.”

Specific comments:

Referee: Line 46 – ‘biochemical’ should perhaps be ‘biogeochemical’

Authors: We changed this.

Referee: Line 63 – ‘related to’ should be ‘relative to’

Authors: We changed this.

Referee: Line 111-114 – It would be helpful to reword the sentence slightly, to clarify that all of the studies being referenced were carried out in Paris.

Authors: We have reworded this sentence as: "However, although the Paris megacity is repeatedly shrouded by particulate pollution episodes, many studies are limited in the Paris megacity and performed over relatively short time frame during field campaigns: NH_3 measurements from May 2010 to February 2011 [Petetin et al., 2016] and nitrate, sulfate, and ammonium aerosol measurements in July 2009 [Zhang et al., 2013], or based on numerical simulations [Skyllakou et al., 2014]."

Referee: Figure 1 – The coloring of the map by the emissions is not easy to see. The colors become a very different shade on the map then on the legend. Is it possible to use a map that doesn't have a green background, or to make the emissions coloring more opaque?

Authors: We changed the background of the map and made the emissions coloring more opaque.

Referee: Figure 6 – would be helpful to have the same months identified on the axis for each year

Authors: We have edited the figure to have the same months for the 2 years.

References: Shephard, M. W., Dammers, E., Kharol, S., and Cady-Pereira, K.: Ammonia measurements from space with the Cross-track Infrared Sounder (CrIS): characteristics and applications, in preparation for ACP, 2019