

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

Viatte Camille<sup>1</sup>, Wang Tianze<sup>1</sup>, Van Damme Martin<sup>2</sup>, Dammers Enrico<sup>3</sup>, Meleux Frederik<sup>4</sup>,  
Clarisse Lieven<sup>2</sup>, Shephard Mark W.<sup>3</sup>, Whitburn Simon<sup>2</sup>, Coheur Pierre François<sup>2</sup>, Cady-Pereira  
Karen E.<sup>5</sup>, and Clerbaux Cathy<sup>1,2</sup>

<sup>1</sup> LATMOS/IPSL, Sorbonne Université, UVSQ, CNRS, Paris, France

<sup>2</sup> Université libre de Bruxelles (ULB), Service de Chimie Quantique et Photophysique, Atmospheric Spectroscopy, Brussels, Belgium

<sup>3</sup> Environment and Climate Change Canada, Toronto, Ontario, Canada

<sup>4</sup> Institut national de l'environnement industriel et des risques, INERIS, Verneuil en Halatte, France

<sup>5</sup> Atmospheric and Environmental Research (AER), Inc., Lexington, USA

## 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 variability with three major  $NH_3$   
23 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 2014 and 2015 the  
27 CHIMERE model shows coefficient of determination of 0.58 and 0.18 when comparing with IASI  
28 and CrIS, respectively. With respect to spatial variability, the CHIMERE monthly  $NH_3$   
29 concentrations in springtime show a slight underrepresentation over Belgium and the United-  
30 Kingdom and overrepresentation in agricultural areas in the French Brittany/Pays de la Loire and  
31 Plateau du Jura region, as well as in the north part of Switzerland. In addition,  $PM_{2.5}$   
32 concentrations derived from the CHIMERE model have been evaluated against surface  
33 measurements from the Airparif network over Paris, for which agreement was found ( $r^2$  of 0.56)  
34 with however an underestimation during spring pollution events.

35 Using HYSPLIT cluster analysis of back-trajectories, we show that  $NH_3$  total columns measured in  
36 spring over Paris are enhanced when air masses originate from the Northeast (e. g., Netherlands  
37 and Belgium), highlighting the importance of long-range transport on the  $NH_3$  budget over Paris.  
38 Variability of  $NH_3$  in the Northeast region is likely to impact  $NH_3$  concentrations in the Parisian  
39 region since the cross-correlation function is above 0.3 (at lag = 0 and 1 day).

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

## 1. Introduction

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

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

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

81 Atmospheric chemical transport models have difficulty representing both  $\text{NH}_3$  and  $\text{PM}_{2.5}$   
82 distributions due to the challenge of reproducing  $\text{NH}_3$  temporal variability [Pinder et al., 2006;  
83 Fortems-Cheiney et al., 2016], long-range transport of pollutants [Moran et al., 2014], and  
84 secondary aerosol formation in the atmosphere [Petetin et al., 2016]. The GEOS-Chem chemical  
85 transport model [Bey et al., 2001] was found to underestimate the observed  $\text{NH}_3$  concentrations  
86 in most regions of the globe [Zhu et al., 2013; Li et al., 2017]. Heald et al. (2012) compared the  
87 IASI observations with the GEOS-Chem model and showed that  $\text{NH}_3$  is likely underestimated in  
88 California, leading to a local underestimate of ammonium nitrate aerosol. Similarly, the French  
89 CHIMERE model [Menut et al., 2013] underestimates the  $\text{NH}_3$  surface concentrations and  
90 emissions over Paris [Petetin et al., 2016; Fortems-Cheiney et al., 2016] because of the mis-  
91 representation of agricultural emissions in terms of intensity and both spatial and temporal  
92 distribution. Often ground and aircraft-based observations are used to provide detailed  
93 representation of the atmospheric state that can be used to evaluate and improve the model  
94 simulations; however, these can be spatially sparse and/or over short sampling periods,  
95 especially globally. Additionally, more recently available (within the last 10-years) sun-  
96 synchronous satellite-based infrared sensors have been providing  $\text{NH}_3$  observations globally  
97 with a spatial resolution of  $\sim 15$  km approximately twice a day. These satellite observations have  
98 limited independent vertical information, but do capture the spatiotemporal variabilities  
99 needed to help address these issues and improve model simulations, especially in remote  
100 locations [Skj  th et al., 2011; Kranenburg et al., 2016].

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

111 Representative measurements of  $\text{NH}_3$  concentrations and spatiotemporal variabilities are  
112 needed to address the link between  $\text{NH}_3$  and  $\text{PM}_{2.5}$  formation and improve model simulations.  
113 This has been attempted previously in some cities around the world, such as in Shanghai [Ye et  
114 al., 2011], Houston [Gong et al., 2013], Santiago City [Toro et al., 2014], and Beijing [Zhao et al.,  
115 2016] for instance. However, although the Paris megacity is repeatedly shrouded by particulate  
116 pollution episodes, many studies are limited to the Paris megacity and performed over relatively  
117 short time frame during field campaigns:  $\text{NH}_3$  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]. Our study is a data-driven regional approach and considers a longer time period to study the seasonal/inter-annual variabilities of  $\text{NH}_3$  and its impact of  $\text{PM}_{2.5}$  formation over the Paris megacity. Specifically in this paper we study concentrations and spatiotemporal variability of atmospheric  $\text{NH}_3$  from the agricultural sector to gain insights on its effects on megacity air quality using: 1) long-term satellite observations derived from IASI (10 years from 2008 to 2017) and CrIS (5 years from 2013 to 2017) at regional scale (400km radius-circle from Paris city center); 2) spatiotemporal patterns of the CHIMERE model evaluated against the IASI and CrIS datasets for 2014 and 2015; and 3) the main meteorological parameters favoring the secondary  $\text{PM}_{2.5}$  formation from  $\text{NH}_3$  in the Paris megacity are analyzed.

## 2. Methodology

### 2.1. Region of analysis

The domain of analysis covers a circular area of 400 km radius around the Paris city center (Figure 1, larger circle) enabling the study of temporal and spatial variabilities of  $\text{NH}_3$  emission sources likely to affect air quality in the Paris megacity. It has been selected for two reasons. First, it includes main regions known for their high  $\text{NH}_3$  emissions, which can be transported and affect air quality over the Parisian region (Ile-de-France –IdF-, smaller circle in Figure 1). Emission regions in the Netherlands, North of Germany, Northwest of Belgium, and the Brittany region in France, are highlighted in darker colors in Figure 1 (emissions values are from the European Monitoring and Evaluation Programme -EMEP- 2015). Second, this area corresponds to the transport of 24 hours back-trajectories from Paris generated from the HYSPLIT model for one year, ensuring that  $\text{NH}_3$  can indeed be efficiently transported from the emitting sources within the selected domain to the IdF region.

### 2.2. Satellite observations of ammonia

For this study we used the available data from IASI and CrIS which are both Fourier transform spectrometers to evaluate the current capacity to observe  $\text{NH}_3$  concentrations from space, and study its variability around IdF. Technical information are summarized in Table 1.

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

IASI is a nadir-viewing spectrometer launched on board the Metop-A and Metop-B satellites and operated by EUMETSAT (European Organisation for the Exploitation of Meteorological Satellites), since October 2006 and September 2012, respectively. These satellites are on similar polar orbits with Equator crossing times at 09:30 (21:30) local mean solar time for the descending (ascending) orbit. IASI measures the thermal infrared radiation of the system Earth-

atmosphere in the spectral range from 645 to 2760  $\text{cm}^{-1}$  with a spectral resolution 0.5  $\text{cm}^{-1}$  apodized. The satellite swath is an area of 2200 km width composed by off-nadir measurements up to 48.3° on both sides of the track. At nadir, the IASI field of view is composed of 4 x 4 pixels of 12 km diameter each [Clerbaux et al., 2009].

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

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 26 minutes for the 1325 days of common measurements. Monthly maps for the 10 years of observations between 2008 and 2017 are obtained by averaging Metop-A and whenever Metop-B (the two instruments are considered jointly for their period of common operation from March 2013 to 2017) with more than  $10^5$  pixels on average over the domain of analysis. The number of available  $\text{NH}_3$  columns depends not only on the satellite overpass time but also on the state of the atmosphere being remotely sensed (e.g. thermal contrast and cloud cover). IASI  $\text{NH}_3$  has been evaluated using the LOTOS-EUROS model over Europe [Van Damme et al., 2014b] and ground-based and airborne measurements [Van Damme et al., 2015b], showing consistency between the IASI  $\text{NH}_3$  and the available datasets. When comparing IASI  $\text{NH}_3$  (previous IASI-NN version) with ground-based Fourier transform infrared (FTIR) observations, a correlation of 0.8 and a slope of 0.73, with a mean relative difference of  $-32.4 \pm (56.3) \%$ , and an underestimation by IASI ranging from 10 to 50 % have been found [Dammers et al., 2016].

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

The CrIS instrument [Zavyalov et al., 2013] is a Fourier Transform spectrometer operated by the Joint Polar Satellite System (JPSS) program on Suomi National Polar-orbiting Partnership (NPP) satellite, launched on 28 October 2011. CrIS is in a sun-synchronous orbit with a mean local daytime overpass time of 13:30 (01:30) in the ascending (descending) node. CrIS measures the atmospheric composition over three wavelength bands in the infrared region (645–1095  $\text{cm}^{-1}$ ; 1210–1750  $\text{cm}^{-1}$ ; 2155–2550  $\text{cm}^{-1}$ ).  $\text{NH}_3$  retrievals are performed from the 645–1095  $\text{cm}^{-1}$  band with a spectral resolution of 0.625  $\text{cm}^{-1}$ . The CrIS instrument scans a 2200 km swath width (+/-

50 °). At nadir, the CrIS field of view consists of a 3 × 3 array of circular pixels of 14 km diameter each.

The CrIS Fast Physical Retrieval (CRPR) [Shephard and Cady-Pereira., 2015] uses an optimal estimation approach [Rodgers, 2000] that minimizes the difference between the CrIS measured atmospheric spectra and a very fast Optimal Spectral Sampling (OSS) [Moncet et al., 2008] forward model simulated spectrum to retrieve atmospheric profiles of ammonia volume mixing ratios. This physical approach provides direct estimates of the retrieval errors and the vertical sensitivity (averaging kernels) of the satellite observations, which is important as they vary from profile-to-profile depending on the atmospheric state. To account for any *a priori* information used in the retrieval (i.e. observation operator) in air quality model comparisons and data assimilation into models, the CRPR provides the retrieved error covariance and averaging kernels. CrIS has been shown to retrieve ammonia surface concentrations values down to ~0.2-0.3 ppbv under favorable conditions [Kharol, et al., 2018]. CrIS comparisons with ground-based FTIR observations show a correlation of 0.77 with a low CrIS bias of +2% in the total column [Dammers et al., 2017]. Initial evaluation against surface observations from the Ammonia Monitoring Network (AMoN) show that even with the inherent sampling differences between the two surface observations they compare well with a correlation of 0.76 and an overall mean CrIS – AMoN difference of ~+15% [Kharol et al., 2018].

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

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

The CHIMERE runs used in this study were obtained in the framework of the Copernicus Atmospheric Monitoring Service (CAMS, <https://atmosphere.copernicus.eu/>), and its annual task devoted to the production of regional reanalysis over Europe. The hindcasts for year 2014 and 2015 (raw simulation without data assimilation) were produced over Europe with a horizontal resolution of 0.1° per 0.1° and 9 vertical levels stretched from the surface up to 500 hPa (~5000m). The input data to feed CHIMERE [Menut et al., 2013; Mailler et al., 2017] were the Integrated Forecasting System (IFS) meteorological data from European Centre for Medium-Range Weather Forecasts (ECMWF), the annual emission inventory provided by the Netherlands Organisation for Applied Scientific Research (TNO) [Kuenen et al., 2014] for year 2011. 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, including the regulated pollutants such as ozone, PM<sub>10</sub>, and NH<sub>3</sub>. The processes that will influence the NH<sub>3</sub> concentrations taken into consideration in CHIMERE are the dry deposition (following [Wesely et al., 1989] and wet deposition due to in-cloud process and precipitation. The gas-particulate phase equilibrium is computed with the ISOROPPIA module [Nenes et al, 1998] which is a thermodynamic equilibrium model for NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. It simulates the NH<sub>4</sub>NO<sub>3</sub> contribution to the particulate matter which is especially large during March-April pollution episodes [Petit et al., 2017].

These datasets were evaluated over Europe for several pollutants before being used for air quality studies (<http://policy.atmosphere.copernicus.eu/Reports.html>).

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

To evaluate the model capacity of reproducing NH<sub>3</sub> 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), NH<sub>3</sub> 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 NH<sub>3</sub> and PM<sub>2.5</sub> events in spring 2014 and 2015 (Figure S1). Thus, these years serve as benchmark to evaluate the model in terms of NH<sub>3</sub> variability and PM<sub>2.5</sub> formation at local and regional scales.

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

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

The purpose here of comparing CrIS and IASI is to assess qualitatively the spatiotemporal patterns of the NH<sub>3</sub> sources derived from the two datasets and use these regional observations to evaluate the CHIMERE model in the domain of analysis at the local time for their respective overpasses: 9:30 and 13:30. CHIMERE outputs, in terms of NH<sub>3</sub> concentrations, have already

been compared to the IASI observations at regional scale (Europe, [Fortems-Cheiney et al., 2016], and to surface measurements at local scale (Paris, [Petetin et al., 2016]), but have never been evaluated against the CrIS observations.

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

The standardized columns have been computed following equation 1:

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

Where  $(X^{data}) = \frac{1}{N} \sum_{i=1}^N X_i^{data}$ ,  $S(X^{data}) = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (X_i - \mu)^2}$ ,  $X^{data}$  corresponds to NH<sub>3</sub> columns derived from a dataset (IASI, CrIS, or CHIMERE), and  $X_{stand}^{data}$  is the corresponding standardized dataset.

In addition, to compare CHIMERE outputs with satellite data/columns, spatial and temporal coincidence criteria have been applied. To compare satellite observations, all CrIS pixels located within a 25-km radius circle from the center of the IASI ground pixels have been considered within the same day of measurements. A spatial criterion of 25 km has been chosen because it optimizes the number of pairs involved in the statistics and improves the correlations. As for the comparisons between the model and the observations: all CHIMERE outputs located within the same 0.15°x0.15° grid box than the satellite and within 1 hour from its measurement have been selected.

### 3. Results

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

### 3.1.1. Seasonal variabilities

First the seasonal variability was investigated over the IdF area. On a monthly basis, the 10-year and 5-year averaged regional  $\text{NH}_3$  total column distributions derived from IASI and CrIS were found to exhibit a high seasonality over the domain (Figures 2 and 3). Note that the distributions in Figures 2 and 3 have been obtained by averaging satellite  $\text{NH}_3$  observations in  $0.25^\circ \times 0.25^\circ$  grid boxes. Both satellite datasets exhibits the same variability over the domain even if the time period is different (10-years versus 5-years) and the sampling hour differs ( $\sim 9.30$  versus  $\sim 13.30$ ). It should be noted that CrIS and IASI  $\text{NH}_3$  columns present small differences in term of  $\text{NH}_3$  total columns in low concentration regimes in the domain of study.

In these figures (2 and 3) high  $\text{NH}_3$  concentrations (up to  $2.10^{16}$  molecules/ $\text{cm}^2$ ) can be observed from March to August at different locations of the domain:

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

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.

In the Champagne-Ardennes region, areas of hotspots do not correspond to vineyards but to field vegetables and root crops (<https://agriculture.gouv.fr/overview-french-agricultural-diversity>, and AGRESTE, Service Central d'Enquêtes et d'Études Statistiques, 2015 <http://agreste.agriculture.gouv.fr/IMG/pdf/R4215A15.pdf>). This is a main region of mineral fertilization used for sugar industry in France [Ramanantenasa et al., 2018]. Hamaoui-Laguel et al. (2014) and Fortems-Cheiney et al. (2016) have previously noted that  $\text{NH}_3$  emissions in this region, mainly due to fertilizer over barley, sugar beet, and potato starch in early March, were higher than what have been reported in the EMEP inventory.

$\text{NH}_3$  concentrations are high from April to August in the northern part of the domain that is known for its animal farming (Eurostat 2014, [http://ec.europa.eu/eurostat/statistics-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 Damme et al., 2014a; Scarlat et al., 2018 – their figure 2]).

In the Pays de la Loire,  $\text{NH}_3$  concentrations are high in April and August and remain relatively high from March to September. Hotspots are found in areas of livestock farming, mainly poultry

[Robinson et al., 2014 - their figure 2c], which might explain the high and relatively constant  $\text{NH}_3$  concentrations over warmer periods in this region.

### 3.1.2. Inter-annual variabilities

As can be seen in Figures 2 and 3,  $\text{NH}_3$  concentrations are enhanced between March and August in the domain. In this section, inter-annual variabilities are discussed regarding meteorological conditions and agricultural practices during this time period.

Inter-annual variability of  $\text{NH}_3$  is higher in springtime than in summer, e.g. in June the variance is 8 times lower than for the other months. To illustrate the inter-annual variability in springtime, maps of monthly mean  $\text{NH}_3$  total columns derived in March-April period from IASI (2008-2017 time period) and from CrIS (2013-2017 time period) are shown in Figure 4. Both satellite distributions exhibit the same inter-annual variability from 2013 to 2017 with higher  $\text{NH}_3$  concentrations in 2015 over the northern part of the domain than the other years.  $\text{NH}_3$  concentrations derived from IASI in 2011 are 150% higher in spring (March and April) compared to 2016 (Figure 4). It has been recently shown that spatial variability of  $\text{NH}_3$  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  $\text{NH}_3$  concentrations over the United-States are dominated by meteorological conditions [Schiferl et al., 2016]. Thus, inter-annual variability of observed  $\text{NH}_3$  total columns is likely to be driven by meteorological conditions and specific agricultural constrains (crop type and phenological stage for instance).

To investigate the impact of meteorological conditions on atmospheric  $\text{NH}_3$  variability, we computed the monthly mean anomalies of total precipitation versus skin temperature derived from ECMWF ERA-interim [Dee et al., 2011], color coded by  $\text{NH}_3$  total columns anomalies derived from IASI, as shown in Figure 5. Monthly mean anomaly is calculated with respect to the 10-year average data (in %). In this figure, monthly  $\text{NH}_3$  total columns are at least 10% higher (positive anomalies, red dots) when skin temperatures are higher and total precipitation are lower than the 10-year average. In contrast, negative monthly  $\text{NH}_3$  total columns anomalies (blue dots, Figure 5) are associated with higher total precipitation and lower skin temperatures than the 10-years average. To further examine the analyses, Figure 1 of the supplement information shows bar plots of monthly mean  $\text{NH}_3$  total columns derived from IASI, total precipitation and skin temperature derived from ECMWF from March to August, plotted in different colors for the different years of measurements from 2008 to 2017.  $\text{NH}_3$  total columns are larger by more than 300% in March-April 2012 compared to 2013 (Figure S2a). Total precipitation is higher (0.4 mm compared to 1 mm, Figure S2b) and skin temperature is lower (281 compared to 288 K, Figure S2c) in March 2013 than in March 2012 on average over the domain. Overall, total precipitation is anti-correlated with  $\text{NH}_3$  concentrations in the

atmosphere ( $R = -0.52$  from March to May for all years, not shown here) likely because of a) the wet deposition importance in the atmospheric  $\text{NH}_3$  removal and b) the absence of fertilization during rainy periods. Skin temperature is relatively correlated with  $\text{NH}_3$  concentrations ( $R = 0.30$  from March to May for all years) since higher temperature increases volatilization of  $\text{NH}_3$  from the surface to the atmosphere.

In addition,  $\text{NH}_3$  concentration is maximum in March 2011 whereas it peaks later in April for 2012 (Figure S2a). Springtime is a fertilizer application period depending on many agricultural and meteorological constrains. When the temperatures are relatively lower as in the case of 2012 (Figure S2b), fertilizer spreading may occur sooner because the phenological growth stage might be more advanced. Fertilizing process period also varies in function of the sowing date which depends on agricultural practices and crop types: corn is fertilized in early spring whereas rapeseed is in late spring.

Overall, our results suggest that variability in meteorological (precipitation and temperature) and farming practices (fertilizer and manure applications) may play an important role in driving the large inter-annual variability in  $\text{NH}_3$  column observed by IASI and CrIS in the domain of study.

### 3.2. Comparisons of $\text{NH}_3$ columns derived from IASI, CrIS, and CHIMERE for 2014 and 2015

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

#### 3.2.1. Annual cycle

Standardized monthly mean concentrations derived from IASI, CrIS, and CHIMERE for 2014 and 2015 are shown in Figure 6.

As can be seen from the plot, the 3 datasets exhibit similar patterns in terms of seasonality: all are enhanced in March-April and in summer, and show a decrease in May. However two major differences can be noted.

First, CrIS standardized  $\text{NH}_3$  columns are higher in winter (November, December, and January) compared to the other dataset which can be also be seen in Figure 3. This could be attributed to a higher number of outliers, given the larger standard deviation (shaded areas, Figure 6) and no attempt to account for potential non-detects when concentrations fall below the instrument detection limits. For these months,  $\text{NH}_3$  levels are low and undetectable by satellite observations (Figures 2 and 3) so these high values could be interpreted as observational noise.

The detection limit depends on the instrument characteristics and atmospheric state, with IASI minimum detection limit of  $\sim 2\text{--}3$  ppbv ( $\sim 4\text{--}6 \cdot 10^{15}$  molecules.cm<sup>-2</sup>) [Clarisse et al., 2010] and CrIS  $\sim 0.5\text{--}1.0$  ppbv ( $\sim 1\text{--}2 \cdot 10^{15}$  molecules.cm<sup>-2</sup>) [Shephard and Cady-Pereira, 2015; Kharol et. al., 2018]. 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 $\leq 0.1$  (Section 2.2.2) favors larger observed columns. Consequently, the normalized seasonal cycle amplitude derived from CrIS is weaker than the IASI one.

Second, the CHIMERE standardized NH<sub>3</sub> columns are enhanced in September 2014, which is not supported by the observations. It has been recently shown that CHIMERE overestimated NH<sub>3</sub> emissions in autumn over Europe [Couvidat et al., 2018]. Generally, the amplitude of the modelled seasonal cycle exceeds the measured ones, which could be explained by higher concentrations measured in winter due to the observational noise and lower emissions. 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.

Over the whole period, the coefficient of determination ( $r^2$ ) between the standardized monthly mean NH<sub>3</sub> 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 ( $p < 0.1$ ) reflecting the significance level of the fits (not shown here). If we only consider months of high NH<sub>3</sub> in the domain from March to August, the correlation between the observational datasets and the model results is weaker with  $r^2$  values between IASI (CrIS) and CHIMERE of 0.29 (0.14) and is not significant ( $p > 0.1$ ) against CrIS, 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 inter-annual variability is likely to be attributed to meteorological conditions changes. However, the values of the  $r^2$  lower than 0.6 (0.2) indicate that the CHIMERE model only reproduces at most half (20%) of the monthly temporal NH<sub>3</sub> variabilities observed by IASI (CrIS) in the domain.

### 3.2.2. Spatial variability of NH<sub>3</sub> in springtime

The IASI and CrIS regional maps have been compared to the CHIMERE model for the March-April period in 2014 and 2015 to evaluate the model's capacity to reproduce the spatial distribution of the episodic emissions from fertilizer spreading practices in springtime, as well as their inter-annual variability. Satellite NH<sub>3</sub> measurements in springtime have been gridded at  $0.15^\circ \times 0.15^\circ$  spatial resolution, and the associated CHIMERE maps have been computed following the coincident criteria described in section 2.4 at the same spatial resolution (Figures 8 and 9).

It can be noted that the spatial distribution of  $\text{NH}_3$  observed in springtime by both satellite instruments are in good agreement, even though their overpass time is different (~4 hours apart). This was already seen in the inter-annual variability agreement seen in Figure 4. In spring 2014, IASI and CrIS both reveal three main regions of enhanced  $\text{NH}_3$  concentrations (North, Champagne-Ardenne, and Brittany/Pays de la Loire region) already identified by the 10-years and 5-years of IASI and CrIS observation maps (Boxes A, B, and C of Figures 2 and 3). In 2015, concentrations of  $\text{NH}_3$  in the northern part of the domain are higher than in 2014, as indicated by both IASI and CrIS observations (Figure 9, upper panels). Overall, satellite observations are able to capture similar spatial distributions of high  $\text{NH}_3$  concentrations in springtime, and their evolution in time.

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

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

Finally, the (model - observations) differences between the standardized  $\text{NH}_3$  column derived from the satellite instruments in springtime 2014-2015 and the corresponding  $\text{NH}_3$  columns derived from the CHIMERE model are shown in Figure 2 of the supplement information. One can see that very similar patterns are presented when comparing the model to independent satellite observations from IASI and CrIS: the modelled  $\text{NH}_3$  concentrations are systematically lower for both years over Belgium and United Kingdom, and higher in the southern part of the domain (green square, Figure S3) including the Pays de la Loire region (box C in Figures 2 and 3), and in the southeastern part of the domain (over the North part of Switzerland and the Plateau du Jura region - between Besancon and Lyon cities – blue box in Figure 8). Reasons of enhanced  $\text{NH}_3$  columns derived from the model in this latter region are not clear yet. An explanation could be that the temporal distribution of the emissions is misrepresented in the model since the modelled concentrations are enhanced in April whereas the two satellite observations are enhanced earlier in March for both years. It is worth noting that there are no EMEP stations measuring surface  $\text{NH}_3$  concentrations in these regions. As for the Brittany/Pays de la Loire region, it has already been shown that the LOTOS-EUROS atmospheric model [Schaap et al.,

2008] using similar chemistry schemes and NH<sub>3</sub> emissions shows higher columns each year in this area [Van Damme et al., 2014b].

### 3.3. Comparisons of PM<sub>2.5</sub> concentrations in IdF derived from the Airparif network and CHIMERE for 2014 and 2015

To evaluate the model capacity to reproduce PM<sub>2.5</sub> concentrations over the Parisian region, comparisons between the Airparif measurements network and the CHIMERE outputs are performed for 2014 and 2015 (Figure 11). For those years, concentrations of PM<sub>2.5</sub> 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 PM<sub>2.5</sub> 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 PM<sub>2.5</sub> 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 PM<sub>2.5</sub> concentrations in spring due to unknown PM<sub>2.5</sub> formation processes, but overestimate them in winter which could be due to uncertainties on NH<sub>3</sub> emissions from wood burning processes. Overall, good agreement is found between the measurements and the model in term of PM<sub>2.5</sub> concentrations over the IdF region given values of  $r^2$  of 0.56 (associated with  $p < 0.05$ ), a slope of  $0.67 \pm 3.51$ , with a slight underestimation of the CHIMERE model given a normalized mean bias (calculated as model-observations/observations) of -18% over 2014 and 2015.

### 3.4. Conditions for PM formation in the Paris megacity

To investigate the impact of intensive agriculture practices on the Paris megacity air quality, we need to better understand the role of NH<sub>3</sub> in the formation of PM<sub>2.5</sub>. This process depends, among others, on specific meteorological conditions such as atmospheric temperature and humidity that alter the gas-particle partitioning. The link between high NH<sub>3</sub> concentrations inducing PM<sub>2.5</sub> formation in the Paris megacity is known [Petetin et al., 2016; Zhang et al., 2013] but quantification of such phenomena is difficult due the lack of long-term NH<sub>3</sub> monitoring in the IdF region. PM<sub>2.5</sub> is however measured hourly at several locations in Paris by the Airparif network (<https://www.airparif.asso.fr/>, Figure 1). Using the 10-years of IASI observations, an observational evidence of PM<sub>2.5</sub> formation in the IdF region (100 km around Paris - black box in Figure 1) is represented in Figure S4. Simultaneous enhancements in March of PM<sub>2.5</sub> measured at the surface and NH<sub>3</sub> columns derived from the IASI observations over the IdF region are clearly visible. However, high concentrations of NH<sub>3</sub> observed in summer are not associated with high PM<sub>2.5</sub> concentrations. This reflects the complexity of the PM<sub>2.5</sub> formation depending on various factors, such as NH<sub>3</sub> emissions, atmospheric chemistry (acidic content of the

atmosphere), transport, and specific meteorological conditions involved in the gas to solid phase conversion between  $\text{NH}_3$  and ammonium salts.

To evaluate the impact of long-range transport on  $\text{NH}_3$  levels observed over the Parisian region (IdF) in spring, back-trajectory analysis was performed. In total 231 24-hours back-trajectories ending in Paris (period from February 15<sup>th</sup> to May 15<sup>th</sup> from 2013 to 2016) were classified into 8 clusters using HYSPLIT (<https://ready.arl.noaa.gov/HYSPLIT.php>). Figure 10 shows the mean trajectories for each cluster associated with the average  $\text{NH}_3$  total columns measured by IASI over the IdF region. In this figure, higher  $\text{NH}_3$  columns are found under the influence of air masses transported from the northern part of the domain (over Belgium and the Netherlands, clusters 4 and 5) and from the Brittany region (cluster 8), which are the major sources regions of  $\text{NH}_3$  in spring in the domain as previously identified (Figures 2 and 3). Indeed,  $\text{NH}_3$  columns over the Netherlands are significantly correlated (at the 95% confidential level) to  $\text{NH}_3$  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). Clusters 2 and 3 (Figure 10) are associated with intermediate  $\text{NH}_3$  levels since air masses moved slowly transporting  $\text{NH}_3$ -rich air from rural regions near IdF (such as the Champagne-Ardennes region - Box A in Figures 2 and 3) to Paris. Finally, low  $\text{NH}_3$  concentrations are measured when air masses originated from ocean regions passing through continental areas with minor  $\text{NH}_3$  sources in spring (clusters 1, 6 and 7, Figure 10). This reflects the importance of long-range transport in the  $\text{NH}_3$  budget observed over the Paris megacity in spring.

To quantitatively assess the influence of meteorological parameters on the formation of  $\text{PM}_{2.5}$  from  $\text{NH}_3$  in the IdF region, timeseries of  $\text{NH}_3$  total columns,  $\text{PM}_{2.5}$  surface concentrations, and five meteorological parameters (temperature at 2 m, boundary layer height, total precipitation, relative humidity, and wind field) derived from ECMWF - ERA-5 [Dee et al., 2011, Copernicus Climate Change Service (C3S), 2017] were analyzed. To compute daily and monthly means, IASI  $\text{NH}_3$  total columns have been averaged over IdF (black box in Figure 1),  $\text{PM}_{2.5}$  concentrations measured between 9 AM and 11 AM have been averaged over the 14 stations (dark points in Figure 1), and ECMWF data have been averaged over a 300 km region around Paris (the blue box in Figure 1). Figure 12 shows all these parameters for spring 2014.

We have flagged pollution episodes in both time series ( $\text{PM}_{2.5}$  and  $\text{NH}_3$ ) by selecting data above 1-sigma standard deviation over the mean of the datasets from 2013 to 2016. This time period was selected to have the most IASI observations (combining Metop-A and B) in the IdF region. Then two cases have been defined to study the temporal correlation between  $\text{NH}_3$  and  $\text{PM}_{2.5}$ : case A in which both  $\text{NH}_3$  and  $\text{PM}_{2.5}$  pollution episodes appear simultaneously, i.e. within the same day or 2 days apart (shaded in red in Figure 12); and case B in which pollution episodes appear at least 3 days apart (shaded in blue in Figure 12). In Figure 12, a strong relationship

between peaks of  $\text{NH}_3$ ,  $\text{PM}_{2.5}$  and meteorological parameters can be seen. For example, between 3 and 19 March 2014 (case A), the boundary layer height is exceptionally low (456 m; compared to 760 m on average); the temperature is relatively low (280 K; 282 K on average); and there is no precipitation (0.01 mm/h; 0.11 mm/h on average). One note that peaks of maximum  $\text{NH}_3$  observed in IdF on 11 and 12 March are associated with air masses coming from the northern part of the domain (clusters 4 and 5 in Figure 10). In contrast, for the case B in which appearance of peaks of  $\text{NH}_3$  and  $\text{PM}_{2.5}$  is not simultaneous, meteorological conditions are different: the boundary layer is thicker (908 m on 23 April 2014), or temperature is higher (285 K on 11 April 2014).

To further investigate the influence of meteorological parameters on the pollution episodes in the IdF region, detailed analysis has been made for the study period. Figure 13 shows the statistical distribution of meteorological parameters corresponding to case A, case B, and all observations. It should be noted that for the study period the boundary layer height is significantly ( $p < 0.01$ ) lower in case A ( $550 \pm 205$  m) than in case B ( $751 \pm 276$  m), and that precipitation is absent in case A (0.019 mm/h) compared to case B (0.085 mm/h). The temperature at 2 meters also differs between the two cases (case A:  $278 \pm 3$  K; case B:  $282 \pm 4$  K), but the humidity is almost the same ( $70\% \pm 17\%$  versus  $75\% \pm 18\%$ ). Results also suggest that simultaneous enhancements of  $\text{NH}_3$  and  $\text{PM}_{2.5}$  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  $\text{NH}_3$  and of  $\text{PM}_{2.5}$  in Paris (i.e. case A): low surface temperatures ( $5^\circ\text{C}$ ), with thin boundary layers ( $\sim 500\text{m}$ ), almost no precipitation, and northeast wind. In addition, the Wilcoxon-Mann-Whitney test ([Wilks, 2011], not shown here) indicates that each single parameter has no significant influence on the  $\text{NH}_3$ - $\text{PM}_{2.5}$  correlation. Therefore only a combination of these different parameters has an impact on secondary aerosol formation from  $\text{NH}_3$ .

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

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  $\text{NH}_4\text{NO}_3$  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  $\text{PM}_{2.5}$  formation in particular since the phase equilibrium leads to  $\text{NH}_4\text{NO}_3$  decomposition above 30 °C.

#### 4. Conclusions

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

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

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

Focusing on the Ile-de-France (IdF, 100 km around Paris) region, we found that air masses originated from rich- $\text{NH}_3$  areas, mainly the northern part of the domain over Belgium and the Netherlands, increase the observed  $\text{NH}_3$  total columns measured by IASI over the urban area of Paris. In this region, we also found that the CHIMERE model is able to reproduce the day-to-day variability of  $\text{PM}_{2.5}$  concentrations ( $r^2$  of 0.56), with however an underestimation during spring pollution events, which could be due to unknown secondary aerosol formation processes.

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

with the presence of atmospheric NH<sub>3</sub> in the IdF region. Based on a more observational approach over large time scale, this work is in agreement with previous studies.

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

#### Code and data availability:

The near-real-time IASI NH<sub>3</sub> (ANNI NH3-v2.1R) data used in this study are freely available through the AERIS database <https://iasi.aeris-data.fr/nh3r-i/> (last access: 03 December 2019). The CrIS data and CHIMERE outputs are currently available upon request. All Matlab codes used to create any of the figures and/or to create the underlying data are available on request.

#### Author contribution:

CV wrote the paper with contributions of all coauthors. CV and CC designed the study. MV, LC, and SW performed IASI retrievals and ED, MWS, and KEC performed the CrIS retrievals. FM ran the CHIMERE simulations. CV and TW analyzed the data with guidance from CC and PFC. All authors discussed the results and contributed to the final paper.

#### Competing interests:

The authors declare that they have no conflict of interest.

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## FIGURES

Figure 1: Region of analysis: 400 km radius-circle around the Paris megacity and 100 km around Paris. The latter is representative of the Ile-de-France (IdF) region where the Airparif PM observational network is located. Black points are the locations of the Airparif stations measuring hourly  $\text{PM}_{2.5}$  concentration at the surface. The black (blue) box delimitates the IdF region in which the IASI  $\text{NH}_3$  (ECMWF) data have been considered. The overlay represents  $\text{NH}_3$  emissions (in Mg per year and per cell of  $0.1^\circ \times 0.1^\circ$ ) derived from the EMEP inventory for 2015. Map provided by GOOGLE EARTH V7.3.2.5776, US Dept. of State Geographer, ©Google, 2019, Image Landsat/Copernicus, Data SIO, NOAA, US, Navy, NGA, and GEBCO.

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

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

Figure 4: Maps of monthly mean  $\text{NH}_3$  total columns ( $\text{molecules/cm}^2$ ) in March-April period derived from IASI from 2008 to 2017 and CrIS from 2013 to 2017.

Figure 5: Scatter plot of monthly mean anomaly (relative to the 10-years – 2008 to 2017 - monthly average) of total precipitation versus skin temperature derived from ECMWF from March to August in the domain, and color coded by the  $\text{NH}_3$  total columns anomaly derived from IASI.

Figure 6: Standardized monthly mean concentrations derived from IASI (red), CrIS (black), CHIMERE sampled at IASI overpass time and space (blue) and CHIMERE sample at CrIS overpass time and space (cyan) for 2014 and 2015. Shaded areas correspond to the one-sigma standard deviation around the means.

Figure 7: Correlation plots between monthly means  $\text{NH}_3$  standardized concentrations derived from satellite observations (IASI in red and CrIS in black) and the CHIMERE outputs for the March to August months of 2014 and 2015. The 1:1 line is represented in the dashed line. Error bars represent the one-sigma standard deviation around the monthly means.

Figure 8: Standardized  $\text{NH}_3$  column derived from the satellite instruments (IASI = top left panel, and CrIS = top right panel) and the corresponding  $\text{NH}_3$  column derived from the CHIMERE model (coincident with IASI – bottom left panel, and coincident with CrIS – bottom right panel) for March-April 2014. Blue dots indicate Paris location. Figure 9: Same as Figure 7 but for March-April 2015.

Figure 10: Cluster analysis of 24-h backward trajectories arriving in spring in Paris (from February 15<sup>th</sup> to May 15<sup>th</sup> for the 2013-2016 period) using HYSPLIT-4 model obtained from the NOAA Air Resources Laboratory. Mean trajectories of the 8 clusters are shown in different colors, associated with the  $\text{NH}_3$  concentrations measured by IASI in the IdF region (in molecules/cm<sup>2</sup>).

Figure 11: Comparison between  $\text{PM}_{2.5}$  concentrations derived from the Airparif network and the CHIMERE model outputs. Left panel: time series of the daily mean  $\text{PM}_{2.5}$  concentrations (in  $\mu\text{g}/\text{m}^3$ ) observed at the surface with the Airparif network (red) and calculated with the CHIMERE model (black), associated with relative differences (in %) calculated as model-observations for 2014 and 2015. Right panel: correlation plots between daily mean  $\text{PM}_{2.5}$  concentrations derived from the CHIMERE model versus the Airparif network.

Figure 12: Average concentrations of  $\text{NH}_3$  total columns derived from IASI (in molecules/cm<sup>2</sup>; orange, upper panel) and  $\text{PM}_{2.5}$  derived from the Airparif network selected within 2 hours from the IASI overpass (in  $\mu\text{g}/\text{m}^3$ ; red, upper panel) for 2014 as example. Periods of simultaneous (independent) enhancements of  $\text{NH}_3$  and PM concentrations are represented with red (blue) areas, i.e. case A (case B). Temperature at 2 meters (in Kelvin; green, upper middle panel), boundary layer height (in meter; blue, upper middle panel), precipitation (in meter; dark blue, lower middle panel), relative humidity (in percent; purple, lower middle panel), and wind speed and directions (lower panel) derived from the ECMWF ERA-5.

Figure 13: Statistical distributions of meteorological parameters corresponding to case A (in which both  $\text{NH}_3$  and  $\text{PM}_{2.5}$  pollution episodes appear simultaneously, i.e. within the same day or 2 days apart), case B (in which pollution episodes appear at least 3 days apart), and all

1006 observations derived from 2013 to 2016. The number of observations (days) are 63 in case A,  
1007 154 in case B and 481 for the ensemble. The medians and the quartiles are presented by center  
1008 lines and borders of the boxes, respectively. The mean values are indicated by red points, and  
1009 the extreme values (i.e. those beyond  $Q1 - 1.5 \text{ IQR}$  and  $Q3 + 1.5 \text{ IQR}$ ) by black points. The IQR is  
1010 the "interquartile range", and it equals to  $Q3 - Q1$  where  $Q3$  and  $Q1$  are the 75<sup>th</sup> and 25<sup>th</sup>  
1011 percentiles. Setting the thresholds at  $Q1 - 1.5 * \text{IQR}$  and  $Q3 + 1.5 * \text{IQR}$  is a common practice to  
1012 determine outliers.

1013

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 (unapodized)	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.

1014 Table 1: Instrumental specifications for the IASI and CrIS satellite instruments.