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1 Atmospheric ammonia variability and link with PM formation: a  
2 case study over the Paris area

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## 12 Abstract

13 The Paris megacity experiences frequent particulate matter ( $PM_{2.5}$ , PM with a diameter less than  
14  $2.5 \mu m$ ) pollution episodes in springtime (March-April). At this time of the year, large parts of  
15 the particles consist of ammonium sulfate and nitrate which are formed from ammonia ( $NH_3$ )  
16 released during fertilizer spreading practices and transported from the surrounding areas to  
17 Paris. There is still limited knowledge on the emission sources around Paris, their magnitude and  
18 seasonality.

19 Using space-borne  $NH_3$  observation records of 10-years (2008-2017) and 5-years (2013-2017)  
20 provided by the Infrared Atmospheric Sounding Interferometer (IASI) and the Cross-Track  
21 Infrared Sounder (CrIS) instrument, regional pattern of  $NH_3$  variabilities (seasonal and inter-  
22 annual) are derived. Observations reveal identical high seasonal variabilities with three major  
23  $NH_3$  hot spots found from March to August. The high inter-annual variability is discussed with  
24 respect to atmospheric total precipitation and temperature.

25 A detailed analysis of the seasonal cycle is performed using both IASI and the CrIS instrument  
26 data, together with outputs from the CHIMERE atmospheric model. For months of high  $NH_3$   
27 concentrations (March to August) the CHIMERE model shows good correspondence with  
28 correlation slopes of 0.98 and 0.71 when comparing with IASI and CrIS, respectively. It is found  
29 that the model is only able to reproduce half of the observed atmospheric temporal  $NH_3$   
30 variability in the domain. In term of spatial variability, the CHIMERE monthly  $NH_3$  concentrations  
31 in springtime show a slight underrepresentation over Belgium and the United-Kingdom and  
32 overrepresentation in agricultural areas in the French Brittany/Pays de la Loire and Plateau du  
33 Jura region, as well as in the north part of Switzerland.

34 Using HYSPLIT cluster analysis of back-trajectories, we show that  $NH_3$  total columns measured in  
35 spring over Paris are enhanced when air masses are originated from the Northeast (e. g.,  
36 Netherlands and Belgium), highlighting the long-range transport importance on the  $NH_3$  budget  
37 over Paris.

38 Finally, we quantify the key meteorological parameters driving the specific conditions important  
39 for the  $PM_{2.5}$  formation from  $NH_3$  in the Ile-de-France region in springtime. Data-driven results  
40 based on surface  $PM_{2.5}$  measurements from the Airparif network and IASI  $NH_3$  observations  
41 show that a combination of the factors, e. g. a low boundary layer of  $\sim 500m$ , a relatively low  
42 temperature of  $5^\circ C$  and a high relative humidity of 70%, contributes to favor  $PM_{2.5}$  and  $NH_3$   
43 correlation.



## 44 1. Introduction

45 Ammonia ( $\text{NH}_3$ ) is an atmospheric pollutant and one of the main sources of reactive nitrogen in  
46 the atmosphere which is involved in numerous biochemical exchanges impacting all ecosystems  
47 [Sutton et al., 2013]. The global budget of reactive N has dramatically increased since the  
48 preindustrial era [Holland et al., 2005; Battye et al., 2017] causing major environmental  
49 damages such as ecosystems and species extinction, as well as soil and water eutrophication  
50 and acidification [Rockström et al., 2009].  $\text{NH}_3$  is a precursor of ammonium salts which can form  
51 up to 50% to particulate matter (PM) total mass [Behera et al., 2013]. Large cities such as Paris  
52 (which is the most populated area in the European Union with 10.5 million people when its  
53 larger metropolitan regions are included) typically experiences strong PM pollution episodes in  
54 springtime. These particles are known to be harmful for human health [Pope III et al., 2009]  
55 inducing 2000 deaths per year in the Paris megacity [Corso et al., 2016] and to impact the  
56 radiative budget of the Earth [Myhre et al., 2013].

57 Because of their impact on the environment, public health, and climate change,  $\text{NH}_3$  emissions  
58 are regulated in several countries in the world. However,  $\text{NH}_3$  emissions of European countries  
59 have increased by 2% over the period 2014-2016 [National Emission Ceilings Directive reporting  
60 status, 2018], where the Gothenburg Protocol set a reduction of 6% by 2020. In France, where  
61 94% of  $\text{NH}_3$  emissions come from the agriculture sector [CITEPA, 2018] as a result of extensive  
62 fertilizer use to increase crop yields [Erisman et al., 2008], policies have been implemented with  
63 the aim to reduce  $\text{NH}_3$  emissions by 13% in 2030 related to 2005 [CEIP, 2016]. However  $\text{NH}_3$   
64 emissions are projected to increase in the future globally with increased population and food  
65 demand [van Vuuren et al., 2011] and  $\text{NH}_3$  volatilization will be enhanced with climate change  
66 [Sutton et al., 2013].

67 Once in the atmosphere,  $\text{NH}_3$  is rapidly removed by wet and dry deposition, and by reactions  
68 with atmospheric sulfuric and nitric acid, leading to a relatively short lifetime between a few  
69 hours and few days [Galloway et al., 2003]. Release of  $\text{NH}_3$  in the atmosphere depends on i)  
70 agriculture practices: spreading season, fertilizer form (urea, ammonium nitrate), fertilizer  
71 application methods, crops, soil conditions such as pH [Hamaoui-Laguel et al., 2014]; and on ii)  
72 meteorological conditions (i.e. wind, temperature, and precipitation). Inter-annual variability of  
73 PM formation over urban area is poorly understood, since it also depends on many factors such  
74 as atmospheric humidity and temperature, which govern the phase equilibrium of secondary  
75 aerosols [Fuzzi et al., 2015]. The variety of factors influencing  $\text{NH}_3$  volatilization and PM  
76 formation illustrates the complexity of predicting their concentrations in the atmosphere  
77 [Behera et al., 2013].

78 Atmospheric chemical transport models have difficulty representing both  $\text{NH}_3$  and  $\text{PM}_{2.5}$   
79 distributions due to the challenge of reproducing  $\text{NH}_3$  temporal variability [Pinder et al., 2006;



80 Fortems-Cheiney et al., 2016], long-range transport of pollutants [Moran et al., 2014], and  
81 secondary aerosol formation in the atmosphere [Petetin et al., 2016]. The GEOS-Chem chemical  
82 transport model [Bey et al., 2001] was found to underestimate the observed  $\text{NH}_3$  concentrations  
83 in most regions of the globe [Zhu et al., 2013; Li et al., 2017]. Heald et al. (2012) compared the  
84 IASI observations with the GEOS-Chem model and showed that  $\text{NH}_3$  is likely underestimated in  
85 California, leading to a local underestimate of ammonium nitrate aerosol. Similarly, the French  
86 CHIMERE model [Menut et al., 2013] underestimates the  $\text{NH}_3$  budget over Paris [Petetin et al.,  
87 2016; Fortems-Cheiney et al., 2016] because of the mis-representation of agricultural emissions  
88 in terms of intensity and both spatial and temporal distribution. Often ground and aircraft-  
89 based observations are used to provide detailed representation of the atmospheric state that  
90 can be used to evaluate and improve the model simulations; however, these can be spatially  
91 sparse and/or over short sampling periods, especially globally. Additionally, more recently  
92 available (within the last 10-years) sun-synchronous satellite-based infrared sensors have been  
93 providing  $\text{NH}_3$  observations globally with a spatial resolution of  $\sim 15$  km approximately twice a  
94 day. These satellite observations have limited independent vertical information, but do capture  
95 the spatiotemporal variabilities needed to help address these issues and improve model  
96 simulations, especially in remote locations [Skjøth et al., 2011; Kranenburg et al., 2016].

97 Aside from the Tropospheric Emission Spectrometer (TES, [Beer et al., 2008]), now  
98 decommissioned but which was first to demonstrate the capability of thermal infrared  
99 instruments to monitoring lower tropospheric  $\text{NH}_3$ , 3 missions are able to measure it now : the  
100 Atmospheric InfraRed Sounder (AIRS, [Warner et al., 2016]), the Cross-track Infrared Sounder  
101 (CrIS, [Shephard and Cady-Pereira, 2015]), and the Infrared Atmospheric Sounding  
102 Interferometer (IASI, [Clarisse et al., 2009]). Recent studies have shown the increased capacity  
103 of space-borne instruments to derived spatial and seasonal distributions of  $\text{NH}_3$  concentrations  
104 globally [Clarisse et al., 2009; Shephard et al., 2011; Van Damme et al., 2014a & 2015a],  
105 regionally [Beer et al., 2008; Clarisse et al., 2010; Van Damme et al., 2014b] and locally [Van  
106 Damme et al., 2018], as well as trends of  $\text{NH}_3$  [Warner et al., 2017].

107 Representative measurements of  $\text{NH}_3$  concentrations and spatiotemporal variabilities are  
108 needed to address the link between  $\text{NH}_3$  and  $\text{PM}_{2.5}$  formation and improve model simulations.  
109 This has been attempted previously in some cities around the world, such as in Shanghai [Ye et  
110 al., 2011], Houston [Gong et al., 2013], Santiago City [Toro et al., 2014], and Beijing [Zhao et al.,  
111 2016] for instance. However, although the Paris megacity is repeatedly shrouded by particulate  
112 pollution episodes, many of studies are limited and performed over relatively short time frame  
113 during field campaigns [Petetin et al., 2016; Zhang et al., 2013], or based on numerical  
114 simulations [Skylakou et al., 2014]. Our study is a data-driven regional approach and considers a  
115 longer time period to study the seasonal/inter-annual variabilities of  $\text{NH}_3$  and its impact of  $\text{PM}_{2.5}$   
116 formation over the Paris megacity. Specifically in this paper we study concentrations and



117 spatiotemporal variability of atmospheric NH<sub>3</sub> from the agricultural sector to gain insights on its  
118 effects on megacity air quality using: 1) long-term satellite observations derived from IASI (10  
119 years from 2008 to 2017) and CrIS (5 years from 2013 to 2017) at regional scale (400km radius-  
120 circle from Paris city center); 2) spatiotemporal patterns of the CHIMERE model evaluated  
121 against the IASI and CrIS datasets for 2014 and 2015; and 3) the main meteorological  
122 parameters favoring the secondary PM<sub>2.5</sub> formation from NH<sub>3</sub> in the Paris megacity are  
123 analyzed.

## 124 2. Methodology

### 125 2.1. Region of analysis

126 The domain of analysis covers a circular area of 400 km radius around the Paris city center  
127 (Figure 1, larger circle) enabling the study of temporal and spatial variabilities of NH<sub>3</sub> emission  
128 sources likely to affect air quality in the Paris megacity. It has been selected for two reasons.  
129 First, it includes main regions known for their high NH<sub>3</sub> emissions, which can be transported and  
130 affect air quality over the Parisian region (Ile-de-France –IdF-, smaller circle in Figure 1).  
131 Emission regions in the Netherlands, North of Germany, Northwest of Belgium, and the Brittany  
132 region in France, are highlighted in darker colors in Figure 1 (emissions values are from the  
133 European Monitoring and Evaluation Programme -EMEP- 2015). Second, this area corresponds  
134 to the transport of 24 hours back-trajectories from Paris generated from the HYSPLIT model for  
135 one year, ensuring that NH<sub>3</sub> can indeed be efficiently transported from the emitting sources  
136 within the selected domain to the IdF region.

### 137 2.2. Satellite observations of ammonia

138 For this study we used the available data from IASI and CrIS which are both Fourier transform  
139 spectrometers to evaluate the current capacity to observe NH<sub>3</sub> concentrations from space, and  
140 study its variability around IdF. Technical information are summarized in Table 1.

#### 141 2.2.1. Infrared Atmospheric Sounding Interferometer (IASI)

142 IASI is a nadir-viewing spectrometer launched on board the Metop-A and Metop-B satellites and  
143 operated by EUMETSAT (European Organisation for the Exploitation of Meteorological  
144 Satellites), since October 2006 and September 2012, respectively. These satellites are on similar  
145 polar orbits with Equator crossing times at 09:30 (21:30) local mean solar time for the  
146 descending (ascending) orbit. IASI measures the thermal infrared radiation of the system Earth-  
147 atmosphere in the spectral range from 645 to 2760 cm<sup>-1</sup> with a spectral resolution 0.5 cm<sup>-1</sup>  
148 apodized. The satellite swath is an area of 2200 km width composed by off-nadir measurements  
149 up to 48.3° on both sides of the track. At nadir, the IASI field of view is composed of 4 x 4 pixels  
150 of 12 km diameter each [Clerbaux et al., 2009].



151 The  $\text{NH}_3$  total columns used here are derived from IASI using an Artificial Neural Network  
152 reanalyzed with ERA-interim data (ANNI-NH3-v2.1R [Van Damme et al., 2017]). This dataset is  
153 consistent in time and suitable for investigating inter-annual variability, which is one purpose of  
154 this study. Note that we have considered here only morning measurements (9:30) since the  
155 evening ones (21:30) are associated with larger relative errors [Van Damme et al., 2017]. IASI  
156 retrievals provide a robust error estimate for each IASI-NH3 observations, allowing to take into  
157 account the variable sensitivity when comparing IASI dataset with independent measurements.  
158 Finally, no filter on relative errors of the IASI datasets has been applied following  
159 recommendations from Van Damme et al. (2017) and outliers for which concentrations exceed  
160 10 standard deviations above the mean in the domain of study have been removed.

161 Over the studied area, Metop-A and Metop-B have an overpass time difference ranging from  
162 only a few seconds to 67 minutes depending on the viewing geometry of the satellite scans; the  
163 average difference is 26 minutes for the 1325 days of common measurements. Monthly maps  
164 for the 10 years of observations between 2008 and 2017 are obtained by averaging Metop-A  
165 and whenever Metop-B (the two instruments are considered jointly for their period of common  
166 operation from March 2013 to 2017) with more than  $10^5$  pixels on average over the domain of  
167 analysis. The number of available  $\text{NH}_3$  columns depends not only on the satellite overpass time  
168 but also on the state of the atmosphere being remotely sensed (e.g. thermal contrast and cloud  
169 cover). IASI  $\text{NH}_3$  has been evaluated using the LOTOS-EUROS model over Europe [Van Damme et  
170 al., 2014b] and ground-based and airborne measurements [Van Damme et al., 2015b], showing  
171 consistency between the IASI  $\text{NH}_3$  and the available datasets. When comparing IASI  $\text{NH}_3$   
172 (previous IASI-NN version) with ground-based Fourier transform infrared (FTIR) observations, a  
173 correlation of 0.8 and a slope of 0.73, with a mean relative difference of  $-32.4 \pm (56.3)\%$  have  
174 been found [Dammers et al., 2016].

### 175 2.2.2. Cross-track Infrared Sounder (CrIS)

176 The CrIS instrument [Zavalyov et al., 2013] is a Fourier Transform spectrometer operated by the  
177 Joint Polar Satellite System (JPSS) program on Suomi National Polar-orbiting Partnership (NPP)  
178 satellite, launched on 28 October 2011. CrIS is in a sun-synchronous orbit with a mean local  
179 daytime overpass time of 13:30 (01:30) in the ascending (descending) node. CrIS measures the  
180 atmospheric composition over three wavelength bands in the infrared region ( $645\text{--}1095\text{ cm}^{-1}$ ;  
181  $1210\text{--}1750\text{ cm}^{-1}$ ;  $2155\text{--}2550\text{ cm}^{-1}$ ).  $\text{NH}_3$  retrievals are performed from the  $645\text{--}1095\text{ cm}^{-1}$  band  
182 with a spectral resolution of  $0.625\text{ cm}^{-1}$ . The CrIS instrument scans a 2200 km swath width (+/  
183  $50^\circ$ ). At nadir, the CrIS field of view consists of a  $3 \times 3$  array of circular pixels of 14 km diameter  
184 each.

185 The CrIS Fast Physical Retrieval (CRPR) [Shephard and Cady-Pereira., 2015] uses an optimal  
186 estimation approach [Rodgers, 2000] that minimizes the difference between the CrIS measured



187 atmospheric spectra and a very fast Optimal Spectral Sampling (OSS) [Moncet et al., 2008]  
188 forward model simulated spectrum to retrieve atmospheric profiles of ammonia volume mixing  
189 ratios. This physical approach provides direct estimates of the retrieval errors and the vertical  
190 sensitivity (averaging kernels) of the satellite observations, which is important as they vary from  
191 profile-to-profile depending on the atmospheric state. The retrieved error covariance and  
192 averaging kernels are also beneficial for air quality model comparisons and data assimilation  
193 into models as any *a priori* information used in the retrieval can be accounted for in a robust  
194 manner (i.e. observation operator). CrIS has been shown to retrieve ammonia surface  
195 concentrations values down to ~0.2-0.3 ppbv under favorable conditions [Kharol, et al., 2018].  
196 CrIS comparisons with ground-based FTIR observations show a correlation of 0.77 with a low  
197 CrIS bias of +2% in the total column [Dammers et al., 2017]. Initial evaluation against surface  
198 observations from the Ammonia Monitoring Network (AMoN) show that even with the inherent  
199 sampling differences between the two surface observations they compare well with a  
200 correlation of 0.76 and an overall mean CrIS – AMoN difference of ~+15% [Kharol et al., 2018].

201 For this study, the CrIS quality flag = 4 has been used, ensuring that retrievals provide some  
202 information from the measurement (degrees-of-freedom- of-signal > 0.1). In addition, outliers  
203 for which concentrations exceed 10 standard deviations above the mean have been removed.

### 204 2.3. Modelling NH<sub>3</sub> from the CHIMERE model

205 The CHIMERE runs used in this study were obtained in the framework of the Copernicus  
206 Atmospheric Monitoring Service (CAMS, <https://atmosphere.copernicus.eu/>), and its annual  
207 task devoted to the production of regional reanalysis over Europe. The hindcasts for year 2014  
208 and 2015 (raw simulation without data assimilation) were produced over Europe with a  
209 horizontal resolution of 0.1° per 0.1° and  
210 9 vertical levels stretched from the surface up to 500 hPa (~5000m). The input data to feed  
211 CHIMERE [Menuet et al., 2013; Mailler et al., 2017] were the Integrated Forecasting System (IFS)  
212 meteorological data from European Centre for Medium-Range Weather Forecasts (ECMWF), the  
213 annual emission inventory provided by the Netherlands Organisation for Applied Scientific  
214 Research (TNO) [Kuenen et al., 2014] for year 2011 and the fire emissions from the Global Fire  
215 Assimilation System (GFAS, [Kaiser et al., 2012]). The model computes hourly concentrations for  
216 more than 180 species, among which are the regulated pollutants such as ozone, PM<sub>10</sub>, and  
217 NH<sub>3</sub>. Within CHIMERE a comprehensive modelling system allows to compute the evolutions of  
218 gaseous species and aerosols taking into account physical and chemical process. More than 30  
219 gaseous species are involved in the chemical scheme and an aerosol module assesses the gas-  
220 particulate phase equilibrium and compute the aerosol composition (inorganic, organic and  
221 natural components). These datasets were evaluated over Europe for several pollutants before  
222 being used for air quality studies (<http://policy.atmosphere.copernicus.eu/Reports.html>).





223 The model NH<sub>3</sub> profiles were integrated vertically along the 9 km model layers to provide a  
224 column that can be compared to that of the satellite measurements. Concretely this makes the  
225 reasonable assumption that all the NH<sub>3</sub> is located within this 0-5km layer (see e.g. Figure 1 in  
226 [Whitburn et al., 2016]).

#### 227 2.4. Relative scales and coincidence criteria for dataset comparisons

228 Direct quantitative comparisons of satellite NH<sub>3</sub> products are difficult because of the different  
229 overpass times and ground footprint sizes of the 2 space borne instruments, which are not  
230 compatible with the high variability of NH<sub>3</sub> in space and time. Therefore, the evaluation of  
231 satellite observations is often made with the use of in situ measurements performed at surface  
232 and onboard aircrafts [Nowak et al., 2012; Van Damme et al., 2015b], or with ground-based  
233 remote-sounding FTIR [Dammers et al., 2016; Dammers et al., 2017].

234 The purpose here of comparing CrIS and IASI is to assess qualitatively the spatiotemporal  
235 patterns of the NH<sub>3</sub> sources derived from the two datasets and use these regional observations  
236 to evaluate the CHIMERE model in the domain of analysis at the local time for their respective  
237 overpasses: 9:30 and 13:30. CHIMERE outputs, in terms of NH<sub>3</sub> concentrations, have already  
238 been compared to the IASI observations at regional scale (Europe, [Fortems-Cheiney et al.,  
239 2016]), and to surface measurements at local scale (Paris, [Petetin et al., 2016]), but have never  
240 been evaluated against the CrIS observations.

241 One aspect that needs to be considered when comparing concentration amounts inferred from  
242 infrared satellite observations is the importance of the algorithm and the a priori information  
243 used in the retrieval, especially for NH<sub>3</sub> which has limited vertical information. Some differences  
244 between the IASI and CrIS observations might arise due to instrument measurement differences  
245 (e.g. sensitivity), difference sampling period (e.g. overpass times of morning/evening vs middle  
246 of day/night), and retrieval algorithm differences, but they have both been validated and shown  
247 to capture well the spatiotemporal variations in lower tropospheric ammonia. Since the purpose  
248 of our study is not to quantitatively compare IASI and CrIS NH<sub>3</sub> data, but rather to use these  
249 independent datasets to assess NH<sub>3</sub> sources patterns over the domain and qualitatively  
250 evaluate the CHIMERE model in term of NH<sub>3</sub> concentrations and variabilities, a standardization  
251 procedure was applied to their retrieved absolute NH<sub>3</sub> columns. We computed “standardized  
252 columns” for each independent dataset (IASI, CrIS, and CHIMERE, separately) for 2014 and 2015  
253 over the domain of study in such a way that the corresponding values have a standard deviation  
254 of 1 and a mean of 0, as in [Wilks, 2011].

255 In addition, to compare CHIMERE outputs with satellite data/columns, spatial and temporal  
256 coincidence criteria have been applied. To compare satellite observations, all CrIS pixels located  
257 within a 25-km radius circle from the center of the IASI ground pixels have been considered



258 within the same day of measurements. A spatial criterion of 25 km has been chosen because it  
259 optimizes the number of pairs involved in the statistics and improves the correlations. As for the  
260 comparisons between the model and the observations: all CHIMERE outputs located within the  
261 same  $0.15^\circ \times 0.15^\circ$  grid box than the satellite and within 1 hour from its measurement have been  
262 selected.

### 263 3. Results

#### 264 3.1. NH<sub>3</sub> regional observations derived from IASI (10-years) and CrIS (5- 265 years)

##### 266 3.1.1. Seasonal variabilities

267 First the seasonal variability was investigated over the IdF area. On a monthly basis, the 10-year  
268 and 5-year averaged regional NH<sub>3</sub> total column distributions derived from IASI and CrIS were  
269 found to exhibit a high seasonality over the domain (Figures 2 and 3). Note that the distributions  
270 in Figures 2 and 3 have been obtained by averaging satellite NH<sub>3</sub> observations in  $0.25^\circ \times 0.25^\circ$   
271 grid boxes. Both satellite datasets exhibits the same variability over the domain even if the time  
272 period is different (10-years versus 5-years) and the sampling hour differs ( $\sim 9.30$  versus  $\sim 13.30$ ).  
273 One note that CrIS and IASI NH<sub>3</sub> columns present small differences in term of NH<sub>3</sub> total columns  
274 in low concentration regimes in the domain of study.

275 In these figures (2 and 3) high NH<sub>3</sub> concentrations (up to  $2.10^{16}$  molecules/cm<sup>2</sup>) can be observed  
276 from March to August at different locations of the domain:

- 277 • The French Champagne-Ardennes region in March and April (Figures 2 and 3, box A),
- 278 • The northern part of the domain corresponding to the Netherlands and the North of Belgium  
279 from April to August (Figures 2 and 3, box B), and
- 280 • The Brittany/Pays de la Loire regions (West of France) mainly in April and August but still  
281 persistent from March to August (Figures 2 and 3, box C).

282 The observed seasonality is related to agricultural practices (fertilizer application period varying  
283 as function of the crop types and farming species) and changes in temperatures, with higher  
284 temperatures favoring volatilization. This explains the high concentration in July and August.

285 In the Champagne-Ardennes region, areas of hotspots do not correspond to vineyards but to  
286 field vegetables and root crops (from the Institut National de la Recherche Agronomique INRA  
287 [https://odr.inra.fr/intranet/carto/cartowiki/index.php/OTEX\\_et\\_Orientation\\_Agricole\\_des\\_terri](https://odr.inra.fr/intranet/carto/cartowiki/index.php/OTEX_et_Orientation_Agricole_des_terri)  
288 toires, and AGRESTE, Service Central d'Enquêtes et d'Études Statistiques, 2015  
289 <http://agreste.agriculture.gouv.fr/IMG/pdf/R4215A15.pdf>). This is a leader region for mineral  
290 fertilization used for sugar industry in France [Ramanantenasoa et al., 2018]. Hamaoui-Laguel et  
291 al. (2014) and Fortems-Cheiney et al. (2016) have previously noted that NH<sub>3</sub> emissions in this



292 region, mainly due to fertilizer over barley, sugar beet, and potato starch in early March, were  
293 higher than what have been reported in the EMEP inventory.

294 NH<sub>3</sub> concentrations are high from April to August in the northern part of the domain that is  
295 known for its animal farming (Eurostat 2014, [http://ec.europa.eu/eurostat/statistics-](http://ec.europa.eu/eurostat/statistics-explained/index.php?title=File:Livestock_density_by_NUTS_2_regions,_EU-28,_2013.png)  
296 [explained/index.php?title=File:Livestock\\_density\\_by\\_NUTS\\_2\\_regions,\\_EU-28,\\_2013.png](http://ec.europa.eu/eurostat/statistics-explained/index.php?title=File:Livestock_density_by_NUTS_2_regions,_EU-28,_2013.png), [Van  
297 Damme et al., 2014a]).

298 In the Pays de la Loire, NH<sub>3</sub> concentrations are high in April and August and remain relatively  
299 high from March to September. Hotspots are found in areas of livestock farming, mainly poultry  
300 and granivorous, which explains the high and relatively constant NH<sub>3</sub> concentrations over  
301 warmer periods in this region.

### 302 3.1.2. Inter-annual variabilities

303 As can be seen in Figures 2 and 3, NH<sub>3</sub> concentrations are enhanced between March and August  
304 in the domain. In this section, inter-annual variabilities are discussed regarding meteorological  
305 conditions and agricultural practices during this time period.

306 Inter-annual variability of NH<sub>3</sub> is higher in springtime than in summer, e.g. in June the variance is  
307 8 times lower than for the other months. To illustrate the inter-annual variability in springtime,  
308 maps of monthly mean NH<sub>3</sub> total columns derived in March-April period from IASI (2008-2017  
309 time period) and from CrIS (2013-2017 time period) are shown in Figure 4. Both satellite  
310 distributions exhibit the same inter-annual variability from 2013 to 2017 with higher NH<sub>3</sub>  
311 concentrations in 2015 over the northern part of the domain than the other years. NH<sub>3</sub>  
312 concentrations derived from IASI in 2011 are 150% higher in spring (March and April) compared  
313 to 2016 (Figure 4). This inter-annual variability is partly driven by meteorological conditions and  
314 specific agricultural constrains (crop type and phenological stage for instance).

315 To investigate the impact of meteorological conditions on atmospheric NH<sub>3</sub> variability, we  
316 computed the monthly mean anomalies of total precipitation versus skin temperature derived  
317 from ECMWF ERA-interim [Dee et al., 2011], color coded by NH<sub>3</sub> total columns anomalies  
318 derived from IASI, as shown in Figure 5. Monthly mean anomalies have been calculated relative  
319 to the 10-years averages (in %). In this figure, monthly NH<sub>3</sub> total columns are at least 10% higher  
320 (positive anomalies, red dots) when skin temperatures are higher and total precipitation are  
321 lower than the 10-year average. In contrast, negative monthly NH<sub>3</sub> total columns anomalies  
322 (blue dots, Figure 5) are associated with higher total precipitation and lower skin temperatures  
323 than the 10-years average. To further detail this analysis, Figure 1 of the supplement  
324 information shows bar plots of monthly mean NH<sub>3</sub> total columns derived from IASI, total  
325 precipitation and skin temperature derived from ECMWF from March to August, plotted in  
326 different colors for the different years of measurements from 2008 to 2017. NH<sub>3</sub> total columns



327 are larger by more than 300% in March-April 2012 compared to 2013 (Figure S1a). Total  
328 precipitation is higher (0.4 mm compared to 1 mm, Figure S1b) and skin temperature is lower  
329 (281 compared to 288 K, Figure S1c) in March 2013 than in March 2012 on average over the  
330 domain. Overall, total precipitation is anti-correlated with  $\text{NH}_3$  concentrations in the  
331 atmosphere ( $R = -0.52$  from March to August for all years, not shown here) because of a) the  
332 wet deposition importance in the atmospheric  $\text{NH}_3$  removal and b) the absence of fertilization  
333 during rainy periods. Skin temperature is relatively correlated with  $\text{NH}_3$  concentrations ( $R = 0.33$   
334 from March to August for all years) since higher temperature increases volatilization of  $\text{NH}_3$   
335 from the surface to the atmosphere.

336 In addition,  $\text{NH}_3$  concentration is maximum in March 2011 whereas it peaks later in April for  
337 2012 (Figure S1a). Springtime is a spreading fertilizer period depending on many agricultural and  
338 meteorological constrains. When temperature are mild, such as in 2012 (Figure S1b), fertilizer  
339 spreading occurs sooner because the phenological growth stage is more advanced. Fertilizing  
340 process period also varies in function of the sowing date which depends on agricultural  
341 practices and crop types: corn is fertilized in early spring whereas rapeseed is in late spring.

342 Overall, all these meteorological (precipitation and temperature) and agricultural (fertilizer and  
343 manure applications) parameters account for the high  $\text{NH}_3$  inter-annual variabilities revealed by  
344 both IASI and CrIS in the domain of study.

### 345 3.2. Comparisons of $\text{NH}_3$ columns derived from IASI, CrIS, and CHIMERE

#### 346 for 2014 and 2015

347 To discuss the representation of agricultural emissions in the models in terms of intensity and  
348 both spatial and temporal distributions, regional satellite observations derived from IASI and  
349 CrIS have been compared to the CHIMERE model in the region of analysis.

#### 350 3.2.1. Annual cycle

351 Standardized monthly mean concentrations derived from IASI, CrIS, and CHIMERE for 2014 and  
352 2015 are shown in Figure 6. These years were selected as  $\text{NH}_3$  total columns were found to vary  
353 a lot, reaching 10% higher in March and 50% lower in May than the 10-years average

354 As can be seen from the plot, the 3 datasets exhibit similar patterns in terms of seasonality: all  
355 are enhanced in March-April and in summer, and show a decrease in May. However two major  
356 differences can be noted. First, CrIS standardized  $\text{NH}_3$  columns are higher in winter (November,  
357 December, and January) compared to the other dataset which can be also be seen in Figure 3.  
358 This could be attributed to a higher number of outliers, given the larger standard deviation  
359 (shaded areas, Figure 6) and no attempt to account for potential non-detects when  
360 concentrations fall below the instrument detection limits. For these months,  $\text{NH}_3$  levels are low



361 and undetectable by satellite observations (Figures 2 and 3) so these high values could be  
362 interpreted as observational noise. The detection limit depends on the instrument  
363 characteristics and atmospheric state, with IASI minimum detection limit of  $\sim 2\text{-}3$  ppbv ( $\sim 4\text{-}6 \cdot 10^{15}$   
364  $\text{molecules}\cdot\text{cm}^{-2}$ ) [Clarisse et al., 2010] and CrIS  $\sim 0.5\text{-}1.0$  ppbv ( $\sim 1\text{-}2 \cdot 10^{15}$   $\text{molecules}\cdot\text{cm}^{-2}$ )  
365 [Shephard and Cady-Pereira, 2015; Kharol et. al., 2018]. Second, the CHIMERE standardized  $\text{NH}_3$   
366 columns are enhanced in September 2014, which is not supported by the observations. It has  
367 been recently shown that CHIMERE overestimated  $\text{NH}_3$  emissions in autumn over Europe  
368 [Couvidat et al., 2018]. Generally, the amplitude of the modelled seasonal cycle exceeds the  
369 measured ones, which could be explained by higher concentrations measured in winter due to  
370 the observational noise and lower emissions.

371 Over the whole period, the coefficient of determination ( $r^2$ ) between the standardized monthly  
372 mean  $\text{NH}_3$  columns derived from IASI (CrIS), and the CHIMERE model is 0.58 (0.18) for the  
373 annual cycles of 2014 and 2015 (not shown here). If we only consider months of high  $\text{NH}_3$  in the  
374 domain from March to August, the correlation between the observational datasets and the  
375 model is good with linear regression slope values between IASI (CrIS) and CHIMERE of 0.98  
376 (0.71), as shown in Figure 7. The seasonal cycle is thus well reproduced by the model, which is  
377 encouraging given the fact that annual total emissions are simply disaggregated with a monthly  
378 profile in the model. However, the values of the  $r^2$  lower than 0.5 indicate that the CHIMERE  
379 model only reproduces at most half of the observed monthly temporal  $\text{NH}_3$  variabilities in the  
380 domain. Similar variabilities are found between the observations and the model outputs since  
381 the coefficients of correlation of the standard deviations are 0.4 and 0.6 between CHIMERE and  
382 IASI and CrIS, respectively.

### 383 3.2.2. Spatial variability of $\text{NH}_3$ in springtime

384 The IASI and CrIS regional maps have been compared to the CHIMERE model for the March-April  
385 period in 2014 and 2015 to evaluate the model's capacity to reproduce the spatial distribution  
386 of the episodic emissions from fertilizer spreading practices in springtime, as well as their inter-  
387 annual variability. Satellite  $\text{NH}_3$  measurements in springtime have been gridded at  $0.15^\circ \times 0.15^\circ$   
388 spatial resolution, and the associated CHIMERE maps have been computed following the  
389 coincident criteria described in section 2.4 at the same spatial resolution (Figures 8 and 9).

390 First one can notice that the spatial distribution of  $\text{NH}_3$  observed in springtime by both satellite  
391 instruments are in good agreement, even though their overpass time is different ( $\sim 4$  hours  
392 apart). This was already seen in the inter-annual variability agreement seen in Figure 4. In spring  
393 2014, IASI and CrIS both reveal three main regions of enhanced  $\text{NH}_3$  concentrations (North,  
394 Champagne-Ardennes, and Brittany/Pays de la Loire region) already identified by the 10-years  
395 and 5-years of IASI and CrIS observation maps (Boxes A, B, and C of Figures 2 and 3). In 2015,  
396 concentrations of  $\text{NH}_3$  in the northern part of the domain are higher than in 2014, as indicated



397 by both IASI and CrIS observations (Figure 9, upper panels). Overall, satellite observations are  
398 able to capture similar spatial distributions of high  $\text{NH}_3$  concentrations in springtime, and their  
399 evolution in time.

400 In spring 2014, the CHIMERE model reproduces the high concentrations in the three regions of  
401 the domain identified in Figures 2 and 3. Additional  $\text{NH}_3$  hot spots in the southeastern part of  
402 the domain including the Po Valley, Switzerland, and the wine region between Besancon and  
403 Lyon (blue box in Figure 8) are indicated by the CHIMERE model.  $\text{NH}_3$  emissions in this latter  
404 region are comparable to average agricultural plains over France. Only dispersion conditions  
405 related to wind speed and boundary layer height can explain high  $\text{NH}_3$  concentrations over this  
406 area.

407 In spring 2015, satellite observations and the CHIMERE model outputs exhibit very similar  
408 patterns in term of high  $\text{NH}_3$  distributions, with however higher  $\text{NH}_3$  concentrations indicated by  
409 the model in the southern part of the domain (blue box in Figure 9).

410 Finally, the (model - observations) differences between the standardized  $\text{NH}_3$  column derived  
411 from the satellite instruments in springtime 2014-2015 and the corresponding  $\text{NH}_3$  columns  
412 derived from the CHIMERE model are shown in Figure 2 of the supplement information. One  
413 can see that very similar patterns are presented when comparing the model to independent  
414 satellite observations from IASI and CrIS: the modelled  $\text{NH}_3$  concentrations are systematically  
415 lower for both years over Belgium and United Kingdom, and higher in the southern part of the  
416 domain (green square, Figure S2) including the Pays de la Loire region (box C in Figures 2 and 3),  
417 and in the southeastern part of the domain (over the North part of Switzerland and the Plateau  
418 du Jura region - between Besancon and Lyon cities – blue box in Figure 8). Reasons of enhanced  
419  $\text{NH}_3$  columns derived from the model in this latter region are not clear yet. An explanation could  
420 be that the temporal distribution of the emissions is misrepresented in the model since the  
421 modelled concentrations are enhanced in April whereas the two satellite observations are  
422 enhanced earlier in March for both years. It is worth noting that there are no EMEP stations  
423 measuring surface  $\text{NH}_3$  concentrations in these regions. As for the Brittany/Pays de la Loire  
424 region, it has already been shown that the LOTOS-EUROS atmospheric model [Schaap et al.,  
425 2008] using similar chemistry schemes and  $\text{NH}_3$  emissions shows higher columns each year in  
426 this area [Van Damme et al., 2014b].

### 427 3.3. Conditions for PM formation in the Paris megacity

428 To investigate the impact of intensive agriculture practices on the Paris megacity air quality, we  
429 need to better understand the role of  $\text{NH}_3$  in the formation of  $\text{PM}_{2.5}$  that depends, among  
430 others, on specific meteorological conditions such as atmospheric temperature and humidity  
431 that alter the gas-particle partitioning. The link between high  $\text{NH}_3$  concentrations inducing  $\text{PM}_{2.5}$



432 formation in the Paris megacity is known [Petetin et al., 2016; Zhang et al., 2013] but  
433 quantification of such phenomena is difficult due the lack of long-term  $\text{NH}_3$  monitoring in the  
434 IdF region.  $\text{PM}_{2.5}$  is however measured hourly at several locations in Paris by the Airparif  
435 network (<https://www.airparif.asso.fr/>, Figure 1). Thanks to the 10 years of IASI observations,  
436 an observational evidence of  $\text{PM}_{2.5}$  formation in the IdF region (100 km around Paris - black box  
437 in Figure 1) is represented in Figure S3. Simultaneous enhancements in March of  $\text{PM}_{2.5}$   
438 measured at the surface and  $\text{NH}_3$  columns derived from the IASI observations over the IdF  
439 region are clearly visible. However, high concentrations of  $\text{NH}_3$  observed in summer are not  
440 associated with high  $\text{PM}_{2.5}$  concentrations. This reflects the complexity of the  $\text{PM}_{2.5}$  formation  
441 depending on various factors, such as  $\text{NH}_3$  emissions, atmospheric chemistry (acidic content of  
442 the atmosphere), transport, and specific meteorological conditions involved in the gas to solid  
443 phase conversion between  $\text{NH}_3$  and ammonium salts.

444 To evaluate the impact of long-range transport on  $\text{NH}_3$  levels observed over the Parisian region  
445 (IdF) in spring, back-trajectory analysis was performed. In total 231 24-hours back-trajectories  
446 ending in Paris (period from February 15<sup>th</sup> to May 15<sup>th</sup> from 2013 to 2016) were classified into 8  
447 clusters using HYSPLIT (<https://ready.arl.noaa.gov/HYSPLIT.php>). Figure 10 shows the mean  
448 trajectories for each cluster associated with the average  $\text{NH}_3$  total columns measured by IASI  
449 over the IdF region. In this figure, higher  $\text{NH}_3$  columns are found under the influence of air  
450 masses transported from the northern part of the domain (over Belgium and the Netherlands,  
451 clusters 4 and 5) and from the Brittany region (cluster 8), which are the major sources regions of  
452  $\text{NH}_3$  in spring in the domain as previously identified (Figures 2 and 3). Clusters 2 and 3 (Figure  
453 10) are associated with intermediate  $\text{NH}_3$  levels since air masses moved slowly transporting  
454  $\text{NH}_3$ -rich air from rural regions near IdF (such as the Champagne-Ardenne region - Box A in  
455 Figures 2 and 3) to Paris. Finally, low  $\text{NH}_3$  concentrations are measured when air masses  
456 originated from ocean regions passing through continental areas with minor  $\text{NH}_3$  sources in  
457 spring (clusters 1, 6 and 7, Figure 10). This reflects the importance of long-range transport in the  
458  $\text{NH}_3$  budget observed over the Paris megacity in spring.

459 To quantitatively assess the influence of meteorological parameters on the formation of  $\text{PM}_{2.5}$   
460 from  $\text{NH}_3$  in the IdF region, timeseries of  $\text{NH}_3$  total columns,  $\text{PM}_{2.5}$  surface concentrations, and  
461 four meteorological parameters (temperature at 2 m, boundary layer height, total precipitation  
462 and relative humidity) derived from ECMWF - ERA-Interim [Dee et al., 2011] were analyzed. To  
463 compute daily and monthly means, IASI  $\text{NH}_3$  total columns have been averaged over IdF (black  
464 box in Figure 1),  $\text{PM}_{2.5}$  concentrations measured between 9 AM and 11 AM have been averaged  
465 over the 14 stations (dark points in Figure 1), and ECMWF data have been averaged over a 300  
466 km region around Paris (the blue box in Figure 1). Figure 11 shows all these parameters for  
467 spring 2014.



468 We have flagged pollution episodes in both time series ( $\text{PM}_{2.5}$  and  $\text{NH}_3$ ) by selecting data above  
469 1-sigma standard deviation over the mean of the datasets from 2013 to 2016. This time period  
470 was selected to have enough IASI observations in the IdF region. Then two cases have been  
471 defined to study the temporal correlation between  $\text{NH}_3$  and  $\text{PM}_{2.5}$ : case A in which both  $\text{NH}_3$  and  
472  $\text{PM}_{2.5}$  pollution episodes appear simultaneously, i.e. within the same day or 2 days apart  
473 (shaded in red in Figure 11); case B in which pollution episodes appear at least 3 days apart  
474 (shaded in blue in Figure 11). In Figure 11, a strong relationship between peaks of  $\text{NH}_3$ ,  $\text{PM}_{2.5}$   
475 and meteorological parameters can be seen. For example, between March 3<sup>rd</sup> and March 19<sup>th</sup>  
476 2014 (case A), the boundary layer height is exceptionally low (456 m; compared to 760 m on  
477 average); the temperature is relatively low (280 K; 282 K on average); and there is no  
478 precipitation (0.01 mm/h; 0.11 mm/h on average). One note that peaks of maximum  $\text{NH}_3$   
479 observed in IdF on March 11<sup>th</sup> and 12<sup>th</sup> are associated with air masses coming from the northern  
480 part of the domain (clusters 4 and 5 in Figure 10). In contrast, for the case B in which  
481 appearance of peaks of  $\text{NH}_3$  and  $\text{PM}_{2.5}$  is not simultaneous, meteorological conditions are  
482 different: the boundary layer is thicker (908 m on April 23<sup>rd</sup> 2014), or temperature is higher (285  
483 K on April 11<sup>th</sup> 2014).

484 To further investigate the influence of meteorological parameters on the pollution episodes in  
485 the IdF region, detailed analysis have been made over the whole dataset. Figure 12 shows the  
486 statistical distribution of meteorological parameters corresponding to case A, case B, and all  
487 observations. One can see that the boundary layer height is significantly lower in case A ( $550 \pm$   
488  $205$  m) than in case B ( $751 \pm 276$  m), and that precipitations are absent in case A (0,019 mm/h)  
489 compared to case B (0,085 mm/h). The temperature at 2 meters also differs between the two  
490 cases (case A:  $278 \pm 3$  K; case B:  $282 \pm 4$  K), but the humidity is almost the same ( $70\% \pm 17\%$   
491 versus  $75\% \pm 18\%$ ). Thus the combination of the following three meteorological parameters favors  
492 simultaneous appearances of  $\text{NH}_3$  and of  $\text{PM}_{2.5}$  in Paris (i.e. case A): low surface temperatures  
493 ( $5^\circ\text{C}$ ), with thin boundary layers ( $\sim 500\text{m}$ ), and rare precipitations. In addition, the Wilcoxon-  
494 Mann-Whitney test ([Wilks, 2011], not shown here) indicates that each single parameter has no  
495 significant influence on the  $\text{NH}_3$ - $\text{PM}_{2.5}$  correlation. Therefore only a combination of these  
496 different parameters has an impact on secondary aerosol formation from  $\text{NH}_3$ .

497 An explanation of these findings might be that anticyclonic conditions (low planetary boundary  
498 layer), preventing pollutant dispersions in the lower atmosphere [Salmond and McKendry,  
499 2005], along with moderate wind fields allow  $\text{NH}_3$  plumes to be transported from rural to urban  
500 regions [Petit et al., 2015]. In addition, thanks to relatively low atmospheric temperatures and a  
501 moderate relative humidity, conversion of gas phase  $\text{NH}_3$  to ammonium salts is then  
502 accentuated via optimal phase equilibrium [Watson et al., 1994; Nenes et al., 1998]. Finally,  
503 with the absence of rain, ammonium salts are stabilized in the aerosols.





504 Our observations are in agreement with previous studies [Bessagnet et al., 2016; Wang et al.,  
505 2015], which have shown that the formation of ammonium salt needs a specific humidity of 60 -  
506 70%, because it corresponds to the deliquescence point of  $\text{NH}_4\text{NO}_3$  in ambient air. This is in  
507 agreement with our results since the mean of relative humidity in case A is 70%. Our results also  
508 support the idea that a relatively low atmospheric temperature favor  $\text{PM}_{2.5}$  formation since the  
509 phase equilibrium leads to  $\text{NH}_4\text{NO}_3$  decomposition above 30 °C.

#### 510 4. Conclusions

511 This study focuses on seasonal and inter-annual variabilities of  $\text{NH}_3$  concentrations in a 400 km  
512 radius-circle area around Paris to assess the evolution of major  $\text{NH}_3$  agricultural sources and its  
513 key role in the formation of the secondary aerosols that affect air quality over the Paris  
514 megacity.

515 Thanks to 10-years and 5-years of regional  $\text{NH}_3$  observations derived from IASI and CrIS, three  
516 main regions of high  $\text{NH}_3$  occurring between March and August were identified. Observed inter-  
517 annual variabilities of  $\text{NH}_3$  concentrations have been discussed with respect to total  
518 precipitations and atmospheric temperature, showing that total precipitations are anti-  
519 correlated with high  $\text{NH}_3$  concentrations, and that mild temperature in late winter causes  
520 precocious fertilizer spreading due to advanced phenological growth stage.

521 To evaluate our knowledge on agricultural emissions in terms of intensity and both spatial and  
522 temporal distributions, coincident CHIMERE model outputs have been compared to satellite  
523 observations of IASI and CrIS for 2014 and 2015. The annual cycle is well reproduced by the  
524 model (correlation slopes of 0.98 and 0.71 between the model and IASI and CrIS, respectively)  
525 but the model is only able to reproduce half of the observed atmospheric  $\text{NH}_3$  variability.  
526 Focusing on spring periods (March-April 2014 and 2015) of episodic  $\text{NH}_3$  emissions, the two  
527 independent satellite observations derived from IASI and CrIS show very similar spatial  
528 distributions of high  $\text{NH}_3$  concentrations, as well as their evolution in time. The comparison  
529 between CHIMERE  $\text{NH}_3$  columns and coincident satellite observations highlights the same  
530 difference spatial patterns with a systematic underestimation of  $\text{NH}_3$  concentrations from the  
531 model over Belgium and an overestimation in the southern part of the domain (French  
532 Brittany/Pays de la Loire and Plateau du Jura regions, as well as North of Switzerland).

533 Focusing on the Ile-de-France (IdF, 100 km around Paris) region, we found that air masses  
534 originated from rich- $\text{NH}_3$  areas, mainly the northern part of the domain over Belgium and the  
535 Netherlands, increase the observed  $\text{NH}_3$  total columns measured by IASI over the urban area of  
536 Paris.

537 To assess the link between  $\text{NH}_3$  and  $\text{PM}_{2.5}$  over the Parisian (IdF) region, the main  
538 meteorological parameters driving the optimal conditions involved in the  $\text{PM}_{2.5}$  formation have



539 been identified. The results show that relatively low temperature, thin boundary layer, coupled  
540 with almost no precipitation, favor the PM<sub>2.5</sub> formation with the presence of atmospheric NH<sub>3</sub> in  
541 the IdF region. Based on a more observational approach over large time scale, this work is in  
542 agreement with previous studies.

543 This study highlights the need for a better representative NH<sub>3</sub> monitoring to improve numerical  
544 simulation of spatial and temporal NH<sub>3</sub> variabilities, especially at fine scales. In order to  
545 compare IASI and CrIS data in absolute values, it would be recommended to derive both  
546 datasets using the same retrieval algorithm. Thus, by combining these datasets bi-daily NH<sub>3</sub>  
547 total columns in absolute values at regional scale would be provided. This would help inferring  
548 variability of top-down NH<sub>3</sub> emissions. Complementarily, long term quantification of NH<sub>3</sub> diurnal  
549 cycle inside Paris would improve comparisons with local PM<sub>2.5</sub> needed to understand secondary  
550 aerosols formations. For this purpose, an ongoing activity consists in the deployment of a mini-  
551 DOAS instrument [Volten et al., 2012] used for long-term and continuous monitoring of  
552 atmospheric NH<sub>3</sub> concentrations in the center of Paris from the QUALAIR platform  
553 (<https://www.ipsl.fr/en/Our-research/Atmospheric-chemistry-and-air-quality/Tropospheric-chemistry/QUALAIR>). Finally, the geostationary-orbit sounder IRS-MTG ([Stuhlmann et al.,  
554 2005], to be launched after 2022) will provide NH<sub>3</sub> columns at very high sampling rate (every 0.5  
555 hour over Europe) with an unprecedented spatial resolution (pixel size of 4 km).

557

#### 558 Author contribution:

559 CV wrote the paper with contributions of all coauthors. CV and CC designed the study. MV, LC,  
560 and SW performed IASI retrievals and ED, MWS, and KEC performed the CrIS retrievals. FM ran  
561 the CHIMERE simulations. CV and TW analyzed the data with guidance from CC and PFC. All  
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578

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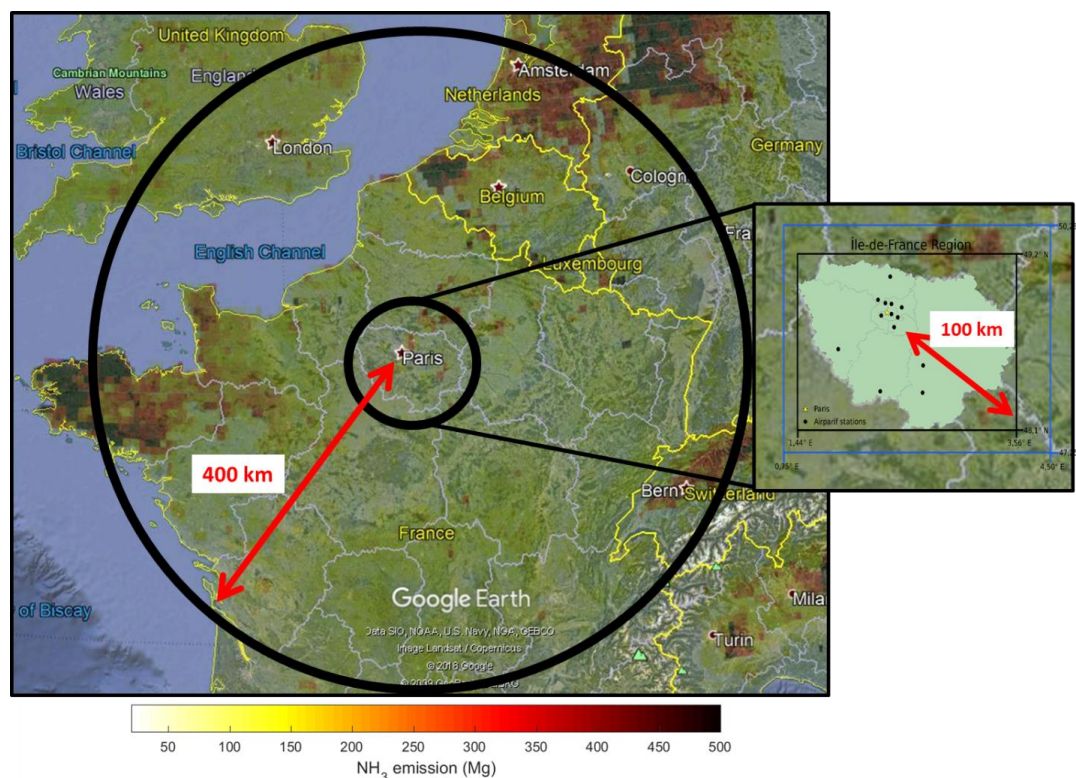


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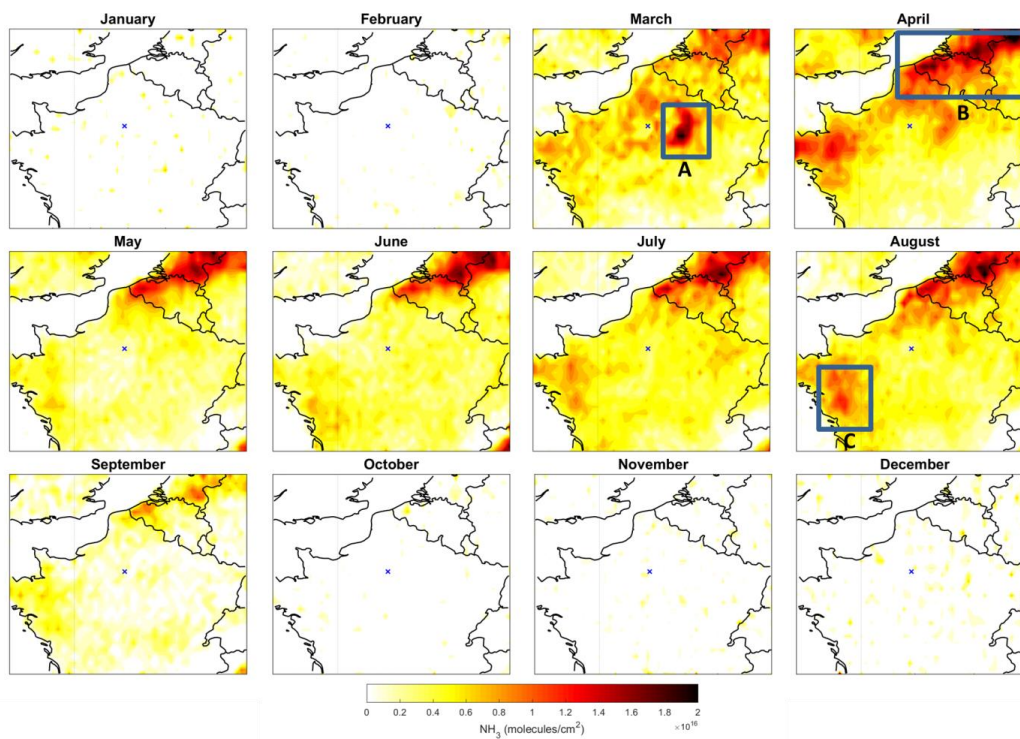
843

## FIGURES



844

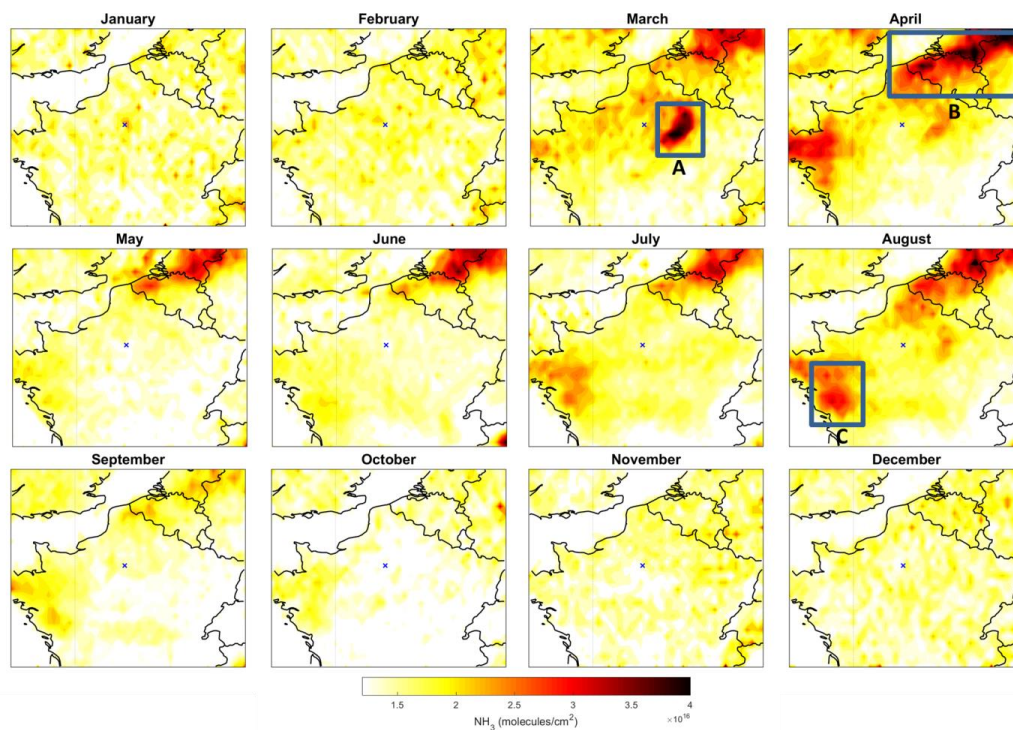
845 Figure 1: Region of analysis: 400 km radius-circle around the Paris megacity and 100 km  
846 Paris. The latter is representative of the Ile-de-France (IdF) region where the Airparif PM  
847 observational network is located. Black points are the locations of the Airparif stations  
848 measuring hourly PM<sub>2.5</sub> concentration at the surface. The black (blue) box delimitates the IdF  
849 region in which the IASI NH<sub>3</sub> (ECMWF) data have been considered. The overlay represents NH<sub>3</sub>  
850 emissions (in Mg per year and per cell of 0.1°x0.1°) derived from the EMEP inventory for 2015.



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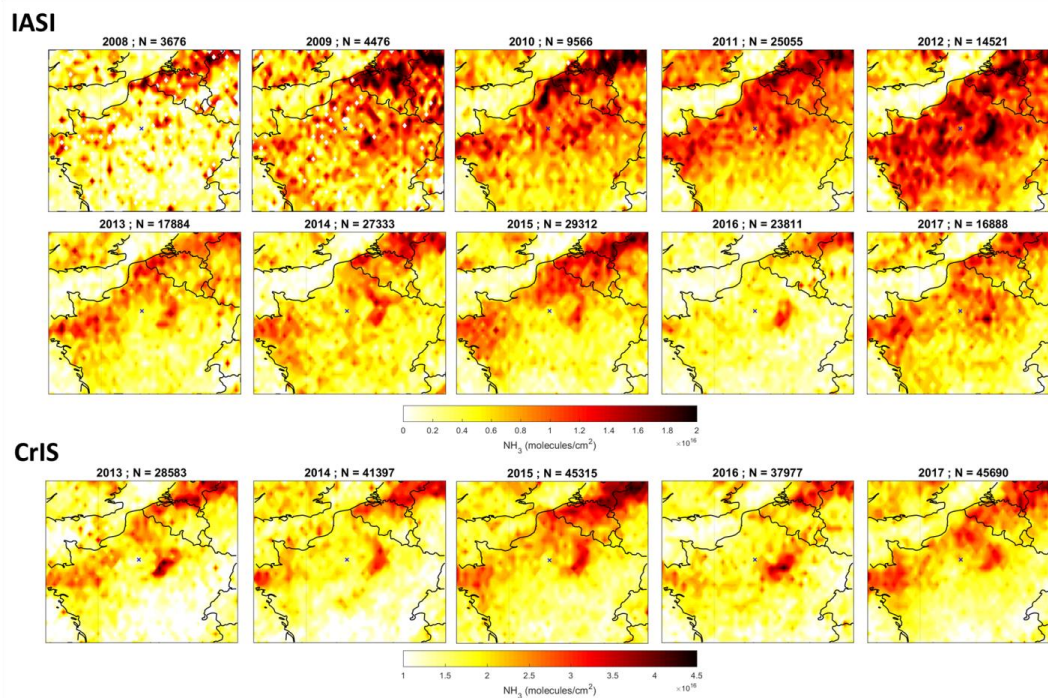
852 Figure 2: Monthly means of  $\text{NH}_3$  total columns ( $\text{molecules}/\text{cm}^2$ ) derived from 10 years (2008-  
853 2017) of IASI  $\text{NH}_3$ -retrieved columns. The blue cross indicates Paris location.

854



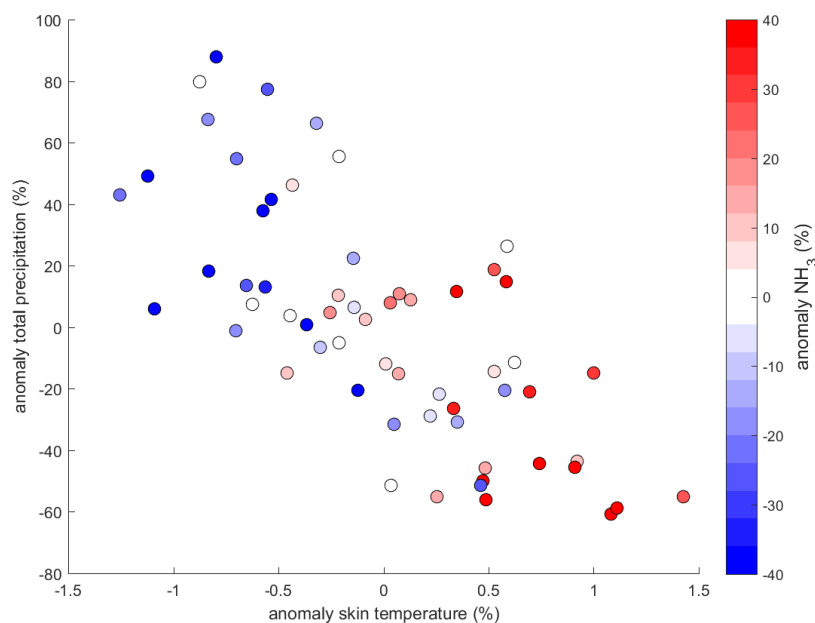
855

856 Figure 3: Monthly means of  $\text{NH}_3$  total columns (molecules/ $\text{cm}^2$ ) derived from 5 years (2013-  
857 2017) of CrIS  $\text{NH}_3$ -retrieved columns. The blue cross indicates Paris location.



858

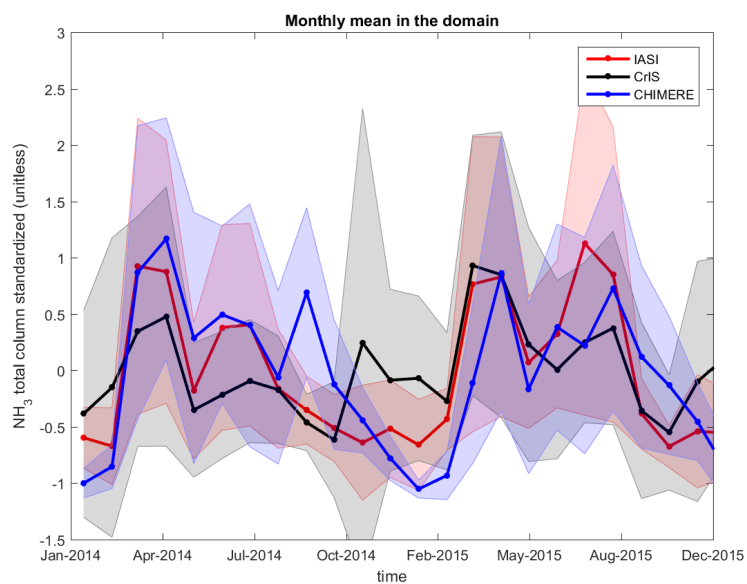
859 Figure 4: Maps of monthly mean NH<sub>3</sub> total columns (molecules/cm<sup>2</sup>) in March-April period  
860 derived from IASI from 2008 to 2017 and CrIS from 2013 to 2017.



861

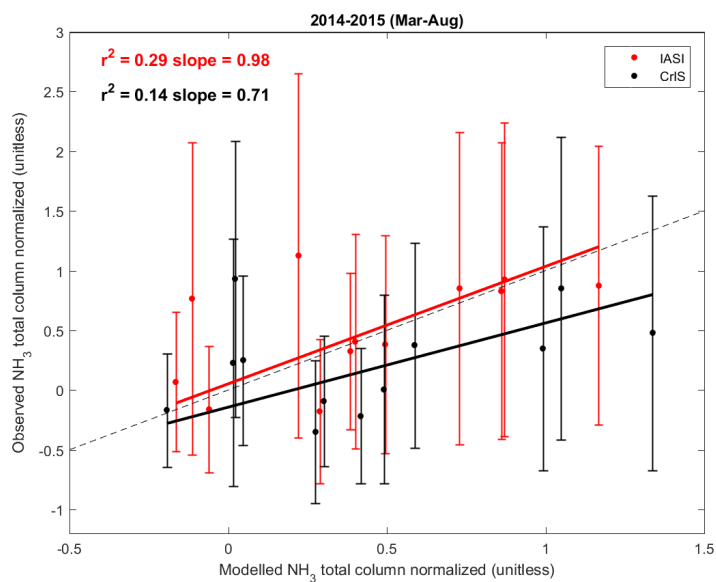
862 Figure 5: Scatter plot of monthly mean anomaly (relative to the 10-years – 2008 to 2017 -  
863 monthly average) of total precipitation versus skin temperature derived from ECMWF from  
864 March to August in the domain, and color coded by the NH<sub>3</sub> total columns anomaly derived  
865 from IASI.





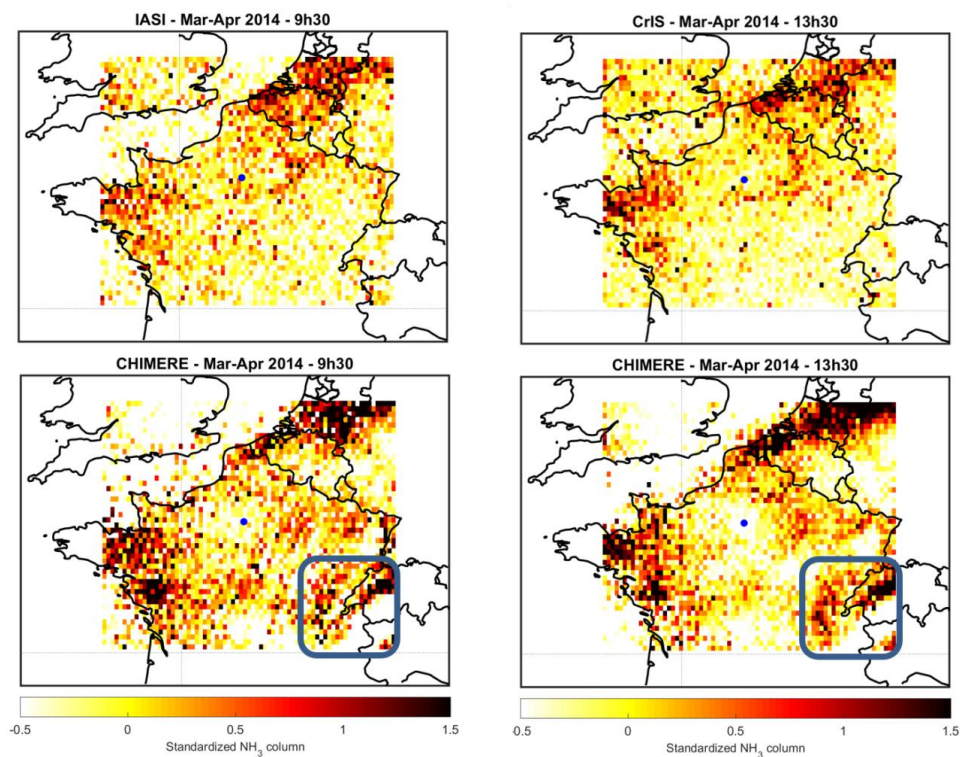
866

867 Figure 6: Standardized monthly mean concentrations derived from IASI (red), CrIS (black) and  
868 CHIMERE (blue) for 2014 and 2015. Shaded areas correspond to the one-sigma standard  
869 deviation around the means.



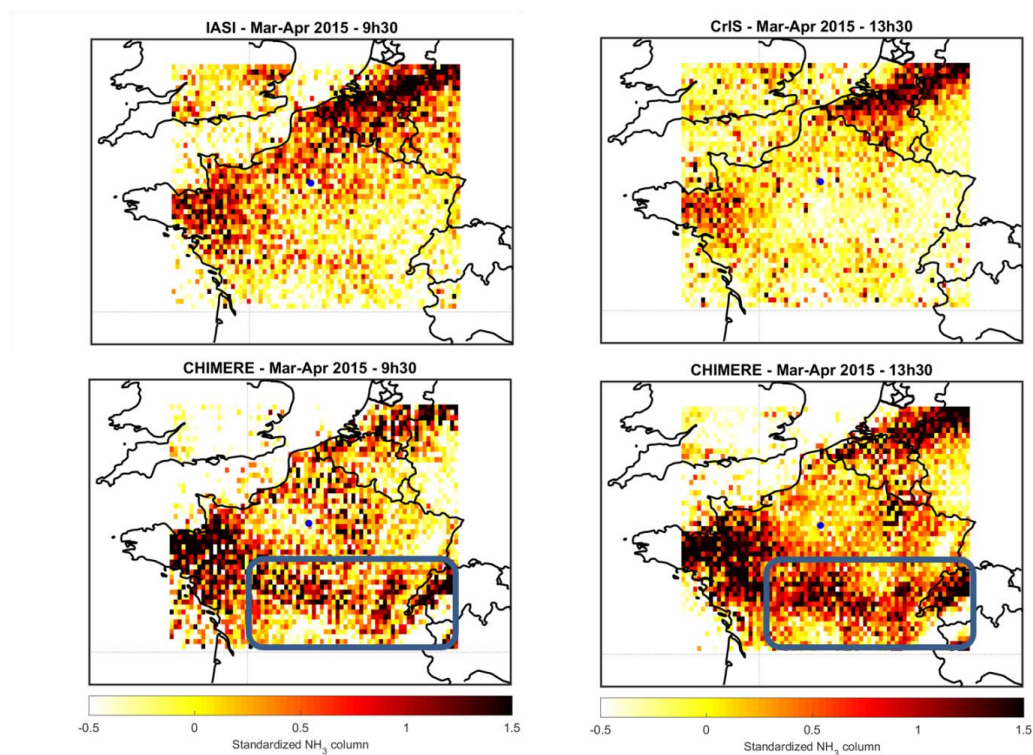
870

871 Figure 7: Correlation plots between monthly means  $\text{NH}_3$  standardized concentrations derived  
 872 from satellite observations (IASI in red and CrIS in black) and the CHIMERE outputs for the  
 873 March to August months of 2014 and 2015. The 1:1 line is represented in the dashed line.



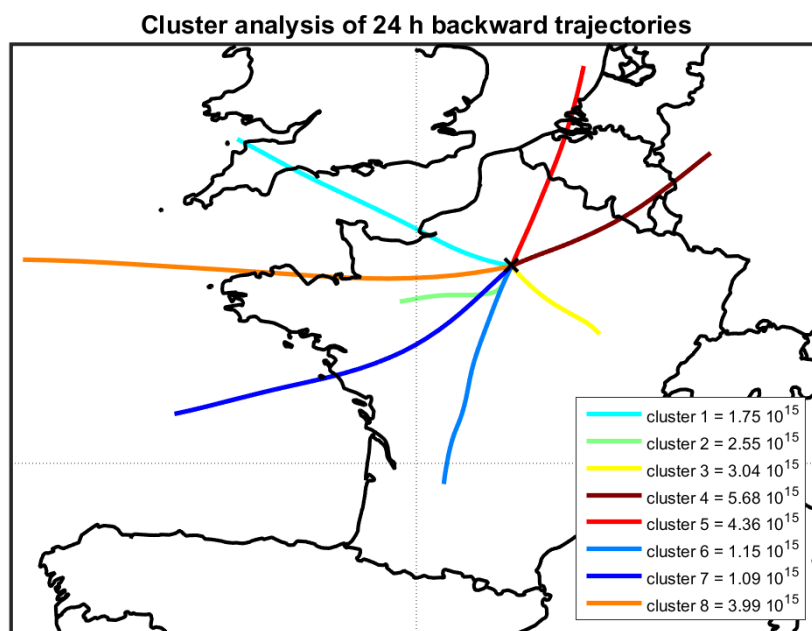
874

875 Figure 8: Standardized  $\text{NH}_3$  column derived from the satellite instruments (IASI = top left panel,  
876 and CrIS = top right panel) and the corresponding  $\text{NH}_3$  column derived from the CHIMERE model  
877 (coincident with IASI – bottom left panel, and coincident with CrIS – bottom left panel) for  
878 March-April 2014. Blue dots indicate Paris location.



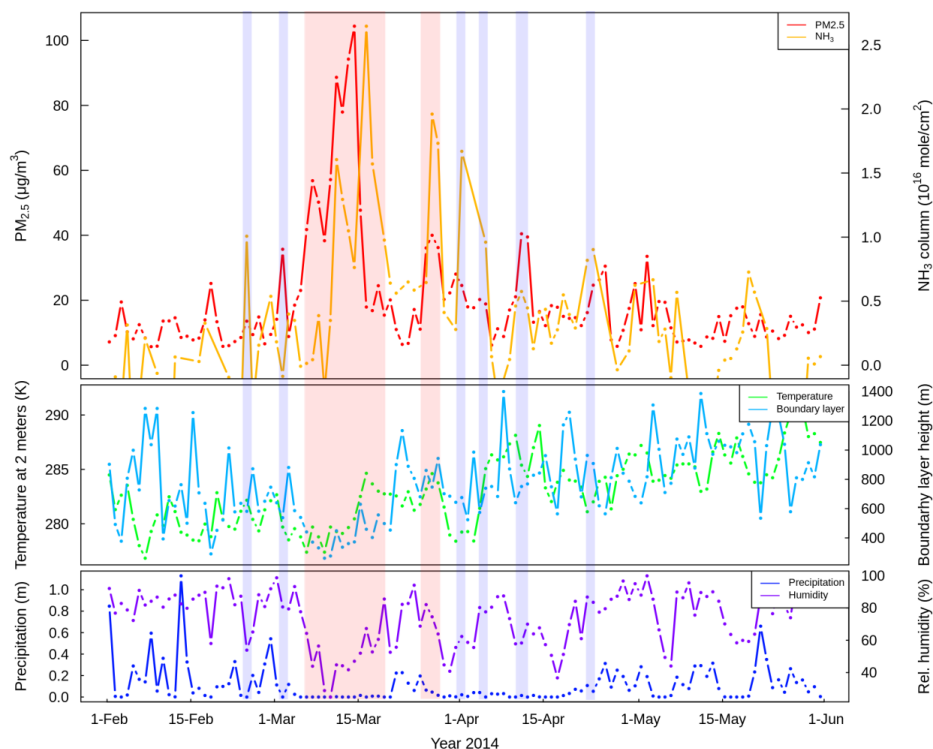
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880 Figure 9: Same than Figure 7 but for March-April 2015.

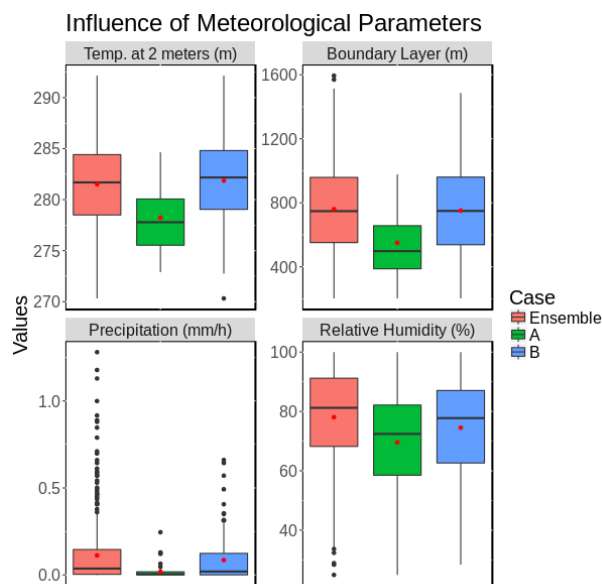


881

882 Figure 10: Cluster analysis of 24-h backward trajectories arriving in spring in Paris (from  
883 February 15<sup>th</sup> to May 15<sup>th</sup> for the 2013-2016 period) using HYSPLIT-4 model obtained from the  
884 NOAA Air Resources Laboratory. Mean trajectories of the 8 clusters are shown in different  
885 colors, associated with the NH<sub>3</sub> concentrations measured by IASI in the IdF region (in  
886 molecules/cm<sup>2</sup>).



887  
888 Figure 11: Average concentrations of  $\text{NH}_3$  total columns derived from IASI (in molecules/ $\text{cm}^2$ ;  
889 orange, upper panel) and  $\text{PM}_{2.5}$  derived from the Airparif network selected within 2 hours from  
890 the IASI overpass (in  $\mu\text{g}/\text{m}^3$ ; red, upper panel) for 2014 as example. Periods of simultaneous  
891 (independent) enhancements of  $\text{NH}_3$  and  $\text{PM}$  concentrations are represented with red (blue)  
892 areas, i.e. case A (case B). Temperature at 2 meters (in Kelvin; green, middle panel), boundary  
893 layer height (in meter; blue, middle panel), precipitation (in meter; dark blue, lower panel), and  
894 relative humidity (in percent; purple, lower panel) derived from the ECMWF ERA-interim.



895

896 Figure 12: Statistical distributions of meteorological parameters corresponding to case A, case B,  
 897 and all observations derived from 2013 to 2016. The medians and the quartiles are presented by  
 898 center lines and borders of the boxes, respectively. The mean values are indicated by red points,  
 899 and the extreme values (i.e. those beyond  $Q1 - 1.5 \text{ IQR}$  and  $Q3 + 1.5 \text{ IQR}$ ) by black points.



900

**TABLE**

Satellite	Overpass time (LT)	Time coverage	Nadir spatial resolution (km)	Spectral range (cm <sup>-1</sup> )	Spectral resolution (cm <sup>-1</sup> )	Spectral Noise* (K) @270K @ 970 cm <sup>-1</sup>	References
<b>IASI</b> Metop-A/B	9.30 (AM/PM)	2006-present	12	645–2760	0.5 (apodized)	~0.2	Clerbaux et al., 2009
<b>CrIS</b> Suomi-NPP	1.30 (AM/PM)	2011-present	14	645–1095; 1210–1750; 2155–2550	0.625; (unapodized)	~0.05	Zavyalov et al., 2013

\*Spectral noise comparison values in main ammonia spectral region (~970 cm<sup>-1</sup>) obtained from Zavyalov et al., 2013.

901 Table 1: Instrumental specifications for the IASI and CrIS satellite instruments.