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1 **NH₃ spatio-temporal variability over Paris, Mexico and Toronto and its link to**
2 **PM_{2.5} during pollution events**

3

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16 **Abstract**

17 Megacities can experience high levels of fine particulate matter ($PM_{2.5}$) pollution linked to ammonia
18 (NH_3) mainly emitted from agricultural activities. Here, we investigate such pollution in the cities of
19 Paris, Mexico and Toronto, each of which have distinct emission sources, agricultural regulations, and
20 topography. Ten years of measurements from the Infrared Atmospheric Sounding Interferometer
21 (IASI) are used to assess the spatio-temporal NH_3 variability over and around the three cities.

22 In Europe and North America, we determine that temperature is associated with the increase in NH_3
23 atmospheric concentrations with coefficient of determination (r^2) of 0.8 over agricultural areas. The
24 variety of the NH_3 sources (industry and agricultural) and the weaker temperature seasonal cycle in
25 southern North America induce a lower correlation factor ($r^2 = 0.5$). The three regions are subject to
26 long range transport of NH_3 , as shown using HYSPLIT cluster back-trajectories. The highest NH_3
27 concentrations measured at the city scales are associated with air masses coming from the
28 surrounding and north-northeast regions of Paris, the south-southwest areas of Toronto, and the
29 southeast/southwest zones of Mexico City.

30 Using NH_3 and $PM_{2.5}$ measurements derived from IASI and surface observations from 2008 to 2017,
31 annually frequent pollution events are identified in the 3 cities. Wind roses reveal statistical patterns
32 during these pollution events with dominant northeast-southwest directions in Paris and Mexico
33 cities, and the transboundary transport of pollutants from the United-States in Toronto. To check
34 how well chemistry transport models perform during pollution events, we evaluate simulations made
35 using the GEOS-Chem model for March 2011. In these simulations we find that NH_3 concentrations
36 are overall underestimated, though day-to-day variability is well represented. $PM_{2.5}$ is generally
37 underestimated over Paris and Mexico, but overestimated over Toronto.



38 1. Introduction

39 Paris, Toronto, and Mexico City are cities with over 2 million inhabitants. When their larger
40 metropolitan regions are included, their populations are 10.5 million for Paris (the most populous
41 area in the European Union), 6.5 million for Toronto (the fourth most populous city in North
42 America) and 9.2 million for Mexico City (most populous city in North America). These cities typically
43 experience strong particulate matter (PM) pollution episodes. Exposure to such particles is harmful
44 to humans and can lead to cardiovascular and respiratory diseases [Murray et al., 2020].

45 A large proportion of the particles' composition is ammonium sulfate and nitrate, which are formed
46 from ammonia (NH₃) [Behera et al., 2013] released in the atmosphere from e.g., fertilizer spreading
47 practices and both transported to cities, reducing the quality of urban air [Pope et al., 2009]. The
48 agricultural sector represents 94%, 90%, and 94% of total NH₃ emissions in France [CITEPA, 2018],
49 Canada [ECCC, 2017] and Mexico [INECC and SEMARNAT, 2018], respectively. NH₃ is the most poorly
50 understood precursor of PM_{2.5} (PM with a diameter less than 2.5 µm), primarily because
51 measurements are difficult [von Bobritzki et al., 2010], sparse, and due to low ambient NH₃
52 concentrations and episodic emissions. Worldwide, only five countries have included NH₃
53 concentrations routine measurements in their air quality monitoring networks [Nair and Yu, 2020].

54 NH₃ emissions are associated with very high uncertainties in all inventories (186% to 294%
55 uncertainties in EDGAR [McDuffie et al., 2020; Van Damme et al., 2018]) due to uncertainties in the
56 reporting of agricultural statistics and emission factors that depend on individual agricultural
57 practices, biological processes, and environmental conditions [Paulot et al., 2014], as well as political
58 disturbances and land-use change [Abeed et al., 2021]. The evaporation of NH₃ in the atmosphere, as
59 well as its transformation into particulate matter, is highly dependent on the thermodynamic
60 conditions of the atmosphere [Sutton et al., 2013]. All these parameters account for the complexity
61 of reproducing NH₃ concentrations in atmospheric models, predicting the associated PM_{2.5} pollution,
62 and, ultimately, implementing relevant regulations to reduce its emissions.

63 Given the crucial role that NH₃ plays in environmental and public health problems, reducing its
64 emissions will therefore be a major challenge. However, NH₃ concentrations are increasing in all of
65 three regions, with a country wide increase of $24 \pm 11\%$, $16.4 \pm 8.6\%$, and $8.4 \pm 5.2\%$ between 2008
66 and 2018 in France, Canada, and Mexico, respectively [Van Damme et al., 2021].

67 In Paris, PM_{2.5} are composed with organic matter (38–47 %), nitrate (17–22 %), non-sea-salt sulfate
68 (13–16 %), ammonium (10–12 %), and to a minor extend with elemental carbon, mineral dust (2–5
69 %) and sea salt [Bressi et al., 2013]. In springtime, it has been shown that NH₃ plays a significant role
70 in PM_{2.5} pollution episodes [Viatte et al., 2021] but long-term observations are needed to properly
71 evaluate the impact of NH₃ to PM_{2.5} formation.

72 In Toronto, secondary nitrate formed with nitric acids (NO_x) and NH₃ account for 36% of the PM_{2.5}
73 sources [Lee et al., 2003] and ammonium nitrate and sulfate accounted for 20–30% of annual PM_{2.5}
74 mass over the 14-year period between 2006 and 2014 [Jeong et al., 2020]. There is a need for a
75 higher number of surface observations to evaluate the NH₃-PM_{2.5} relationship and its evolution over
76 time [Larios et al., 2018].

77 In Mexico, PM_{2.5} concentrations often exceed the standard of 65 µg/m³ [Moya and Huey, 2007;
78 INECC and SEMARNAT, 2018]. Secondary inorganic aerosols account for 30% of the chemical
79 composition of PM_{2.5}, which are dominated by ammonium sulfate with an average of 14% [Vega et
80 al., 2010]. A better understanding of the particulate pollutants processes in Mexico is still needed
81 [Ojeda-Castillo et al., 2019].



To assess the role of NH_3 in the formation of particulate matter, the AmmonAQ (Ammonia air quality) project was designed to quantify NH_3 spatio-temporal variabilities in regional domains around these three cities. The main objective of this project is to determine the impact of intensive agricultural practices on NH_3 and urban air quality, with a focus on Paris, Toronto and Mexico as benchmark case studies. A schematic representation of the AmmonAQ project and the domains of study are shown in Figure 1. The so-called “Europe”, “North America”, and “southern North America” domains represent the extended area with NH_3 sources that can impact on the Paris, Toronto, and Mexico cities air composition. The three cities are investigated with the use of different datasets: satellite measurements and model simulation data, and surface measurements when available (see section 2).

These cities have been chosen as the focus of this study because of the availability of NH_3 and $\text{PM}_{2.5}$ measurements. These three cities differ in terms of:

1. The regulation of NH_3 emissions: French policies aim to reduce NH_3 emissions by 13% in 2030 relative to 2005 [CEIP, 2016] following EU ratification of the Gothenburg Protocol in 2017, whereas in Canada and Mexico there are no federal regulations for NH_3 emissions yet [Bittman et al., 2017];
2. Agricultural practices affecting NH_3 emissions differ in each region as farmers depend on meteorological conditions for fertilizer use;
3. Meteorological/climate conditions are very different in each of the regions: drier winter and wetter summer in Toronto compared to Paris, and weak winds and strong temperature inversions in Mexico-city. This influences the NH_3 lifetime and chemistry leading to the formation of $\text{PM}_{2.5}$;
4. Topography: Toronto is adjacent to Lake Ontario, Paris is inland, and Mexico-city is a basin surrounded by mountains. This will impact the trajectories of air masses.

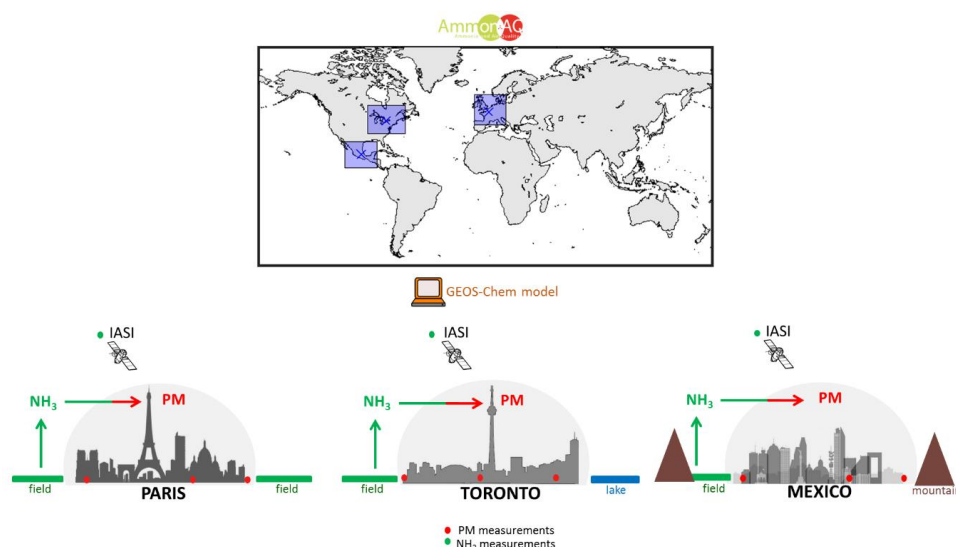


Figure 1: schematic representation of the AmmonAQ project. Upper panel: the three study regions investigated (in blue rectangles). Lower panel: presentation of each city and regional domain and different datasets used.



110 2. Methodology

111 2.1. NH₃ observations derived from IASI

112 The Infrared Atmospheric Sounding Interferometer (IASI) was launched onboard the Metop-A/B/C
113 satellites in 2006, 2012, and 2018, respectively [Clerbaux et al., 2009]. IASI provides twice daily total
114 column measurements of NH₃ globally at 9:30 and 21:30 local solar time. With its polar orbit and a
115 swath of 2400 km, IASI pixel size is 12 km in diameter at nadir. In this work, we use version 3 of the
116 ANNI-NH₃ product [Van Damme et al., 2021; Guo et al., 2021] from IASI Metop-A/B morning
117 overpasses over the period 2008 to 2017.

118 2.2. PM_{2.5} dataset derived from surface network measurements

119 To study local scale PM_{2.5} pollution events in the Paris, Toronto, and Mexico cities, PM_{2.5} observations
120 of surface concentrations from 2008 to 2017 are used.

121 For Paris, we use hourly observations of PM_{2.5} concentrations derived from fourteen stations of the
122 Airparif network (<https://data-airparif-asso.opendata.arcgis.com/>). For Toronto, we analyze hourly
123 PM_{2.5} observations derived from eleven stations supported by the Ministry of the Environment,
124 Conservation and Parks of Ontario (<http://www.airqualityontario.com/>). For Mexico, PM_{2.5}
125 concentrations are derived from 27 stations of the Red Automática de Monitoreo Atmosférico
126 (RAMA, <http://www.aire.cdmx.gob.mx/default.php?opc=%27aKBh%27>) network.

127 All these stations are located in a 50-km radius-circle around the city centers of Paris, Toronto, and
128 Mexico City.

129 2.3. NH₃ and PM_{2.5} from the GEOS-Chem model

130 We generate model outputs for March of 2011 using version 12.7.2 of the GEOS-Chem chemical
131 transport model [Bey et al., 2001] driven by the MERRA-2 reanalysis product, including nested
132 domains over Europe and North America at a 0.5° × 0.625° horizontal resolution from which we
133 extract modeled surface values for each city. Boundary conditions for these two nested domains are
134 created using a global simulation for the same months at 2° × 2.5° resolution. Output for the
135 analyzed month of March includes monthly means, as well as hourly means for selected diagnostics,
136 and is preceded by two months of discarded model spinup time for the global simulation, and one
137 month for each nested run. Anthropogenic emissions are taken primarily from the global Community
138 Emissions Data System (CEDS) inventory [Hoesly et al., 2018], with regional emissions from the 2011
139 National Emissions Inventory produced by the US EPA (NEI2011) used to override global values over
140 the United States. Biogenic non-agricultural ammonia, as well as ocean ammonia sources, are taken
141 from the Global Emission Inventories Activities database (GEIA, [Bouwman et al., 1997]). Open fire
142 emissions are generated using the GFED 4.1s inventory [Randerson et al., 2017]. Sulfate-nitrate-
143 ammonium aerosol processes are calculated using version 2.2 of the ISORROPIA thermodynamic
144 module [Fountoukis and Nenes, 2007]. Black carbon is handled as described in Wang et al. (2014),
145 while secondary organic aerosol is produced using the simplified irreversible scheme described in Pai
146 et al., (2020).

147 2.4. Back-trajectories analysis from the HYSPLIT model

148 To determine the effect of long-range transport affecting the local air quality of the three cities, we
149 use the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT, [Stein et al., 2015]).
150 One note that unlike the GEOS-Chem model, HYSPLIT does not include atmospheric chemistry. For
151 the runs, meteorological data are from the National Centers for Environmental Prediction (NCEP) /



National Center for Atmospheric Research (NCAR) reanalysis at 2.5-degree global latitude-longitude projection. First, we run daily 24-hours back-trajectories ending in the city-centers at the overpass time of the IASI instrument covering the period 2008 to 2017. Then, for each day we calculate the mean of NH_3 total columns derived from IASI observations in a 50-km radius circle around the cities associated with each back-trajectory. Finally, every back-trajectory are combined in clusters and associated with the corresponding local-scale IASI NH_3 concentrations.

2.5. ERA-5 meteorological data

The meteorological variables used in this study are extracted from the hourly ECMWF's reanalysis (ERA5, [Hersbach et al., 2020]). ERA5 data are at $0.25^\circ \times 0.25^\circ$ resolution (native horizontal resolution of ERA5 is $\sim 31\text{km}$) and are interpolated in time and space to the IASI observation. The meteorological parameters considered here are the skin temperature (T_{skin} , which is the physical temperature of the Earth's surface), total precipitation (in meter of water equivalent - accumulated liquid and frozen water, comprising rain and snow -) and relative humidity up to 2 meters above the surface calculated from dew and air temperature at 2m from ERA5.

3. Results

3.1. NH_3 source regions identification and spatio-temporal variability over the Europe, North America, and southern North America domains

Using 10-years of IASI observations, the main source regions of NH_3 in the 3 domains of study are identified (Figure 2) and listed in Table 1. We identify 10, 9, and 19 NH_3 source regions over the Europe, North America, and southern North America regions, respectively. All of the sources over the Europe, North America domains are mostly related to agricultural practices (farming and spreading practices). This is in agreement with previous calculation of worldwide nitrogen inputs from fertilizer and manure [Potter et al., 2010]. Around southern North America, three sources are related to fertilizer or soda ash industries (listed with C, G, O in Figure 2 and Table 1, [Van Damme et al., 2018]), the rest is agricultural.

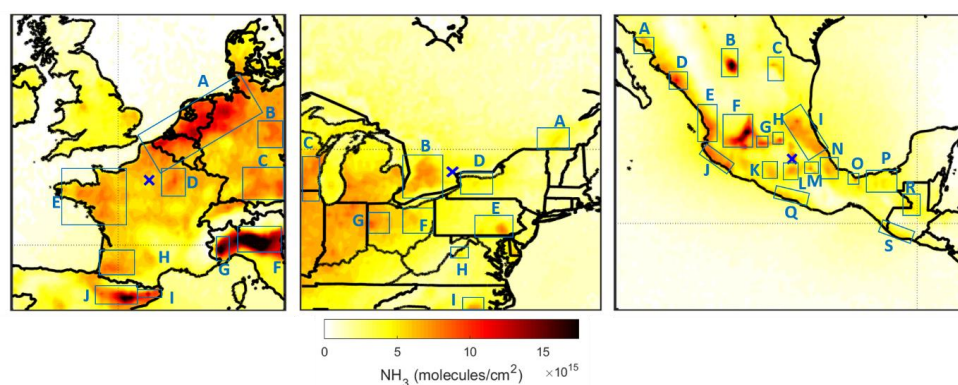


Figure 2: Source region identification of NH_3 derived from 10 years average of IASI total columns (molecules/cm^2) from 2008 to 2017. The blue crosses indicate Paris, Toronto, and Mexico cities locations.

Spatio-temporal variabilities of NH_3 in the atmosphere in the three regions (Figure 2) are not expected to be similar: NH_3 emissions from industries in the region of southern North America are released all year long, whereas NH_3 emissions from agricultural practices (i.e. major over Europe and North America), depend on various surface and meteorological conditions. In order to investigate



184 this, NH_3 concentrations using 10-years of IASI observations are assessed against atmospheric
185 temperature and precipitation derived from the ERA5 reanalysis over the three domains in Figure 3.
186 It shows the seasonal evolution of NH_3 from IASI over the three regions (left panel), along with the
187 seasonal evolution of temperature and precipitation (right panel).

188 Table 1: List of NH_3 source regions identified using 10-years average of IASI total columns (molecules/ cm^2) over
189 the Europe, North America, and southern North America regions.

Europe [41°-59°N ; -11.25°- 16.25°E]		North America [35°-53°N ; 93.75°-63.75°W]		Southern North America [9°-29°N ; 113.75°-86.25°W]	
A	The North-European plain ^{1,2}	A	Granby	A	Obregon (Mexico) ¹
B	Saxe Anhalt plain (Germany)	B	Elmira-Kitchener-Guelph	B	Torreon (Mexico) ^{1,2}
C	Munich - Mangfall (Germany)	C	Brillion area	C	Garcia (Mexico) ^{**1}
D	Champagne-Ardenne (France)	D	New-York state	D	Culiacancito (Mexico) ^{1,2}
E	Bretany-Pays de la Loire (France) ²	E	Lancaster county	E	Nayarit (Mexico)
F	Pô Valley (Italy) ^{1,2}	F	Wayne county	F	Jalostotitlan-San Juan de Los Lagos (Mexico) ^{1,2}
G	Valley of piedmont (Italy) ^{1,2}	G	Celina-Coldwater ¹	G	Salamanca – Villagran (Mexico) ^{*1}
H	Landes area (France)	H	Shenandoah Valley- Bridgewater ¹	H	Ezequiel Montes (Mexico) ^{1,2}
I	Vic - Manlleu (Spain) ^{1,2}	I	Lenoir County	I	Tampaon, Loma Alta (Mexico) ¹
J	Ebro river basin (Spain) ^{1,2}			J	Tecoman (Mexico)
				K	Coyuca de Catalan (Mexico)
				L	Morelos (Mexico)
				M	Tochtepec-Tehuacan (Mexico) ¹
				N	South of Veracruz (Mexico)
				O	Cosolaecaque (Mexico) ^{*1}
				P	Tabasco (Mexico)
				Q	Guerrero (Mexico)
				R	Chisec (Guatemala)
				S	Texcuaco (Guatemala)

*Fertilizer industry ** Soda ash industry

¹ Van Damme et al., 2018; Clarisse et al., 2019

² Dammers et al., 2019

190

191 For Europe and North America, NH_3 total columns are the highest in spring and summer. In fact, NH_3
192 concentrations over Europe exhibit two seasonal maxima in March/April and July/August
193 (supplementary material, Figure S1) and in North America the maxima are in May and September
194 (Figure S2). This is consistent with agricultural practices (i.e. fertilizer application) and higher air
195 temperature favoring NH_3 volatilization in the atmosphere.

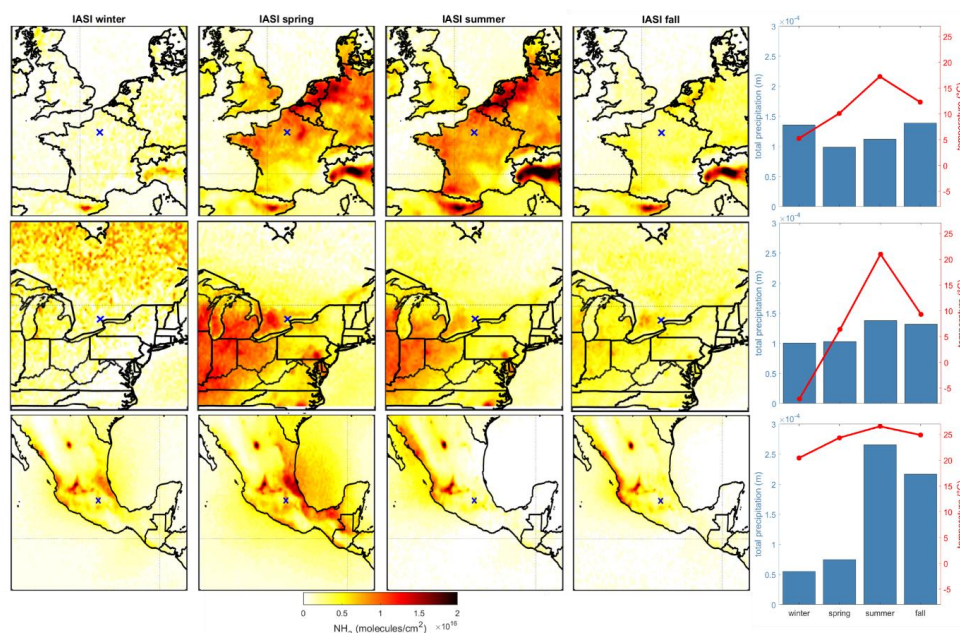
196 The right panel of Figure 3 shows how temperature (red lines) and precipitation (blue bars)
197 seasonally evolve over the three regions. In winter, atmospheric temperatures are below 5 °C in
198 Europe and North America, and IASI observations reveal almost no NH_3 hot spots (left panel, Figure
199 3). This can be due to the lack of NH_3 abundance, lower volatilization in this temperature range, no
200 agricultural emissions in winter and/or the reduced sensitivity of the IASI NH_3 retrievals in winter
201 [Van Damme et al., 2017].

202 In southern North America, NH_3 seasonal variations are less pronounced than in the other two
203 regions. Figure 3 shows that the NH_3 concentrations over several sources, such as Torreon and San
204 Juan de Los Lagos (boxes B and F in Figure 2 right panel) are high during all seasons, which could be
205 associated with the weak seasonal cycle of temperature in this region close to the equator.

206 In spring, seasonal precipitations are the lowest for the three regions. This is reflected in high NH_3
207 concentrations on the left panel. Over Europe and North America, this can be related to agricultural
208 spreading practices period and higher atmospheric temperature favoring NH_3 volatilization. In
209 southern North America, NH_3 concentrations observed by IASI are the highest in spring when
210 atmospheric temperatures are high and precipitations rates are low. In addition, biomass burning,



that are often encountered during this period could explain higher atmospheric NH_3 concentrations in spring. NH_3 reach maximum values in April/May (Figure S3) just before the start of the rain season, potentially reducing observed NH_3 concentrations due to the wet deposition of atmospheric gaseous ammonia [Asman et al., 1998].



215

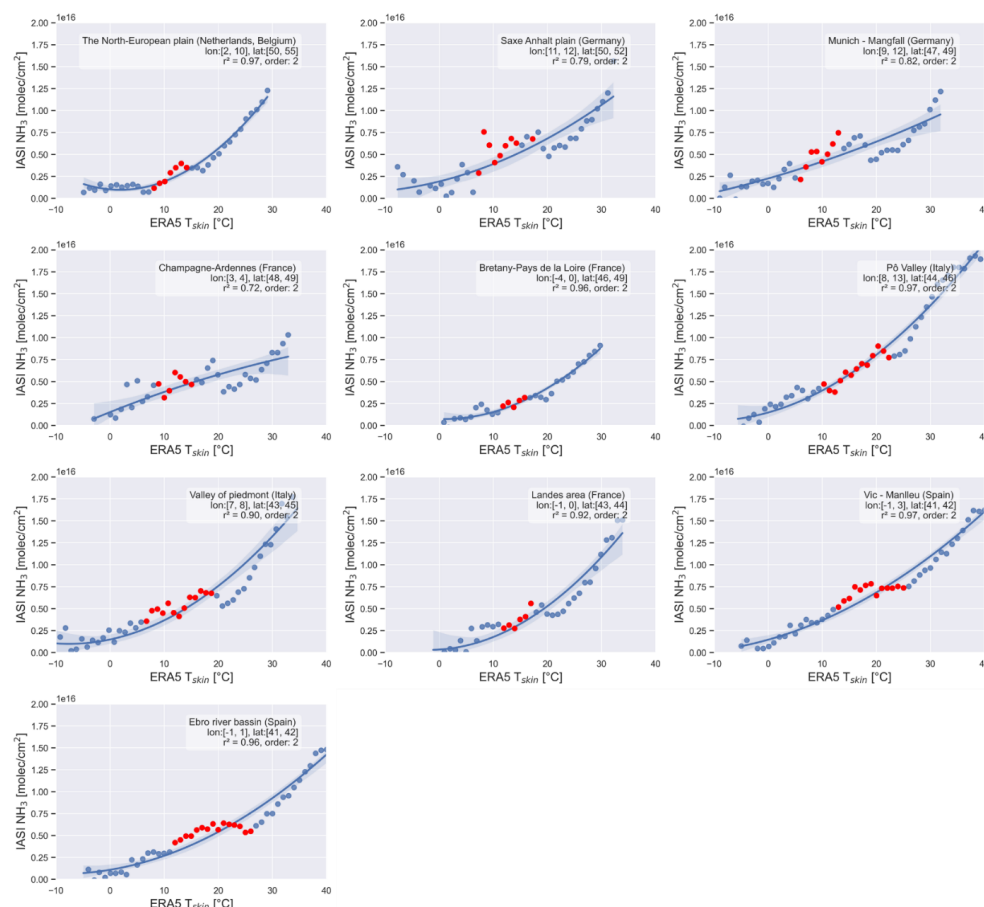
216 Figure 3: Seasonal maps of NH_3 total columns (molecules/cm²) derived from 10 years (2008-2017) of IASI
217 observations, along with seasonal means of atmospheric temperature (red line) and precipitation (blue bar
218 chart) over the Europe (upper panels), North America (middle panels), and southern North America (lower
219 panels) regions.

220 Since in Europe and North America NH_3 sources are mostly agriculture-related (with a mild
221 contribution from industries), the temperature/ NH_3 relationship is expected to be relatively easy to
222 interpret: when the land surface temperature increases, volatilization of ammonia from the
223 fertilized/manured soil is favored, and atmospheric ammonia increases. The corresponding
224 determination factors r^2 for this relationship in Europe and North America are 0.85 and 0.80
225 respectively (polynomial fit of second order). This is not the case in southern North America, in which
226 some of the ammonia sources are also industrial and they contribute greatly to the atmospheric NH_3 ,
227 the concentrations of ammonia are therefore not directly temperature dependent, as we can see on
228 the right upper panel in Figure S4 ($r^2 = 0.46$). There is nonetheless a relationship in southern North
229 America that is due to the fact that we have constant high ammonia sources and temperatures
230 (Figure 3). In fact, the relationships between NH_3 and temperature on one hand, and
231 precipitation/relative humidity on the other hand, are not linear; this has been equally shown in a
232 previous study [Sutton et al., 2013].

233 To further investigate the temperature/ NH_3 relationship, we show in Figure 4 the evolution of NH_3
234 with respect to land surface temperature over different sub-regions of the Europe domain (listed in
235 Table 1). Similar Figures for the North America and southern North America domains are shown in
236 the supplement information (Figure S5 and S6). We observe a peak of NH_3 followed by a local



237 maximum plateau between 10 and 25°C approximately in all of the regions of the Europe domain
 238 (Figure 4). In fact, the NH_3 detected in this range of temperature can indicate the fertilizer application
 239 period, since most of them (up to 80%) were detected during the spring and fall seasons. For
 240 instance, over the Po valley (region F in Table 1, Figure 4), 36% of the NH_3 detected in the bins 10 –
 241 25°C correspond to the spring season, whereas 35% correspond to the fall season (not shown here).
 242 In Celina-Coldwater (region G in Table 1), 82% of the NH_3 detected between 10 and 25°C correspond
 243 to the spring and the fall seasons, the percentage is split equally (Figure S5).



244
 245 Figure 4: Yearly IASI NH_3 total columns (molecules/ cm^2) averaged per bins of ERA5 skin temperatures ($^{\circ}\text{C}$), with
 246 an interval of 1°C between each consecutive bin. The red circles denote the growing seasons, at least 60% of
 247 the NH_3 is detected during March-May and Sept-Nov periods. See Figure 2 and Table 1 for the localization of
 248 the sub-regions around Europe.

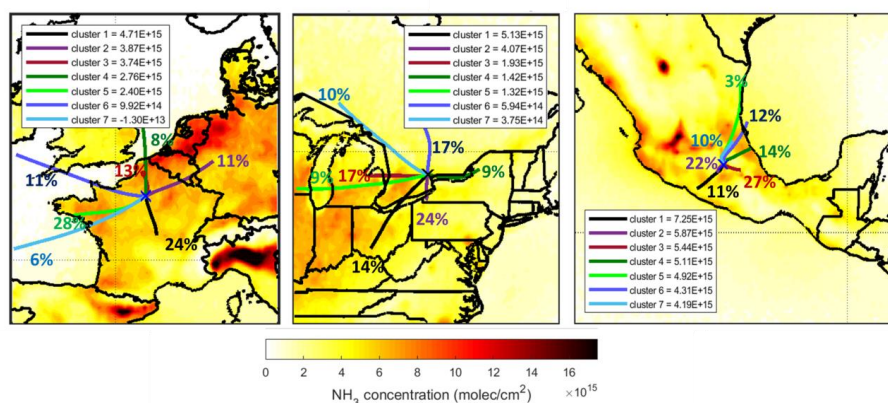
249 We choose to show the sub regions in the vicinity of the Europe domain, since they are mostly
 250 agricultural sources. The “bumps” corresponding to the fertilizer application are very clear in all of
 251 the sub-regions. This bump was detected to a lower extent for agricultural regions affecting North
 252 America (supplementary material Figure S5). Over the agricultural regions in the southern North
 253 America domain, the bumps are clear in the regions A to D (Figure S6, a). When the seasonal
 254 temperatures do not fluctuate during the fertilizer application, any increase in atmospheric NH_3 is



255 due to the sudden addition of nitrogen fertilizers in the soil. In southern North America, the regions E
256 to M show that the highest NH_3 concentrations were observed as the temperature increased during
257 the growing seasons (Figure S6). A possible explanation to the resemblance among the regions A to D
258 is that they share similar climate properties (Steppe and Desert) unlike the rest of the sub-regions in
259 the same domain (tropical/subtropical). Since the temperatures in the Europe and southern North
260 America domains are higher (Figure 3, right panels) in spring and fall seasons (fertilizer application
261 period) than those in North America, this bump is clearer in the latter. The bumps seen for the
262 Europe regional domain are clearer than those of southern North America, possibly related to the
263 fact that in autumn in Europe precipitation is lower than those in southern North America, leading to
264 lower NH_3 loss through wet deposition.

265 3.2. NH_3 budget over the cities of Paris, Toronto, and Mexico

266 Temperature, relative humidity, and precipitation are not the only factors affecting the NH_3
267 concentrations. More locally, and to analyze the impact of long-range transport on NH_3
268 concentrations measured over the cities (and not domains) of Paris, Toronto, and Mexico, HYSPLIT
269 back-trajectories have been used. For each day of IASI NH_3 observations made in a 50-km radius
270 circle from the city-center, a 24-hours back-trajectory has been performed from 2008 to 2017. There
271 are between 3643 and 4008 back-trajectories for Paris, Toronto, and Mexico cities. Then, a seven-
272 cluster analysis has been applied to these datasets and NH_3 mean concentrations measured inside
273 the cities by IASI have been allocated to the different mean cluster trajectories. The result is shown in
274 Figure 5.



275

276 Figure 5: Seven cluster-mean backward trajectories over the Europe, North America, and southern North
277 America regions for the whole time period between 2008 and 2017. Back-trajectories are color-coded in
278 function of the corresponding NH_3 concentrations measured inside the cities. The numbers indicate the
279 percentage of trajectories allocated to a cluster.

280 For Paris, 1/4 of all back-trajectories (875) that are associated with the most NH_3 concentrations, i.e.
281 4.71×10^{15} molecules/ cm^2 on average, are coming from the surrounding south regions (black line,
282 Figure 5). Clusters 2 and 3 are also associated with high NH_3 concentrations and are coming from the
283 north-northeast. This is consistent with previous analyses using HYSPLIT [Viatte et al., 2020] and
284 FLEXPART models [Viatte et al., 2021]. As expected, the back-trajectories coming from the ocean are
285 related with almost no NH_3 concentrations (light and dark blue lines, left panel).



Over Toronto, the highest NH_3 concentrations (24% and 14%) measured in the city are allocated to long-range transport located south-southwest (black and purple lines, middle panel) coming from the United-States where most of the feedlots are. 9 to 17% of NH_3 concentrations are coming from the west and the east of Toronto (cluster 3, 4, and 5) where sources emissions have increased in the last decade [Yao and Zhang, 2019]. The 2 back-trajectory clusters that are related to low NH_3 concentrations are coming from the north (light and dark blue lines) where no NH_3 sources have been identified.

In the southern North America domain, back-trajectories are coming from relatively close regions since orographic conditions around Mexico-city limit long-range transport. In this city, the highest NH_3 concentrations are associated with air masses coming from the southwest (11%, black line, 22%, purple line, right panel) and southeast (27%, red line). Air parcels coming from the north are associated with relatively low NH_3 concentrations measured in Mexico City.

3.3. Pollution events over Paris, Toronto, and Mexico cities from 2008 to 2017

After assessing the NH_3 distribution under average climate conditions, we focus now on pollution events occurring at the 3 cities. These are identified by applying the Fourier series of order 3 [Yamanouchi et al., 2021; Herrera et al., 2022] on the surface $\text{PM}_{2.5}$ and satellite NH_3 observations at cities scale (i.e. 50-km radius circle from city-centers). The Fourier fit accounts for the “natural” variability (seasonality) in the time-series, and helps identify pollution events that are above this natural variability. It is a robust method commonly used to quantify trends and identify enhancements in long-term timeseries [Zellweger et al., 2009]. Pollution events occurrence per year and per city are shown in Figure 6.

The figure shows that NH_3 pollution episodes are found to be annually frequent at the 3 cities. In Toronto and Mexico cities, $\text{PM}_{2.5}$ pollution events are encountered annually (with higher number in Mexico) whereas no events are detected in 2009, 2015, and 2017 in Paris.

Numbers of identified days of $\text{PM}_{2.5}$ pollution events are 88, 58, and 50 in Mexico City, Toronto, and Paris, respectively. For NH_3 pollution events, they occur more in Toronto than in Mexico City and Paris, with number of days of 94, 73, and 56, respectively. Common days of high NH_3 and $\text{PM}_{2.5}$ concentrations are found in all 3 cities, especially in spring (not shown here), coinciding with the high seasonal NH_3 concentrations shown in Figure 3.

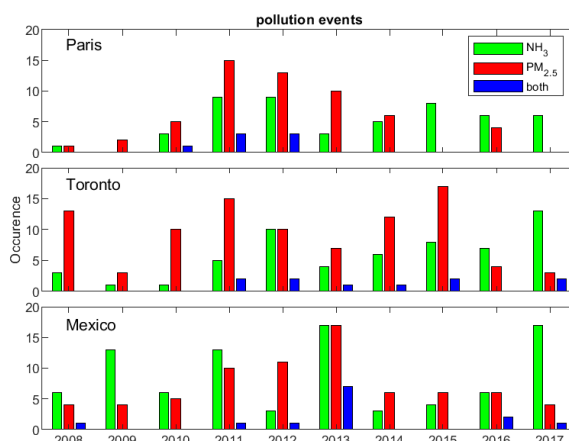




Figure 6: Annual occurrence of pollution events of NH_3 (green bars), $\text{PM}_{2.5}$ (red bars), and NH_3 and $\text{PM}_{2.5}$ simultaneous (blue bars) detected from 2008 to 2017 in Paris (upper panel), Toronto (middle panel), and Mexico (lower panel) cities.

To further investigate the impact of transport on pollution events occurring at the 3 cities, we have analyzed the wind fields patterns for different cases: i) for the whole dataset (i.e. ensemble 2008-2017), ii) for days of NH_3 and $\text{PM}_{2.5}$ pollution events occurred separately, and iii) for days when both high concentrations are monitored. Figure 7 shows wind roses computed for the ensemble and these different types of pollution events (i.e. $\text{PM}_{2.5}$, NH_3 and both occurring during the same day). In general, wind speed is lower at Mexico City (max 3 m.s^{-1}) compared to Toronto and Paris (up to 10 m.s^{-1}) because of the mountainous topography that blocks and slows air masses exchange in Mexico.

In Paris, the ensemble wind-roses show a dominant northeast-southwest pattern. NH_3 pollution events are associated with wind coming from various directions at all wind speeds which was suggested by the HYSPLIT cluster analysis (Figure 5), whereas $\text{PM}_{2.5}$ events are present mainly under high northeast wind. When both NH_3 and $\text{PM}_{2.5}$ high concentrations are observed in Paris, the wind field can have two patterns: low wind speed coming from all direction (except from the south) or high wind speed coming from the northeast. This confirms the importance of transport of NH_3 and $\text{PM}_{2.5}$ from the northeast and could suggest the inter-conversion of $\text{PM}_{2.5}$ to NH_3 at low wind speed.

In Toronto, the ensemble show that dominant wind pattern is coming from the south. For all the pollution events (NH_3 , $\text{PM}_{2.5}$, and both) the wind is coming from the southwest, confirming the long-range transport of pollutants from the United-States.

In Mexico City, the dominant pattern (ensemble) is southwest-northeast wind fields. For days of NH_3 pollution events, wind is mainly coming from the south-southwest, and for $\text{PM}_{2.5}$, wind come from all direction with an important northeast wind pattern. Days of both pollution events are associated with wind coming from the west-southwest only.

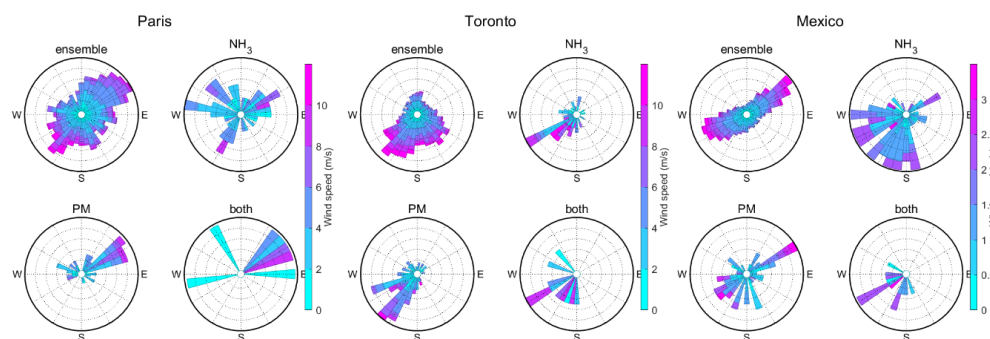


Figure 7: Wind roses corresponding to the ensemble of all observations, the NH_3 , $\text{PM}_{2.5}$, and both NH_3 and $\text{PM}_{2.5}$ simultaneous pollution events derived from 2008 to 2017 over Paris (left panels), Toronto (middle panels), and Mexico (right panels) cities.

3.4. Case study: NH_3 and $\text{PM}_{2.5}$ concentrations comparison with the GEOS-Chem model in March 2011

The occurrence of pollution events varies from year to year (Figure 6). However, in 2011, all 3 cities experienced $\text{PM}_{2.5}$ and NH_3 separate and combined pollution events. For this reason, GEOS-Chem



348 model simulations were performed in March 2011 to interpret the events and evaluate the model
349 performance.

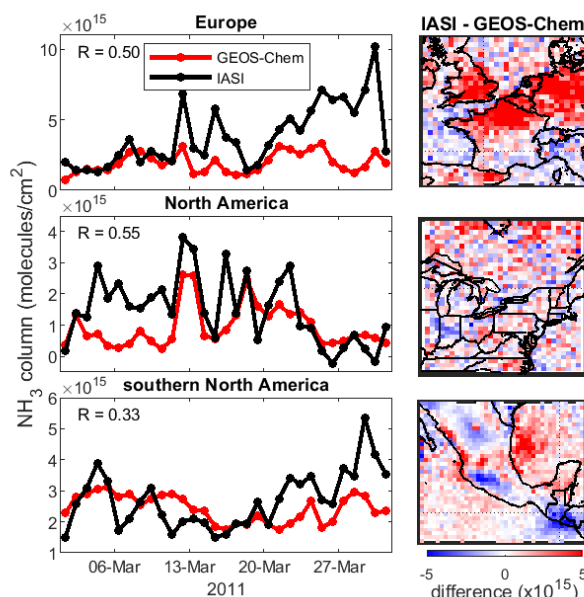
350 Spatial and temporal coincidence criteria have been applied to GEOS-Chem outputs to compare with
351 IASI morning observations. We have selected collocated model outputs between 8.30 and 11.30 AM
352 coincident with IASI overpasses. Averages of numbers of IASI observations are 1324, 1138, and 3000
353 over the Europe, North America, and southern North America domains of study during March 2011.

354 Figure 8 shows the one-month comparison between the two datasets. Over the regional domains,
355 the coefficient of correlation between daily model NH_3 concentrations and IASI NH_3 observations are
356 $R = 0.50$, $R = 0.55$, and $R = 0.33$, over Europe, North America, and southern North America,
357 respectively, with related p-values < 0.01 . NH_3 columns derived from the GEOS-Chem model are
358 overall underestimated with Mean Relative Difference ($\text{MRD} = (\text{observations} - \text{model}) / \text{model}$) of
359 104%, 109%, and 12% over Europe, North America, and southern North America, respectively.

360 Over Europe and North America, day-to-day variabilities are in agreement since IASI and GEOS-Chem
361 exhibit same enhancements (on March 12, 15, and 30 over Europe, and March 12, 13, and 18 over
362 North America). In southern North America, the underestimation of the GEOS-Chem NH_3 columns is
363 less pronounced (MRD is 12%) than in the other regions but the day-to-day variability is not well
364 represented in the model.

365 The GEOS-Chem model NH_3 total columns are lower than those from IASI in March 2011 over specific
366 locations in the southern North America and Europe domains (Figure 8, right panels). For the Europe
367 region, GEOS-Chem NH_3 columns are smaller than the IASI ones over the north of France, Belgium,
368 the Netherlands, north of Spain (in particular sources A, B, C, D, E, I, and J of Figure 2) and the United
369 Kingdom. For the southern North America domain, GEOS-Chem NH_3 columns are smaller than the
370 IASI ones over the west Mexican coast (sources A, D, E, J of Figure 2/Table 1), central (source F, G, H
371 of Figure 2) and southeast (sources O and P of Figure 2) of Mexico City and over the Pacific Ocean,
372 whereas they are higher in Guatemala (source S, R of Figure 2), and West of Mexico City.

373 Over the North America domain, spatial distribution of the differences between NH_3 columns derived
374 from GEOS-Chem and IASI are less pronounced than in the Europe and southern North America
375 domains. IASI NH_3 columns are smaller than GEOS-Chem outputs over the south of the United-States
376 and over the Lancaster County (sources E and I of Figure 2) and higher over Indiana in the United
377 States.

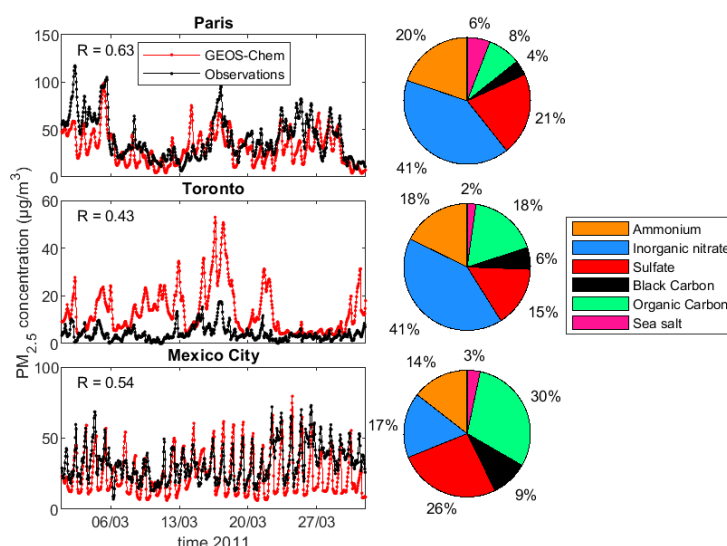


378

379 Figure 8: Left: time-series of daily NH_3 columns derived from IASI (black lines) and the GEOS-Chem model (red
380 lines) over Europe (upper panel), North America (middle panel), and southern North America (lower panel).
381 Right: maps of NH_3 columns (in molecules/ cm^2) differences between IASI and GEOS-Chem model for March
382 2011.

383 At the city scales of Paris and Mexico City, the daily model NH_3 columns are in relatively good
384 agreements with IASI observations within a 50-km radius circle from the city-centers (not shown
385 here), since the coefficient of correlation are $R = 0.42$ and $R = 0.52$, respectively. Similar to the
386 regional domains, GEOS-Chem NH_3 columns are relatively underestimated at the city scales of Paris
387 and Mexico City, with a MRD of 14% and 72%. At the city scale of Toronto, the correlation between
388 the NH_3 columns derived from the model and observed by IASI is poor, with a coefficient of
389 correlation of $R = -0.32$, and an overestimation of the modelled NH_3 concentrations is found with a
390 MRD of -81%.

391 Local comparison of $\text{PM}_{2.5}$ concentrations at the city scale (over Paris, Toronto, and Mexico) is shown
392 in Figure 9, left panels. They show that $\text{PM}_{2.5}$ concentrations calculated by the model in March 2011
393 are in relatively better agreement with the surface observations with $R = 0.63$, $R = 0.43$, and $R = 0.54$
394 in Paris, Toronto and Mexico City. In Paris and Mexico City, $\text{PM}_{2.5}$ concentrations values derived from
395 the observations are overall higher than the GOES-Chem concentrations with MRD values of 55% and
396 65%, respectively, whereas GEOS-Chem $\text{PM}_{2.5}$ concentrations are higher than the observations in
397 Toronto with MRD value of -59%.



398

399 Figure 9: left: Time-series of hourly $PM_{2.5}$ ($\mu g/m^3$) derived from surface observations (black lines) and the GEOS-
400 Chem model (red lines) over Paris (upper panel), Toronto (middle panel), and Mexico (lower panel) cities for
401 March 2011. Right: $PM_{2.5}$ speciation (% in total mass) derived from the GEOS-Chem run for March 2011.

402 The right panels of Figure 9 show the chemical composition of the $PM_{2.5}$ from GEOS-Chem. These
403 inform us about the different pollution sources. Organic matter sources split equally between the
404 primary emissions and the oxidation of volatile organic compounds [Day et al., 2015]. SNA (sum of
405 sulfate, nitrate, and ammonium) sources originate in chemical transformation of gaseous precursors
406 in the atmosphere, whereas black carbon comes from primary emissions of industrial and traffic
407 combustion.

408 According to the GEOS-Chem model, SNA dominates the $PM_{2.5}$ chemical composition mass in March
409 2011 over the 3 cities, meaning that the dominant source of $PM_{2.5}$ mass comes from the secondary
410 oxidation path. This partition of SNA in March 2011 from the model is higher than what have been
411 reported based on 1-year-measurements performed in 2013: 43%, 42%, and 33% of the $PM_{2.5}$ mass
412 composition in Paris, Toronto, and Mexico City, respectively [Cheng et al., 2016].

413 In Toronto, $PM_{2.5}$ speciation is monitored by the National Air Pollution Surveillance Program (NAPS,
414 <https://www.canada.ca/en/environment-climate-change/services/air-pollution/monitoring-networks-data/national-air-pollution-program.html>) network. Observations in March 2011 reveal
415 that inorganic nitrate burden is overestimated by a factor 2 in the GEOS-Chem run (41% in the model
416 compared to 20% in the observations), whereas sulfate and black carbon abundances are
417 underestimated by a factor 2 (15 and 6% in the model compared to 27 and 12% in the observations).
418

419 In Mexico City, the organic matter represents the most abundant fraction of the aerosol, which is
420 consistent with measurements made during several campaigns performed in the dry season of 2006
421 during the Megacity Initiative: Local And Global Research Observations (MILAGRO, [Molina et al.,
422 2010]) and Aerosoles en Ciudad Universitaria (ACU) in 2015 [Salcedo et al., 2018]. Daily cycles appear
423 overexaggerated in the model with maxima well represented and minima greatly underestimated.



424 This could suggest model issues in term of atmospheric dynamics (removal/transport or planetary
425 boundary layer dynamics) due to coarseness of grid.

426 **4. Conclusion**

427 The AmmonAQ project aims to determine the impact of intensive agricultural practices on urban
428 pollution in the Paris, Toronto, and Mexico metropolitan areas. For this purpose, PM_{2.5} and NH₃
429 measurements from in situ instruments and satellite infrared spectrometers, and atmospheric model
430 simulations, have been combined.

431 Using 10-years of IASI observations, NH₃ sources regions have been identified. All of the sources are
432 from the agricultural sector (husbandry and fertilizer application) in the Europe and North America
433 domains, whereas, some of them are industrial in the southern North America region. Consequently,
434 the spatio-temporal variability of NH₃ is different, with stronger seasonal variabilities in Europe and
435 North America. A strong correlation is found between NH₃ total columns and surface temperature
436 (T_{skin}) for all regions, with higher correlation over agricultural regions, and when the temperature
437 seasonal cycle is pronounced. We find that the timing of the fertilizer application can be detected
438 through local maxima in the NH₃/T_{skin} relationship curve.

439 According to HYSPLIT cluster analysis, the highest NH₃ concentrations measured at the city scales are
440 associated with air masses coming from the surrounding regions and the north-northeast of Paris,
441 the south-southwest of Toronto, and the southeast/southwest of Mexico City. These will lead to the
442 exacerbation of the degradation of air quality in each of the 3 cities.

443 Pollution episodes are found to be annually frequent at the 3 cities, especially in springtime when
444 high NH₃ and PM_{2.5} are observed. In Paris and Mexico, winds are coming from the northeast-
445 southwest directions, whereas, in Toronto, the transboundary transport of pollutant from the
446 United-States is dominant during pollution events.

447 The evaluation of the GEOS-Chem outputs in March 2011 reveals that NH₃ concentrations are overall
448 underestimated by the model at the regional scale, with, however, a good representability of the
449 day-to-day variability in Europe and North America domains. NH₃ columns derived from IASI and the
450 GEOS-Chem model exhibit substantial spatial differences in the Europe and southern North America
451 areas. In term of PM_{2.5} concentrations at the city scales, we show that they are underestimated in
452 Paris and Mexico, but overestimated in Toronto.

453 The IASI thermal infrared remote sensors have proved to be valuable to monitor pollution events
454 over cities. The main limitations are associated with the low revisit time (at the beginning and at the
455 end of the day), the lack of sensitivity to the surface in particular in winter, and some areas are not
456 well covered during cloudy scenes. In the near future the next generation of instruments will have
457 improved capabilities to sound deeper in the atmosphere [Crevoisier et al., 2014]. The IRS-MTG
458 satellite instrument that should be launch in 2024 in geostationary orbit will offer the capacity to
459 enhance this research over Europe thanks to better temporal (measurements every 30-45 minutes)
460 and spatial (4 km x 4 km pixel) resolution.

461 **Data availability**

462
463 The near-real-time IASI NH₃ (ANNI NH3-v3) data used in this study are freely available through the
464 AERIS database <https://iasi.aeris-data.fr/nh3-i/> (Van Damme et al., 2021) (last access: 1 April 2022).
465 All hourly observations of PM_{2.5} concentrations are available from the Airparif network ([https://data-
466 airparif-asso.opendata.arcgis.com/](https://data-airparif-asso.opendata.arcgis.com/)), the Ministry of the Environment, Conservation and Parks of
467 Ontario (<http://www.airqualityontario.com/>), and the Red Automática de Monitoreo Atmosférico



468 (RAMA, <http://www.aire.cdmx.gob.mx/default.php?opc=%27aKBh%27>) network (last access: 1 April
469 2022). The GEOS-Chem outputs are currently available upon request. All MATLAB/PYTHON codes
470 used to create any of the figures and/or to create the underlying data are available on request.

471 **Author contributions**

472 CV, CC, SY, and KS designed the AmmonAQ project. MV and LC provided the IASI data. WP provided
473 the GEOS-Chem outputs. CV and RA analyzed the data. CV, RA, and SS wrote the manuscript draft.
474 BH, MG, KS, P-FC, and CC reviewed and edited the manuscript.

475 **Competing interests**

476 The authors declare that they have no conflict of interest.

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