Review 1 of "NH3 Spatio-temporal variability over Paris, Mexico and Toronto and its link to PM2.5 during pollution events"

Referee: General comments:

The manuscript of egusphere-2022-413 presented the result of a unique project of the AmmonAQ that targeted different three areas of Paris, Toronto, and Mexico City. Towards better air quality by mitigating NH3 emissions, the finding of this study will contribute to improving the atmospheric environment. I generally agree with this manuscript being published; however, some points are concerned. Especially, I am wondering about the uncertainty of the satellite NH3 measurement dataset analyzed in this study. Please address the following specific points.

Authors: We would like to thank the referee for this positive review and all the relevant comments that we have addressed in the following document.

Specific comments:

P3, L52: Please specify these five countries.

The five countries are United-States, China, Netherlands, United-Kingdom, and Canada. We have included this list in the revised manuscript.

P3, L65: Are these increasing trends explained by the expansion of NH3 emissions, or meteorological variability (e.g., temperature)?

In Europe, NH_3 emissions are relatively stable (with a decrease of 4 % between 2008 and 2012 followed by an increase of 3% between 2013 and 2018). However, IASI observations reveal an increase that could be associated with meteorological conditions, with high temperature and drought recorded in 2018.

In Canada, emissions are also relatively constant between 2008 and 2018, but biomass burning sustains increased NH₃ emissions in the northern hemisphere.

In Mexico, the EDGAR inventory shows an increase in NH₃ emissions.

These conclusions must be tempered by the fact that the lifetime of NH₃ in the atmosphere increases with decreasing concentrations of nitrogen oxides and sulfur.

We have added a sentence in the revised manuscript to explain the trends: "These trends are likely explained by increasing emissions, partly due to increased temperature (Europe) and biomass burning (Canada). However, decreasing concentrations of nitrogen and sulfur oxides e.g. in Europe and China also increase the ammonia atmospheric lifetime and plays a role in the reported upward trends."

P3, L77: Does "the standard" indicate the standard in Mexico? Because this study conducted the comparison over three regions, it will be better to explicitly state it.

We have included 'national' standard to explicitly state it. In addition, we have modified the standard value for Mexico because it has recently changed in October 2021. Therefore, we have modified the sentence as follows: "In Mexico, $PM_{2.5}$ concentrations often exceed the national standard of 41 μ g/m³ for the 24-hour mean [NOM-025-SSA1-2021, 2021]".

P5, L111 (Section 2.1): Because of the recent progress in satellite NH_3 measurement, I would like to strongly suggest including the discussion of the uncertainty of satellite data, such as the detection limit (https://doi.org/10.5194/acp-19-12261-2019).

In this section of the revised manuscript, we have added description about the detection limit: "The detection limit depends both on the atmospheric state (mainly thermal contrast and NH_3 abundance) and the instrument characteristics. For IASI, the minimum detection limit is found to be $4-6\times10^{15}$ molecules/cm² [Clarisse et al., 2010]."

What is the mottled pattern found over Canada during winter in Figure 3?

The sensitivity of IASI measurements is intimately related to the thermal contrast between the surface and the first layers of the atmosphere [Clerbaux et al., 2009]. When the detection is possible (with good thermal contrast), the peak sensitivity for NH₃ is in the boundary layer [Clarisse et al., 2010]. The high value over Canada and the Arctic in winter can be associated with high uncertainties in the NH₃ retrievals due to low thermal contrast and high emissivity from snow. We have added this sentence in the revised manuscript to clarify: "The high value over Canada and the Arctic in winter can be associated with high uncertainties in the NH₃ retrievals due to low thermal contrast."

Can all satellite measured NH3 close to zero be used in Figure 4?

Yes, removing or keeping these values won't change the relationship between temperature and the ammonia averages, therefore the discussion of the following figure will not be affected. In Figure R1, we show the same plots as Figure 4 (in the manuscript) but with the values of NH₃ $\leq 0.25 \times 10^{16}$ molecules cm⁻² removed. Note that the r² did not change much, in the presence and absence of these values.





Is it available AK when comparing GEOS-Chem? The information on AK and how to calculate it in the comparison with the model is not described.

The IASI retrieval algorithm for NH₃ does not provide averaging kernels. We have qualitatively compared IASI NH₃ columns with GEOS-Chem NH₃ columns using all the morning IASI measurements available, following the recommendation provided in Van Damme et al. [2017]. Previous studies have demonstrated good agreement with surface and FTIR measurements (e.g., Clarisse et al., 2010; Van Damme et al., 2015; Dammers et al., 2017; Viatte et al., 2021; Van Damme et al., 2021), demonstrating that IASI retrievals are sensitive to NH₃ located in the lower layers of the atmosphere.

P5, L115: What is the actual gridded data (e.g., Figure 2) analyzed in this study?

We have gridded the IASI data at 0.25° x 0.25° degrees. This information has been included in the revised manuscript as follow: "In this work, we use version 3 of the ANNI-NH₃ product [Van Damme et al., 2021; Guo et al., 2021] from IASI Metop-A/B morning overpasses over the period 2008 to 2017 gridded a spatial resolution of 0.25° x 0.25°".

P5, L130: Although we can find the reason to choose the model simulation period of 2011 in P12, L344-P13, L349, it is better to be shortly explained here.

We have added a short sentence in this section: "because all three cities experienced both separate and combined $PM_{2.5}$ and NH_3 pollution events during this period."

P6, L178: Are these three panels shown with the same horizontal distance? If different, the scaler might be helpful.

The three panels are approximatively shown at the same horizontal distance, but we have inserted a scaler in each panel to help the reader.



Figure R2: Same as Figure 2 in the revised manuscript.

P6, L152: Too coarse reanalysis resolution to investigate air mass trajectories on 50 km radius-circle at each city?

We have run 24-hour HYSPLIT back-trajectories every day for the whole IASI dataset from 2008 to 2017. The idea is to determine the effect of long-range transport affecting air quality within the cities during this decade. Running 3652 daily back-trajectories (10 years) using a finer meteorological reanalysis would have been very time consuming. In addition, results derived from a finer resolution meteorological dataset are very similar. We have performed a test for a sub dataset (July 2008) running 24h-backtrajectories ending in Paris using NCEP at 2.5° resolution and GDAS at 1° resolution (Figure R1). Results show no significant differences when using a finer meteorological dataset. We have inserted in the revised manuscript a sentence to address this concern: "Note that results using a finer meteorological dataset (GDAS at 1° resolution) show no significant differences."



Figure R3: 24-h HYSPLIT back-trajectories ending in Paris using the meteorological dataset of GDAS (at 1° resolution, left panel) and NCEP (at 2.5° resolution, right panel) for July 2008.

P7, L188: Same to Europe and southern North America, source information of "(Canada)" or "(U.S.A.)" can be useful in this Table 1.

We have added information about the sources countries in the revised Table 1 as follows:

	Europe		North America		Southern North America	
	[41°-59°N ; -11.25°- 16.25°E]	[35°-53°N ; 93.75°-63.75°W]		[9°-29°N ; 113.75°-86.25°W]	
Α	The North-European plain ^{1,2}	Α	Granby (Canada)	Α	Obregon (Mexico) ¹	
В	Saxe Anhalt plain (Germany)	В	Elmira-Kitchener-Guelph (Canada)	В	Torreon (Mexico) ^{1,2}	
С	Munich - Mangfall (Germany)	С	Brillion area (U.S.A)	С	Garcia (Mexico)**1	
D	Champagne-Ardennes (France)	D	New-York state (U.S.A)	D	Culiacancito (Mexico) ^{1,2}	
Е	Bretany-Pays de la Loire (France) ²	Е	Lancaster county (U.S.A)	Е	Nayarit (Mexico)	
F	Pô Valley (Italy) ^{1,2}	F	Wayne county (U.S.A)	F	Jalostotitlan-San Juan de Los Lagos (Mexico) ^{1,2}	
G	Valley of piedmont (Italy) ^{1,2}	G	Celina-Coldwater (U.S.A) ¹	G	Salamanca – Villagran (Mexico)*1	
н	Landes area (France)	н	Shenandoah Valley- Bridgewater (U.S.A) ¹	Н	Ezequiel Montes (Mexico) ^{1,2}	
I.	Vic - Manlleu (Spain) ^{1,2}	Т	Lenoir County (U.S.A)	T	Tampaon, Loma Alta (Mexico) ¹	
J	Ebro river bassin (Spain) ^{1,2}			J	Tecoman (Mexico)	
				К	Coyuca de Catalan (Mexico)	
				L	Morelos (Mexico)	
				Μ	Tochtepec-Tehuacan (Mexico) ¹	
				Ν	South of Veracruz (Mexico)	
				0	Cosolaecaque (Mexico)*1	
				Ρ	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

P13, L358: Should the denominator be "observations" when comparing observation and model? Why model is referred to as a criterion?

We agree with the referee that the model is not referred here as a criterion. Therefore, we have changed the denominator to be observations. The result doesn't change much the MRD, so the discussion remains valid.

P13, L359: Are these values positive? If model underestimation, are these negative?

To calculate the Mean Relative Difference (MRD), we have revised the formula to be more intuitive as follows: MRD = (model - observations) / observations) as suggested above. Thus, when the MRD is positive, model data are higher than the observations. Conversely, when the MRD is negative, model data are smaller than the observations. In the latter case, a negative MRD means that the model underestimate compared to the observations.

P14, L379: From the spatial mapping over Europe, this seems to be simply led to model overestimation, and this is not consistent with the timeseries and relevant discussion in the main text. Please confirm this figure.

In the revised figure (see figure R4), we choose to be consistent and show (GEOSChem-IASI) NH_3 columns. Therefore, if this difference is negative (blue colour in the figure), then IASI NH_3 columns are higher than the model ones, leading to an underestimation of the model. To clarify, we have added "(model- observations)" in the caption of the revised manuscript.



Figure R4: same as Figure 8 in which we choose to show the difference (model-observations) to be consistent throughout of the revised manuscript.

P15, L413-418: From this comparison on PM2.5 component, I am suspicious about the result in other cities of Paris and Mexico City. When we considered this poor performance for PM2.5 components, the result in Figure 9 and the relevant discussion seems to be meaningless. Is this performance for PM2.5 component useful (worse or better than other studies)? If not, I would like to request to reconsider this final section in P14, L391-P16, L425.

The component comparison is important in Toronto because it helps explain why the model is performing so poorly there.

Unfortunately, to our knowledge, there are no $PM_{2.5}$ chemical composition observations available to compare individual components in Paris and Mexico City in March 2011. However, we found in the literature relevant results that could strengthen the final discussion.

In Paris, the March 2011 pollution episode has indeed been analyzed in terms of geographical origins and aerosols properties [Chazette et al., 2017] but not in term of aerosol speciation.

Comparing the GEOS-Chem outputs used in this study with two years of observations of aerosol chemical composition in Paris (2011-2013) [Petit et al., 2015], we found that sulfate component is slightly higher in the GEOS-Chem model than in the springtime observations (21% compared to 11%) whereas modelled organic carbon is lower than the observations (8% compared to 33%). This springtime underestimation of organics in atmospheric models has previously been reported in Paris [Sciare et al., 2010; Petit et al., 2015; Lanzafame et al., 2021] and could be associated with an underestimation of the organic matter emissions from residential contribution [Van der Gon et al., 2015].

Regarding the secondary aerosol, observations in Paris during the March 2015 pollution event show that it accounts for more than 50% of the PM concentration [Petit et al., 2017], which is in agreement with the SNA partition simulated in our GEOS-Chem model.

In Mexico City, a very recent paper [Retama et al., 2022] shows that during the dry-warm season of 2019 (between March and June), SNA correspond to 30% of the aerosol mass concentration, which is consistent with what has been reported before [Cheng et al., 2016] and the chemical composition modelled in our study. The organic fraction is found to be dominant in the observations [Retama et al., 2022] as suggested in the GEOS-Chem model over Mexico City.

We have inserted part of this discussion in the revised manuscript as follows:

"In Paris, the March 2011 pollution episode has been analyzed in terms of geographical origins and aerosols properties [Chazette et al., 2017] but not in terms of aerosol speciation.

Comparing the GEOS-Chem outputs used in this study with two-years observations of aerosol chemical composition in Paris (2011-2013) [Petit et al., 2015], we found that the sulfate component is slightly higher in the GEOS-Chem model than in the springtime observations (21% compared to 11%) whereas modelled organic carbon is lower than the observations (8% compared to 33%). This springtime underestimation of organics in atmospheric models has previously been reported in Paris [Sciare et al., 2010; Petit et al., 2015; Lanzafame et al., 2021] and could be associated with an underestimation of the organic matter emissions from residential contribution [Van der Gon et al., 2015]. Regarding the secondary aerosol, observations in Paris during the March 2015 pollution event show that it accounts for more than 50% of the PM concentration [Petit et al., 2017], which is in agreement with the SNA partition in our GEOS-Chem model simulation.

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

In Mexico City, the organic matter represents the most abundant fraction of the aerosol, which is consistent with measurements made during several campaigns performed in the dry season of 2006 during the Megacity Initiative: Local And Global Research Observations (MILAGRO, [Molina et al.,

2010]) and Aerosoles en Ciudad Universitaria (ACU) in 2015 [Salcedo et al., 2018]. Observations performed during the dry-warm season of 2019 reported that SNA correspond to 30% of the aerosol mass concentration, which is consistent with what has been reported before [Cheng et al., 2016] and the chemical composition modelled in our study. The organic fraction is found to be dominant in the observations [Retama et al., 2022] as suggested in the GEOS-Chem model over Mexico-City. Daily cycles appear overexaggerated in the model with maxima well represented and minima greatly underestimated. This could suggest model issues in term of atmospheric dynamics (removal/transport or planetary boundary layer dynamics) due to coarseness of grid."

Technical corrections:

Authors: All technical corrections have been addressed in the revised manuscript.

P10, L281: 4.71 "×" 1015?

P12, L324 and L325: "m.s-1"? Does it need the period?

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