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Interactive comment

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

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"Atmospheric ammonia variability and link with PM formation: a case study over the Paris area" by Camille Viatte et al. Anonymous Referee #2

Referee: In this study, Viatte et al. use satellite observations (CrIS, IASI) to a) characterize the spatial and inter annual variability of ammonia column over Western Europe and its drivers and b) examine the connection between NH3 and PM2.5 over Paris. The material presented is interesting and well suited for ACP However, I have some significant concerns regarding the robustness of some of the conclusions and the lack of connection between a) and b). These need to be addressed before I publication can be considered. Authors: We would like to thank the referee for his/her insightful com-

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Discussion paper

ments. We have performed additional analyses and adapted the manuscript to fully address those comments.

General Comments Referee: a) there are places when the authors make fairly definitive claims with insufficient support/references. For instance Line 49: it is stated that N causes species/ecosystem extinction. A specific reference is needed. Authors: We have added 2 references for this sentence: [Isbell et al., 2013; Hernandez et al., 2016]

Referee: Line 341 and discussion above. This discussion is too speculative and needs to be much better supported. Was more corn planted in 2011 than in 2012? Were planting dates shifted earlier in 2011 relative to 2012? This is critical since the authors then state that they have shown that meteorology and farming practices account for the interannual variability in $NH_3$ column. Authors: We have toned down our language to indicate that these are possible/likely explanations rather than the only ones.

Referee: Line 374 It is stated that the correlation is "good" based on Fig. 7 ($r^2<0.3$) . What is the p value, what is the uncertainty on the slopes given the large error bars shows in Fig. 7? In general, the authors need to be more quantitative when reporting statistics: always give p value for correlation (e.g ., line 331 and 333) and uncertainty for slopes. Authors: We have changed "good" to "rather good". As proposed by the other referee, the values of the slopes are not that meaningful since each dataset has already been standardized. Therefore we have removed the slope values and added the p-values for each $r^2$ values, as you suggested. "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 r2 lower than 0.5 indicate that the CHIMERE model only reproduces at most half of the observed monthly temporal NH3 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: b) there is very little connection between a) and b) in the current manuscript. In part b), the authors focus on the relationship between PM2.5 and NH3 in two (fairly similar) years (2014, 2015). The main conclusion is that meteorology (temperature, local PBL) probably controls whether NH3 contributes to PM2.5. This is interesting although very much expected from studies performed in other regions. From part a), I was instead expecting the authors to consider whether the considerable variability in NH3 sources over Belgium/Netherlands could impact PM2.5 over Paris. From part a), I was also expecting to have the authors show whether CHIMERE is able to capture the observed correlation between PM2.5 and NH3. This could help understand whether the observed PM2.5 enhancement results from production of ammonium nitrate in Ile de France or from transport of ammonium nitrate/sulfate or other aerosols from Belgium. I fully appreciate that such analysis will require significant work. However, without a significantly stronger connection between part a) and b), I would recommend the paper be split, with part a) being more readily publishable. Authors: We have added a section (3.3) and a Figure (new Figure 11) to evaluate the capacity of the model to reproduce PM2.5 over the Parisian region. "Comparisons of PM2.5 concentrations in IdF derived from the Airparif network and CHIMERE for 2014 and 2015 To evaluate the model capacity to reproduce PM2.5 concentrations over the Parisian region, comparisons between the Airparif measurements network and the CHIMERE outputs have been performed for 2014 and 2015 (Figure 11). For those years, concentrations of PM2.5 are measured hourly from the surface at 13 Airparif stations distributed over the IdF region (black dots, Figure 1). To compare with the CHIMERE model, we have extracted the hourly surface PM2.5 outputs in the IdF region, i. e. within a 50 km-radius circle from Paris. Results of the comparison are shown in Figure 11. Day-to-Day variability of PM2.5 concentrations at the surface is well represented by the CHIMERE model with however differences during pollution events in March/April and in December for both years. The model may underestimate PM2.5 concentrations in spring due to unknown PM2.5 formation processes, but overestimate them in winter which could be due to uncertainties on NH3 emissions from wood burning processes. Overall, good agreement is found between the measurements and the model in term of PM2.5 concentrations over the IdF region given values of r2 of 0.56 (associated with p-value of 6 10-133), a slope of 0.67 $\pm$ 3.51, with a slightly underestimation of the CHIMERE model given a mean relative difference (calculated as model-observations/observations) of -18% over 2014 and 2015." We have also added a sentence in the conclusion about this analysis: "In this region, we also found that the CHIMERE model is able to reproduce the day-to-day variability of PM2.5 concentrations (r2 of 0.56), with however an underestimation during spring pollution events, which could be due to unknown secondary aerosol formation processes." Finally, we have added a sentence in the abstract section about PM2.5 concentrations evaluation from CHIMERE: "In addition, PM2.5 concentrations derived from the CHIMERE model have been evaluated against surface measurements from the Airparif network over Paris. Agreement was found (r2 of 0.56) with however an underestimation during spring pollution events." To investigate whether the variability in NH3 sources over the northeast part of the domain could impact NH3 over Paris, we have studied the cross-correlation function of NH3 concentrations between the Northeast part of the domain (over the Netherlands) and the IdF region (see Figure R1 and Figure S5 in the supplement information). The cross-correlation function (CCF) is calculated between the daily averaged mean of the IASI NH3 columns observed over these two regions (both are average values of available pixels of the same day). From the CCF plot, we can see that when lag = 0 (i.e. within the same day), the cross-correlation is maximum with CCF = 0.37, and the CCF is above 0.3 when lag=$\pm$1 (i.e. 1 day before or after) for the whole time period (2008-2016). Therefore, correlation between NH3 concentrations over the northeast part of the domain and the IdF region is relatively correlated. This confirms the result suggested by the back-trajectory analysis in Figure 10. We have also computed the CCF over these two regions considering months with high NH3: the maximum CCF between March and August and between March and April are 0.35 and 0.26, respectively. Therefore we have added a sentence about this analysis in the new section 3.4: "Indeed, NH3 columns over the Netherlands are relatively correlated to NH3 columns measured over IdF since the cross-correlation function is 0.37 at lag = 0 and above 0.3 at lag = $\pm$1 day over the whole time period (2008-2016 - Figure S5)." and we add a sentence in the abstract : "Variability of NH3 in the Northeast region is likely to impact NH3 concentrations in the Parisian region since the cross-correlation function is above 0.3 (at lag = 0 and 1). "

Figure R1: Cross-correlation analysis of NH3 concentrations between the Northeast part of the domain (over the Netherlands) and the IdF region. In addition, to study the effect of transport on NH3 and PM2.5 concentrations observed over the Parisian region, we have included wind fields analysis in Section 3.4 (old Section 3.3). In Figure 12 (old Figure 11) in the lower panel, we have added wind fields parameters (direction and speed) from ERA-5 and included wind roses for studies cases (ensemble, case A, and case B) in the supplement information. Results of the statistic show that cases involving simultaneous enhancements of NH3 and PM2.5 concentrations in Paris (cases A) are associated with wind fields dominantly coming from the Northeast. Airmasses coming from this area are thus likely to favor simultaneous enhancements of NH3 and PM2.5 over Paris. We have added few sentences in the new Section 3.4 and the conclusion about this: Section 3.4: "Results also suggest that simultaneous enhancements of $NH_3$ and PM2.5 over Paris (cases A) are mainly associated with wind fields dominantly coming from the Northeast part of the domain (Figure S6). Thus the combination of the following four meteorological parameters favors simultaneous appearances of $NH_3$ and of PM2.5 in Paris (i.e. case A): low surface temperatures (5°C), with thin boundary layers (∼500m), rare precipitations, and northeast wind." In the conclusion section: "To assess the link between $NH_3$ and PM2.5 over the Parisian (IdF) region, the main meteorological parameters driving the optimal conditions involved in the PM2.5 formation have been identified. The results show that relatively low temperature, thin boundary layer, coupled with almost no precipitation and wind coming from the northeast, favor the PM2.5 formation with the presence of atmospheric $NH_3$ in the IdF region."

Technical comments Referee: Section 2.3 the description of CHIMERE is far too short (especially with respect to the treatment of ammonia. For instance: -> how is dry deposition represented? Does it include the bidirectional exchange between land and atmosphere -> what is the temporal resolution of the emissions? Does it include a diurnal cycle? It would be useful to show the seasonality of the emissions in a few regions, to help the reader better analyze Figs 2 and 3 -> how is the gas/aerosol partitioning of $NH_3$ represented (ISORROPIA?) -> I assume that $NH_3$/$NH_4$/$NH_4NO_3$ in CHIMERE have been evaluated previously? Please provide reference for these studies at this stage. I also encourage the authors to show how the configuration of CHIMERE that is used here performs against surface observations (e.g., EMEP wet deposition/concentrations). This could be briefly discussed in the main text, with figures in the supplementary materials. Authors: We have detailed the description of the model by adding this section: "These annual emissions are then distributed in hourly data to feed CHIMERE using seasonal, weekly and hourly factors. Fire emissions come from the Global Fire Assimilation System (GFAS, [Kaiser et al., 2012]). The model computes hourly concentrations for more than 180 species, among which are the regulated pollutants such as ozone, PM10, and $NH_3$. The processes that will influence the $NH_3$

concentrations taken into consideration in CHIMERE are the dry deposition (following [Wesely et al., 1989] and wet deposition due to in-cloud process and precipitations. The gas-particulate phase equilibrium is computed with the ISOROPPIA module [Nenes et al, 1998] which is a thermodynamic equilibrium model for NH4+, NO3- and SO42-. It evaluates the NH4NO3 contribution to the particulate matter which is especially large during March-April pollution episodes [Petit et al., 2017]."

Referee: Section 3.1.1 It would be useful to include a map showing the distribution of livestock and major crops in Western Europe so that the reader can see the relationship between NH3 emissions and the different sources described by the authors. This would be especially helpful as some of the material the authors refer to is in French. Authors: We have added specific references for livestock mapping and found English versions of the references: âĂć https://agriculture.gouv.fr/overview-french-agricultural-diversity ; âĂć Scarlat et al., 2018 – their figure 2], âĂć [Robinson et al., 2014 - their figure 2c].

Referee: Fig. 5. This figures shows first and foremost that there is good correlation between skin temperature and precipitation at the regional level. I think it would be more relevant to show the relationship between temperature/precipitation and NH3 anomaly. In addition, I assume that the precipitation/temperature anomalies exhibit some significant spatial variability? Do you weigh the anomaly by the average NH3 column? High NH3 columns only cover a small fraction of your domain and it's unclear to me why it would respond to the average temperature change (vs the local change). Authors: We have tried the analysis suggested by the referee. Anomalies of NH3 and temperature/precipitation over the domain are shown in Figure R2. The results suggests strong relationships exists between anomalies of NH3 and skin temperature (correlation R = 0.72), and total precipitation (anti-correlation R = -52).

Figure R2: monthly mean anomaly (relative to the 10-years – 2008 to 2017 - monthly average) of total precipitation/skin temperature derived from ECMWF from March to August in the domain, versus NH3 total columns anomaly derived from IASI. When computing the anomalies, temperature and precipitation anomalies were not weighting by NH3 total column.

Referee: Section 3.2. I am a little confused by the need for the standardization. CrIS and IASI seem reasonably close, so why not use the model absolute NH3 column. In addition, Fig. 6 only show one CHIMERE time series, shouldn't there be two, one for CHIMERE sampled at the IASI overpass time and one at the CrIS overpass time (with AK).. Authors: The CrIS and the IASI data are not close in absolute values: CrIS is higher than IASI in the region of interest (of about 1.1016 molecule/cm2). In addition, the CHIMERE output concentrations are closer to IASI observations than CrIS's ones (see Figure R3), which is why we wanted to standardized each dataset independently. We have also tested the comparison between CrIS and CHIMERE by taking into account the different vertical sensitivity (smoothing by the AK) but results were not improved.

Figure R3: Time series of dailymean NH3 concentrations (in molecules/cm2) 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). As for Figure 6, we have changed it to include the CHIMERE time series sampled in space and time with IASI and CrIS, as you suggested.

Referee: Line 351 I am not sure I understand the motivation for picking this years. Why not use the climatological seasonality? Why are these years more useful to benchmark the model? They look fairly similar as far as I can tell from the supporting material. Authors: In the frame of evaluating the model capacity of reproducing NH3 variability in space and time at regional scale and its impact on air quality at local scale, those two years are interesting for the following reasons. At regional scale (over the 400 km radius around Paris), NH3 total columns derived from IASI in 2014 and 2015 are highly variable in time throughout the years and especially in spring, reaching 10% higher in March and 50% lower in May than the 10-years average. Since ammonia emission variability depends on seasonal timing of fertilizer applications in France [Ramanantenasoa et al., 2018], this period is crucial to assess the model capacity. Second, for those two years NH3 concentrations over the IdF region (100 km radius around Paris) are also extremely high in March (Figure R4, upper panel). These extreme events might have affected the Parisian air quality since PM2.5 concentrations are also enhanced, especially in 2014 (Figure R4, lower panel). We have added this Figure in the Supplementary Information (Figure S1). Therefore, we think these years could serve as benchmark to evaluate the model in terms of NH3 variability at regional scale, and PM2.5 formation at local scale. We have changed the manuscript to explain the motivation for choosing these years in section 2.3 dedicated to the CHIMERE model: "To evaluate the model capacity of reproducing NH3 variability in space and time at regional scale and its impact on air quality at local scale, comparisons have been performed in 2014 and 2015 for the following reasons. At regional scale (over the 400 km radius around Paris), NH3 total columns derived from IASI in 2014 and 2015 are highly variable in spring, reaching 10% higher in March and 50% lower in May than the 10-years average. Since ammonia emission variability in France depends on seasonal timing of fertilizer applications [Ramanantenasoa et al., 2018], this period is crucial to assess the model capacity. Second, the IdF region (100 km radius around Paris) also experiences high NH3 and PM2.5 events in spring 2014 and 2015 (Figure S1). Thus, these years serve as benchmark to evaluate the model in terms of NH3 variability and PM2.5 formation at local and regional scales."

Figure R4: Time series of daily mean NH3 concentrations (in molecules/cm2) derived from IASI (upper panel) and PM2.5 concentration (in in $\mu$g/m3) observed over the IdF region between 2013 and 2016.

Technical comments Referee: They are a few issues with language. It sometimes (rarely) makes it challenging to understand the manuscript. Referee: line 28: regression slope. Remove slope Authors: We have removed slope Referee: line 63: related->relative Authors: We have changed this. Referee: Line 112: many of studies? Authors: We have deleted "of" Referee: Line 283: farming species? Do you mean livestock? Authors: Yes, we have changed it to livestock. Referee: Line 300. What are non-poultry granivorous (animals)? Authors: We have deleted granivorous. Referee: Fig. 7 What do the error bars correspond to? Authors: The error bars correspond to the 1-sigma standard deviation around the mean. We have clarified it in the figure caption. Referee: Fig. 9: Same than Fig.7 -> “Same as Fig. 8” Authors: We have changed this. Referee: Fig. 12: Define IQR Authors: We added: The IQR is the "interquartile range", and it equals to Q3 - Q1 where Q3 and Q1 are the 75th and 25th percentiles. Setting the thresholds at Q1 - 1.5 * IQR and Q3 + 1.5 * IQR is a common practice to determine outliers. Referee: Line 220: I don’t understand the distinction between inorganic, organic and natural aerosols? Authors: We have deleted this part of the text to include more specific description of the model. Referee: Line 487. Why is the value given on line 476 different (mean/median?) Authors: The first value refers to the example given in the manuscript, i. e. from March 3rd and March 19th 2014, whereas the second value represents the mean value for the case A over the whole dataset. We have added ‘over the whole dataset’ in the latest sentence to avoid confusion.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-138/acp-2019-138-AC2-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-138, 2019.

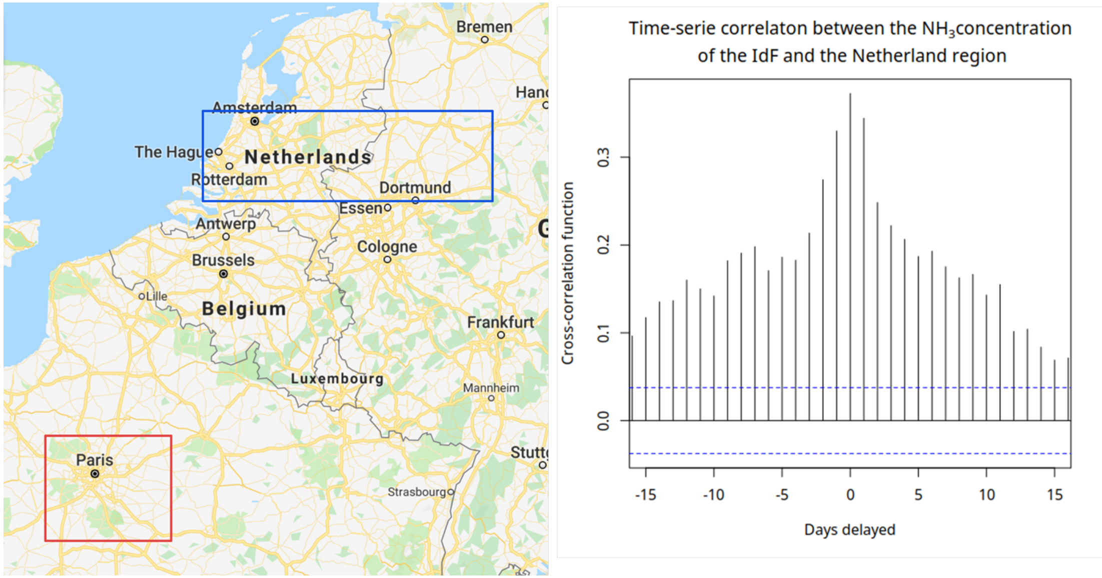

Bremen
Amsterdam
The Hague
Netherlands
Rotterdam
Dortmund
Essen
Antwerp
Cologne
Brussels
Lille
Belgium
Frankfurt
Luxembourg
Mannheim
Paris
Strasbourg
Time-serie correlaton between the $NH_3$ concentration of the IdF and the Netherland region
Cross-correlation function
0.0
0.1
0.2
0.3
-15
-10
-5
0
5
10
15
Days delayed

**Fig. 1.**

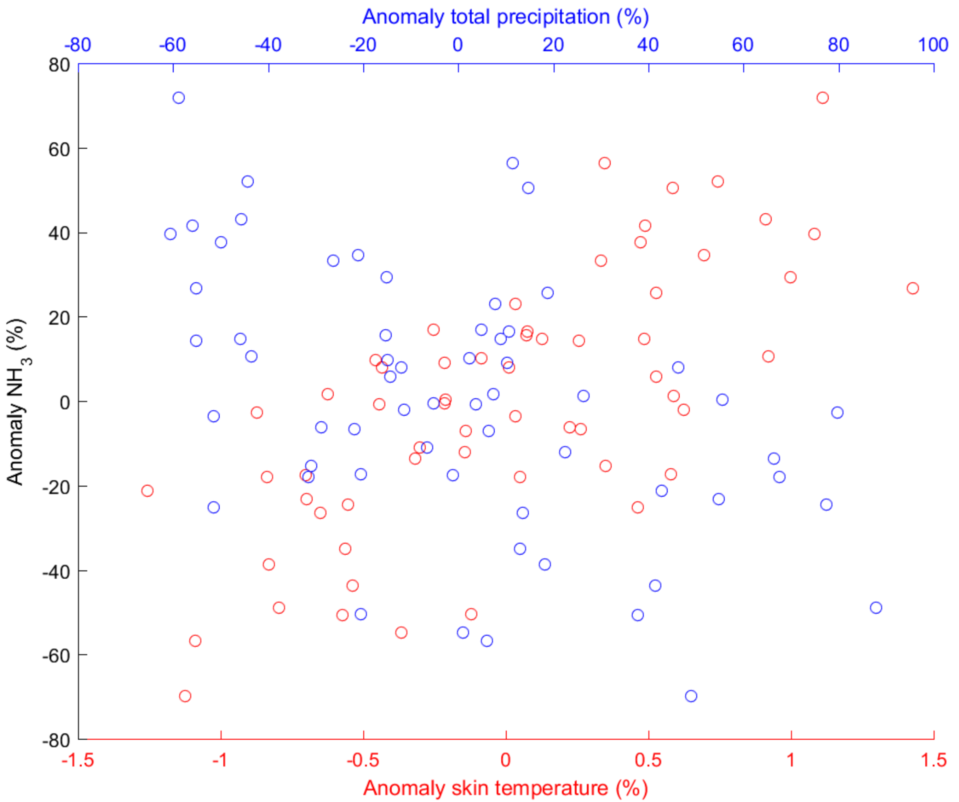
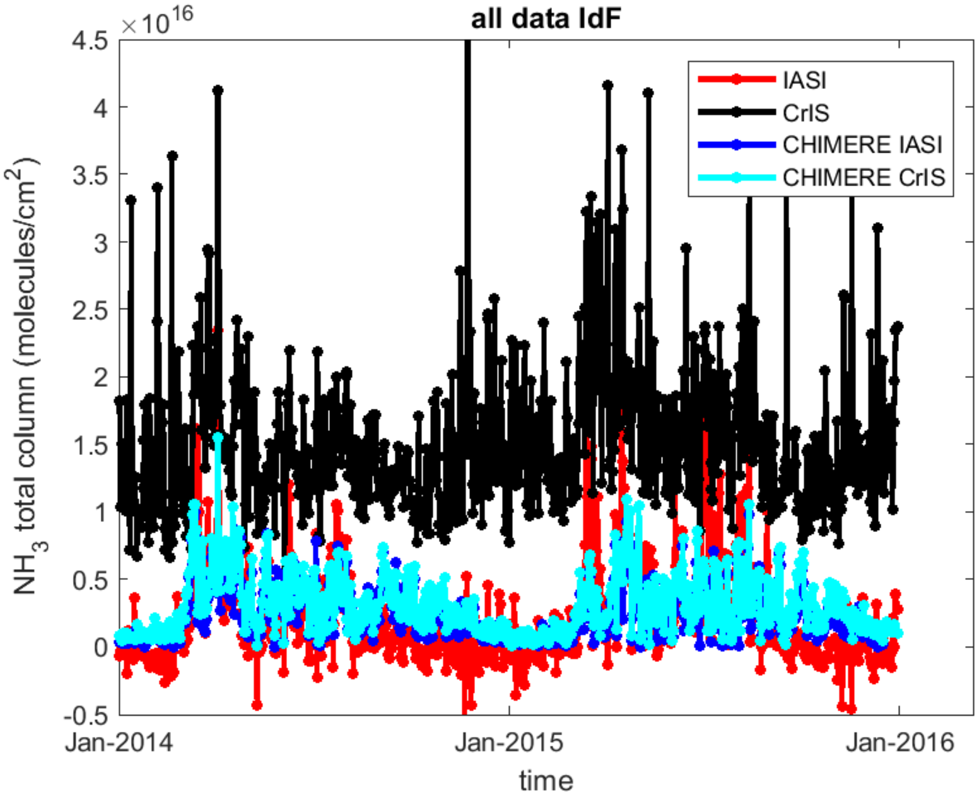
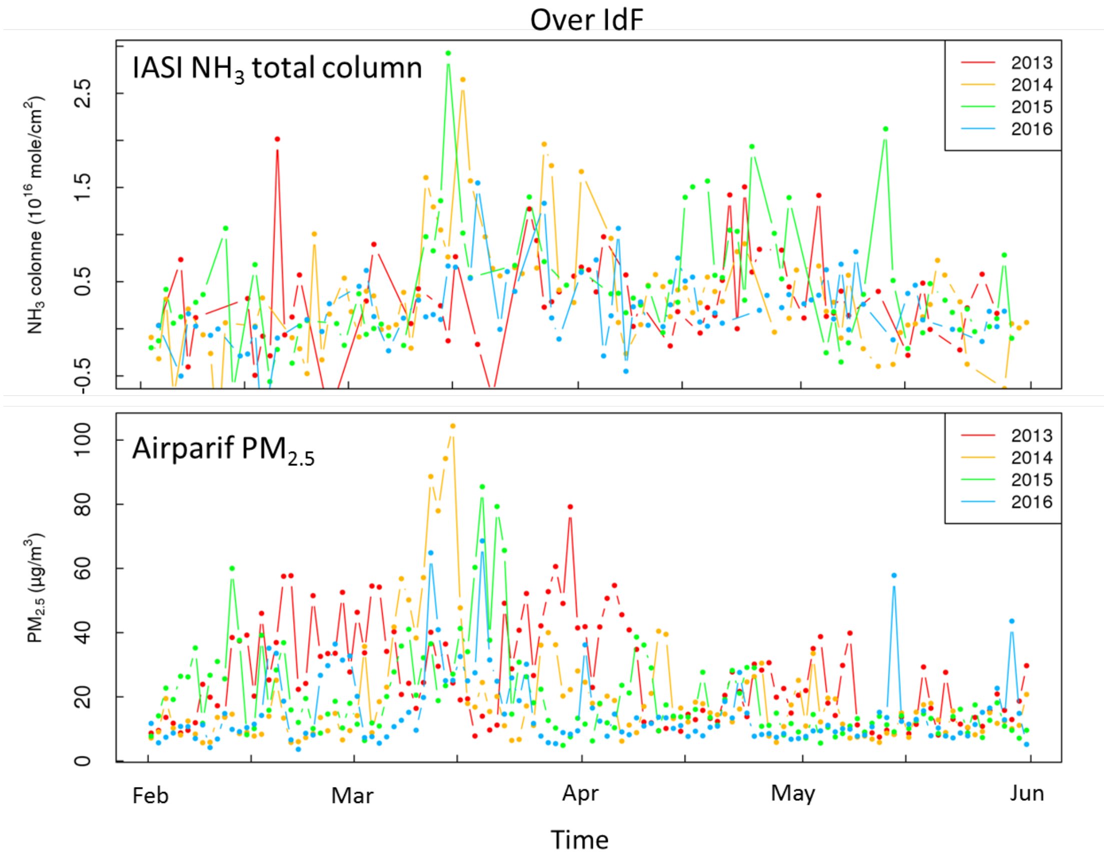

Anomaly total precipitation (%)
-80
-60
-40
-20
0
20
40
60
80
100
Anomaly NH3 (%)
80
60
40
20
0
-20
-40
-60
-80
-1.5
-1
-0.5
0
0.5
1
1.5
Anomaly skin temperature (%)

**Fig. 2.**



all data IdF
×10^16
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
NH3 total column (molecules/cm2)
IASI
CrIS
CHIMERE IASI
CHIMERE CrIS
Jan-2014
Jan-2015
Jan-2016
time


**Fig. 3.**



Over IdF
IASI $NH_3$ total column
2013
2014
2015
2016
$NH_3$ colonne ($10^{16}$ mole/cm$^2$)
-0.5
0.5
1.5
2.5
Airparif $PM_{2.5}$
2013
2014
2015
2016
$PM_{2.5}$ (µg/m$^3$)
0
20
40
60
80
100
Feb
Mar
Apr
May
Jun
Time


**Fig. 4.**