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Measurement report: Evolution and distribution of NH₃ over Mexico City from ground-based and satellite infrared spectroscopic measurements

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20 **Abstract.** Ammonia (NH₃) is the most abundant alkaline compound in the atmosphere, with consequences for the
environment, human health, and radiative forcing. In urban environments, it is known to play a key role in the formation of
secondary aerosols through its reactions with nitric and sulphuric acids. However, there are only a few studies about NH₃ in
Mexico City. In this work, atmospheric NH₃ was measured over Mexico City between 2012 and 2020 by means of ground-
based solar absorption spectroscopy using Fourier transform infrared (FTIR) spectrometers at two sites (urban and remote).
25 Total columns of NH₃ were retrieved from the FTIR spectra and compared with data obtained from the Infrared Atmospheric
Sounding Interferometer (IASI) satellite instrument. The diurnal variability of NH₃ differs between the two FTIR stations
and is strongly influenced by the urban sources. Most of the NH₃ measured at the urban station is from local sources, while
the NH₃ observed at the remote site is most likely transported from the city and surrounding areas. The evolution of the
boundary layer and the temperature play a significant role in the recorded seasonal and diurnal patterns of NH₃. Although the
30 vertical columns of NH₃ are much larger at the urban station, the observed annual cycles are similar for both stations, with
the largest values in the warm months, such as April and May. The IASI measurements underestimate the FTIR NH₃ total
columns by an average of 32.2 ± 27.5 % but exhibit similar temporal variability. The NH₃ spatial distribution from IASI
shows the largest columns in the northeast part of the city. In general, NH₃ total columns over Mexico City exhibited an



average annual increase of $92 \pm 3.9 \times 10^{13}$ molecules/cm² yr (urban) and $8.4 \pm 1.4 \times 10^{13}$ molecules/cm² yr (remote) was
35 observed in Mexico City at both FTIR stations and a decadal increase of 62 % with IASI data.

1 Introduction

Atmospheric ammonia (NH₃) is the most abundant basic gas in ambient air (Behera et al., 2013). It predominantly reacts
with sulfuric acid (H₂SO₄) and nitric acid (HNO₃) vapor to neutralize a significant fraction of the atmospheric acidity and
form ammonium sulfate and ammonium nitrate salts (Seinfeld and Pandis, 2006). Rich NH₃ environments thus promote the
40 formation of secondary inorganic aerosols, which can account for up to 50% of the mass in the total particulate matter (PM)
(Behera et al., 2013). PM_{2.5} (PM with an aerodynamic diameter < 2.5 μm) is associated with premature human mortality
(Paulot and Jacob, 2014; Giannakis et al., 2019), highlighting the importance of taking action to reduce the health impacts
due to air pollution, particularly in densely populated environments.

NH₃ has a short lifetime, on the order of hours to a few days (Dammers et al., 2016, 2019; Nair and Yu, 2020; Evangelidou et
45 al., 2021), and exhibits a strong temporal and spatial variability that ranges over three orders of magnitude near the surface
(Shepherd et al., 2011). NH₃ emissions and deposition strongly depend on environmental conditions. The primary sources of
atmospheric NH₃ are related to agricultural activities (mainly livestock and fertilizers), as well as natural sources, biomass
burning, vehicular emissions, humans and pets (Bouwman et al., 1997; Sutton et al., 2008, 2013). Human NH₃ emissions
strongly depend on temperature and skin exposure, for example, one adult can emit 0.4 mg of NH₃ per hour at 25 °C but 1.4
50 of NH₃ per hour at 29 °C (Li et al., 2020). In countries with intensive livestock production, NH₃ is the main contributor to
nitrogen fluxes. Emitted NH₃ can be transported by winds and removed from the atmosphere by wet and dry deposition
(Neiryneck and Ceulemans, 2008; Behera et al., 2013). NH₃ deposition also has an important role in the acidification and
eutrophication of ecosystems (Krupa, 2003; Sutton et al., 2008), with multiple effects on water, air, soil, climate and
biodiversity (Sutton et al., 2013).

55 NH₃ accounts for almost half of all reactive nitrogen released in the atmosphere, with total NH₃ emissions doubling from
1860 to 1993 and possibly doubling again by 2050 (Krupa, 2003; Galloway et al., 2004; Clarisse et al., 2009) mainly driven
by the increasing use of fertilizers. Recent advances in satellite remote sensing have resulted in a better knowledge of global
NH₃ concentrations, however, uncertainties in the total NH₃ budget, along with the specific emission sources across different
spatial scales, remain high mainly due to the lack of observations on land (Clarisse et al., 2009; Behera et al., 2013; Sutton et
60 al., 2013).

The number and size of the world's cities is increasing, with some of them becoming megacities, hosting more than 10
million inhabitants. The urban population worldwide is expected to continue this increase in the coming years, adding about
ten more megacities by 2030 (United Nations, 2018). These massive concentrations of people and their activities present



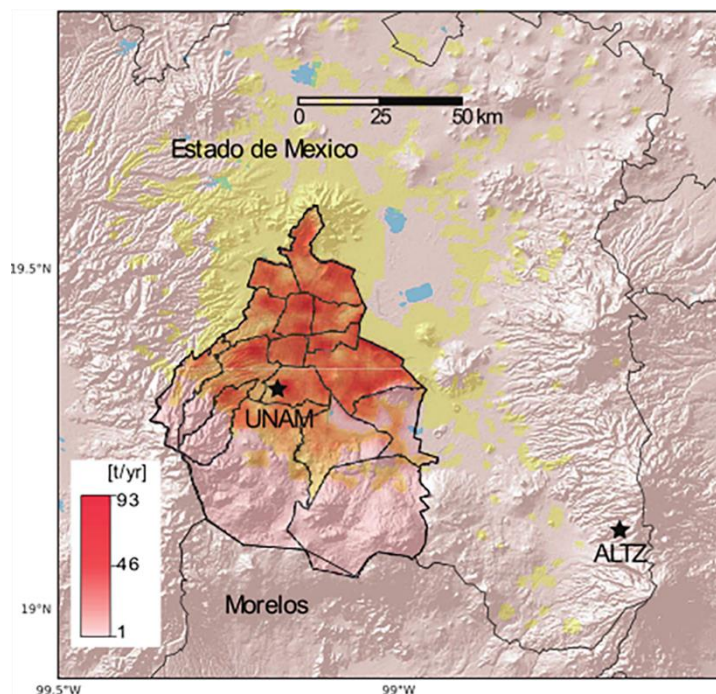
65 significant challenges for the global environment, especially in terms of air pollution, climate, and human health. One of the
largest metropolitan areas in the world, and the largest in North America, is the Mexico City Metropolitan Area (MCMA), a
megacity of >21 million inhabitants that presents poor air quality during many days of the year. It is located in a basin
surrounded by mountains and volcanoes, complicating the ventilation of the polluted air (Molina et al., 2020) that is
dominated by the dynamics of the boundary layer (Stremme et al., 2013; Dammers et al., 2016). The Mexico City Emissions
Inventory for 2016 (SEDEMA, 2018), reports that the MCMA hosts almost 6 million vehicles and 2300 regulated industries,
70 and emits a total of 14895 tonnes of NH_3 /yr only in the Mexico City's area and 47717 tonnes of NH_3 /yr in the MCMA,
including part of the Estado de Mexico. According to the inventory, 0.1% of NH_3 emissions in Mexico City are coming from
“point sources” such as industry, 6% from “mobile sources” such as vehicles, and 94% from “area sources” including urban
waste (0.12%), agriculture (1.66%), livestock (2.42%) and other (89%); within the other category are: urban and forest fires
and paved and unpaved roads. The inventory also strongly attributes the NH_3 sources to a range of population activities and
75 feces from domesticated animals. Despite the frequent pollution episodes due to PM, the local government has not
implemented policies regulating NH_3 emissions.

A few studies have investigated atmospheric NH_3 in the Mexico City area. Surface NH_3 concentrations between 10 and 40
ppbv were measured using an open-path Fourier transform infrared (FTIR) spectrometer, with the highest mixing ratios
observed in the morning hours during a two-month period (Moya et al., 2004). FTIR- NH_3 time series between 2012 and
80 2015 contributed to a validation study of Infrared Atmospheric Sounding Interferometer (IASI) (Dammers et al., 2016) and
Cross-track Infrared Sounder (CrIS) (Dammers et al., 2017) NH_3 satellite products. In terms of NH_3 emissions in Mexico
City, Yokelson et al. (2007) reported NH_3 emission factors from forest fires in the mountains surrounding Mexico City in
2006 and Christian et al., (2010) reported emission factors from garbage burning and domestic and industrial biofuel use in
central Mexico. A more recent study by Cady-Pereira et al. (2017) investigated the impact of biomass burning events on
85 pollution over the MCMA using trace gas data, including NH_3 , from the Tropospheric Emission Spectrometer (TES)
instrument onboard the Aura satellite. That study concluded that biomass burning events can impact pollution levels in
Mexico City, specifically the south part of the MCMA and particularly during the March-April-May period. Recently,
Clarisse et al. (2019) and Viatte et al. (2022) reported NH_3 hotspots near Mexico City at Tochtepec (18.84°N, 97.80°W),
Ezequiel Montes (20.68°N, 99.93°W), and Tehuacan (18.45°N, 97.31°W), with all of them classified as agricultural sources.
90 Finally, Van Damme et al. (2021) reported an increasing trend of NH_3 over Mexico of $(2.5 \pm 1.5) \times 10^{13}$ molecules cm^{-2} yr^{-1}
using 11 years of IASI satellite data (2008-2018).

In this work, the diurnal and seasonal variability of NH_3 over Mexico City is investigated using datasets from two ground-
based FTIR spectrometers, including an extension of the FTIR- NH_3 total column time series of the station in Mexico City
used in Dammers et al. (2016), and of the FTIR- NH_3 total columns measured at Altzomoni, a remote high-altitude station
95 close to Mexico City, that are retrieved for the first time. The locations of these two sites are shown in Figure 1. The analysis



is complemented with IASI satellite observations over the region, and back-trajectories that were constructed for anomalous NH_3 columns detected at the urban site to assess the influence of local and remote sources.



100 **Figure 1:** Study area in central Mexico. Mexico City is shown in the middle, with the red shading corresponding to NH_3 emissions reported in the Mexico City Emissions Inventory 2016 (SEDEMA, 2008) in tons per year. The stars indicate the location of the UNAM and Altzomoni stations and the yellow shading indicates the extension of the MCMA.

2 Methodology

2.1 Ground-based FTIR stations and retrieval of NH_3 total columns

105 This study utilizes NH_3 total columns retrieved from solar absorption spectra measured with ground-based FTIR spectrometers at two sites in and around the MCMA. The urban FTIR station is located at the south of Mexico City within the campus of the Universidad Nacional Autónoma de México on the rooftop of the Instituto de Ciencias de la Atmósfera y Cambio Climático (UNAM, 19.33°N, 99.18°W, 2280 m.a.s.l.). A custom-built solar tracker directs solar radiation to the entrance of a FTIR spectrometer (Bruker Optik GmbH model Vertex 80) that has a maximum unapodized resolution of 0.06 cm^{-1} . The instrument is equipped with a KBr beamsplitter and two detectors (HgCdTe and InGaAs). The HgCdTe detector is
110 cooled with liquid nitrogen. For more details about this system, see Bezanilla et al. (2014). Measurements from the remote FTIR site were made at the Altzomoni Atmospheric Observatory (ALTZ, 19.12°N, 98.66°W, 3985 m.a.s.l.), a high-altitude station located 60 km from the UNAM urban site and within the Izta-Popo National Park surrounded by nature. This site is part of the Network for the Detection of Atmospheric Composition Change (NDACC) (De Mazière et al., 2018) contributing



115 data from a high-resolution FTIR spectrometer since 2012. This instrument (Bruker Optik GmbH model IFS 120/125 HR) can record solar spectra with a maximum spectral resolution of 0.0035 cm^{-1} , and is equipped with KBr and CaF_2 beamsplitters and HgCdTe, InSb, and InGaAs detectors. For details of the site and the instrument see Baylon et al. (2017).

120 The FTIR spectra used for the retrieval of NH_3 were collected with the HgCdTe detector at both sites with a spectral resolution of 0.005 cm^{-1} at Altzomoni, and 0.1 cm^{-1} (prior to 2014) and 0.075 cm^{-1} at UNAM, using an optical band pass filter to enhance the region between 700 and 1400 cm^{-1} . In this study, we extend the UNAM time series used in a previous 2012-2015 comparison between IASI and FTIR (Dammers et al., 2016) with improvements to the retrieval, and we present for the first time, Altzomoni FTIR- NH_3 retrievals for the period between April 2012 and May 2020. The analysis presented here focuses on the region around the MCMA, also using the IASI satellite product and a back-trajectory evaluation, as described below.

125 For both sites, the solar FTIR spectra were analysed using PROFFIT version 9.6 for the retrievals (Hase et al., 2004) to obtain the NH_3 total columns. A retrieval strategy based on that reported by Dammers et al. (2015) was used, comprising two microwindows (929.1 - 931.8 and 963.7 - 970.0 cm^{-1}) to cover the NH_3 absorption lines from the ν_2 vibrational band in the mid-IR region. The trace gases H_2O , CO_2 , O_3 , CO and N_2O were taken into account as interfering species for the retrieval for both stations, and the temperature and pressure profiles were obtained from the US National Centers for Environmental Prediction (NCEP). Spectroscopic parameters were obtained from the high-resolution transmission molecular absorption 130 database HITRAN 2008 (Rothman et al., 2009), and the *a priori* profile information about the interfering gases was obtained from 40-year averages of simulations from the Whole Atmosphere Community Climate Model (WACCM) (Eyring et al., 2007; Marsh et al., 2013). Since NH_3 profiles are not available from WACCM, scaled *a priori* profiles derived from the global chemical transport model GEOS-Chem v11 NH_3 were used instead. Constructed scaled *a priori* profiles have been used previously from GEOS-Chem simulations for the retrieval of trace gases (Shephard et al., 2011; Shephard and Cady- 135 Pereira, 2015; Bader et al., 2017). A total of 7992 NH_3 columns were retrieved for the UNAM station and 4031 for ALTZ. The resulting uncertainties obtained with PROFFIT averaged over the entire time series in molecules/ cm^2 at UNAM were 1.25×10^{15} (random), 8.40×10^{14} (systematic), and 1.52×10^{15} or 11.50% (total); and 3.09×10^{14} (random), 3.14×10^{14} (systematic), and 4.42×10^{14} or 51.37% (total) at ALTZ. The average degrees of freedom for signal (DOFS) averaged over the entire time series were 2.03 for UNAM and 1.04 for ALTZ.

140 2.2 IASI- NH_3 data product and comparison methodology

IASI measures the infrared thermal radiation emitted by the Earth's surface and the atmosphere from a Sun-synchronous orbit on board the MetOp platform. Spectra are recorded in the 645 - 2760 cm^{-1} spectral range at a spectral resolution of 0.5 cm^{-1} (Clerbaux et al., 2009). The instrument crosses the equator at mean local solar times of 09:30 and 21:30, providing global coverage of the Earth twice a day. IASI has a field-of-view composed of four circular footprints each with a diameter



145 of 12 km at the nadir view and up to 20 km x 39 km elliptical pixels outside the nadir depending on the satellite viewing
angle, complemented by scanning along a swath width of 2200 km off-nadir perpendicular to the ground track (Clarisse et
al., 2009; Van Damme et al., 2014, 2015). The IASI-NH₃ retrieval products are based on Artificial Neural Networks (ANNI)
that link the Hyperspectral Range Index (HRI, a dimensionless index that represents the amount of NH₃ in the column), to
other parameters such as temperature, pressure, and humidity profiles, to derive the NH₃ total column (Van Damme et al.,
150 2014, 2017; Whitburn et al., 2016). The retrieval scheme does not produce averaging kernels, however, under conditions of
high NH₃ and a favourable thermal contrast, IASI has maximum sensitivity to NH₃ in the boundary layer (Clarisse et al.,
2010). An error estimate is provided with each individual IASI observation. IASI's average detection limit for NH₃ under
large thermal contrast is about 3 ppbv, and can be as low as 1 ppbv under conditions of well-mixed NH₃ throughout a thick
boundary layer (Clarisse et al., 2010).

155 For this study, eleven years of the IASI-A NH₃ total columns (ANNI-NH3-v3) between 2008-2018 were used; details of this
version 3 can be found in Appendix A of Van Damme et al. (2021), and was also used by Yamanouchi et al. (2021) and
Viatte et al. (2022). The spatial distribution of NH₃ over Mexico City was obtained by averaging all the IASI-A morning
observations between January 2008 and December 2018 over this region. The FTIR-NH₃ total columns at UNAM were
compared against the IASI-NH₃ total columns over Mexico City to assess the agreement between both data sets. Due to the
160 high spatiotemporal variability of NH₃, the temporal and spatial coincidence criteria were tested and assessed using the
correlations (both *R* and slope). In addition, as suggested in Dammers et al. (2016), an elevation filter (FTIR station altitude
minus IASI observation < 300 m) was applied. The criteria resulting in the best correlations were elevation filter < 300 m,
spatial sampling difference < 20 km, maximum temporal sampling difference ± 40 min, and maximum IASI-NH₃ retrieval
error of 100%. The seasonal variability comparison and annual averages were performed using only FTIR-NH₃ retrievals
165 between 9:00 and 10:59 a.m. (Local Time), corresponding to the IASI overpass time over Mexico City, and the < 20 km
spatial criterion for IASI-NH₃ total columns. Alzomoni correlation plots with IASI-NH₃ data were not included due to the
few coincidences between the FTIR and IASI, a consequence of the station's high-altitude location.

2.3 Back-trajectory analysis

To determine the primary sources of NH₃ measured at the UNAM station and to assess the dominant atmospheric transport
170 pathways during the events with the largest NH₃ columns in the time series, trajectory cluster analysis (Reizer and Orza,
2018) was applied. The 8-hour back-trajectory was selected to capture only air masses traversing the MCMA. Using the
UNAM station as the receptor, back-trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated
Trajectory (HYSPLIT) model (Stein et al., 2015, Draxler et al., 1997) at 100 m above the UNAM station level (2280
m.a.s.l.). The 100 m cluster was considered the most representative because NH₃ is more concentrated near the surface.



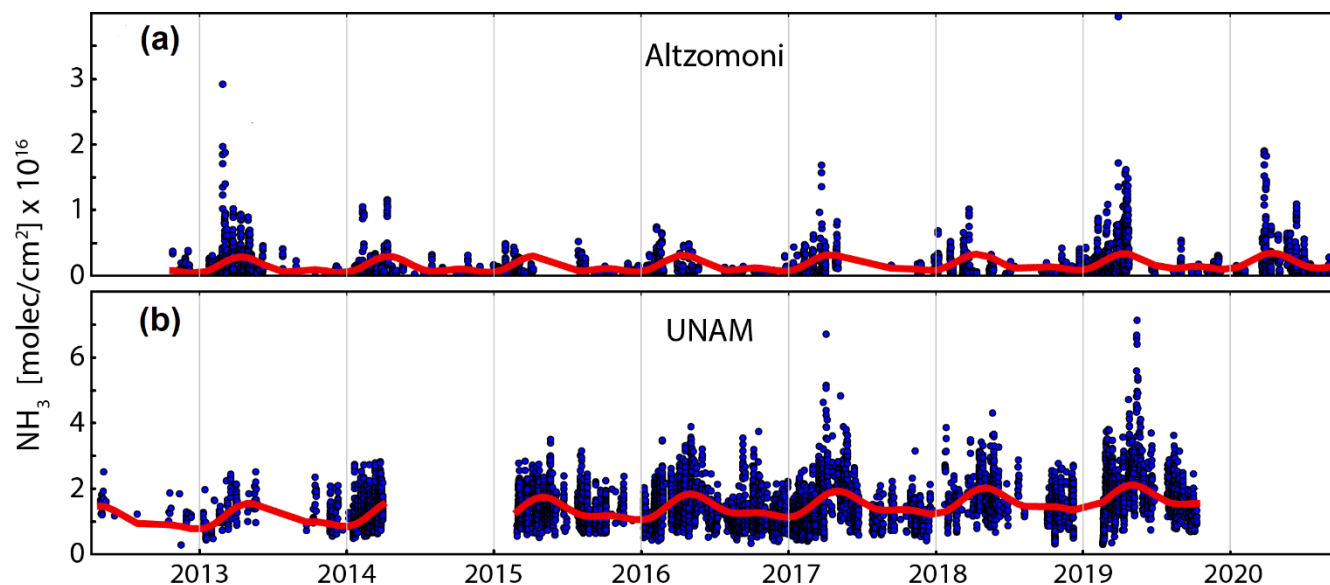
175 3 Results and Discussion

3.1 FTIR-NH₃ time series and temporal variability

The NH₃ total column time series retrieved at both FTIR stations are shown in Figure 2. The urban UNAM columns, shown in the top panel, are about one order of magnitude larger than the high-altitude Altzomoni columns. The entire period average NH₃ total columns of $1.46 \times 10^{16} \pm 0.64$ molecules/cm² measured at UNAM and $1.87 \times 10^{15} \pm 2.40$ molecules/cm² at Altzomoni are listed and compared to values reported for stations in other parts of the world in Table 1. The Mexico City NH₃ total columns are comparable with those reported in Bremen, while they are about twice as large as those measured at Toronto (Canada), Paris (France), and Lauder (New Zealand). Jungfraujoch, a remote high-altitude station in Switzerland with similar characteristics to Altzomoni, presents a significantly lower average NH₃ column and also has much lower variability. The reason for this might be that Altzomoni is impacted more frequently by biomass burning events in the dry season and also by the regional boundary layer, receiving polluted air from Mexico City and other large urban centres in the afternoon (Baumgardner et al., 2009).

Table 1: Mean NH₃ total columns reported from ground-based FTIR stations.

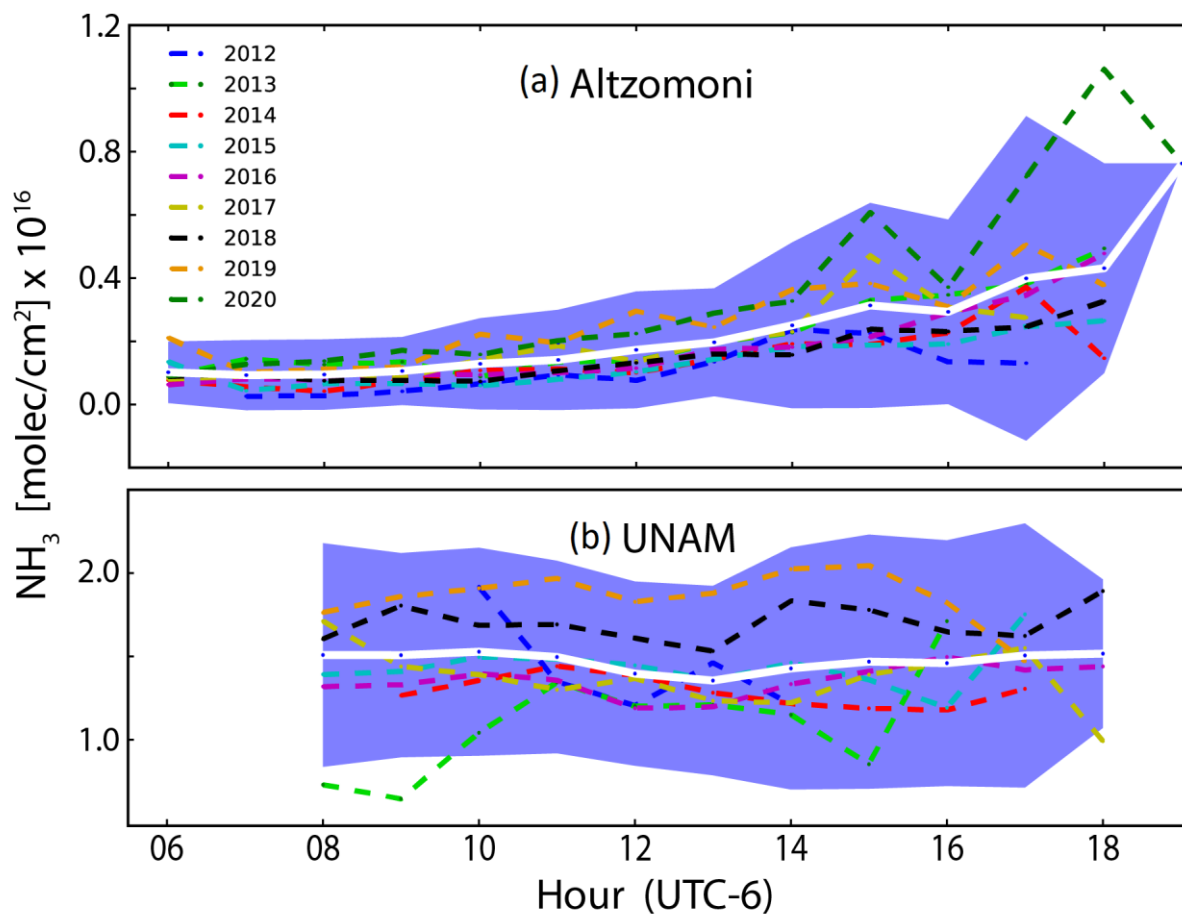
Station	Location	Time period	Average NH ₃ total column (molecules/cm ²) x 10 ¹⁵	Station characteristics	Reference
Bremen, Germany	53.10° N, 8.85° E 27 m.a.s.l	2004-2013	13.7 ± 4.24	Urban, fertilizers, livestock	Dammers et al. (2015)
Paris, France	48.79°N, 2.44°E, 56 m.a.s.l	2009-2017	8.4 ± 8.6	Urban, surrounding agricultural sources	Tournadre et al., (2020)
Jungfraujoch, Switzerland	46.55°N, 7.98°E, 3580 m.a.s.l	2004-2013	0.18 ± 0.07	Remote and high altitude, no large sources	Dammers et al. (2015)
Toronto, Canada	43.66°N, 79.40°W, 174 m.a.s.l	2002-2005	5.94 ± 5.14	Urban, fertilizers, biomass burning	Yamanouchi et al. (2021)
		2015-2018	8.13 ± 7.88		
UNAM, Mexico	19.33°N, 99.18°W, 2280 m.a.s.l	2012-2019	14.6 ± 6.39	Urban, large sources	This study
Altzomoni, Mexico	19.12°N, 98.66°W, 3985 m.a.s.l	2012-2020	1.87 ± 2.40	Remote and high altitude, no local sources, biomass burning	This study
Reunion, Indian Ocean	20.90°S, 55.5°E, 85 m.a.s.l	2004-2012	0.80 ± 0.54	Remote, fertilizers, fires	Dammers et al. (2015)
Lauder, New Zealand	45.04°S, 169.68°E, 370 m.a.s.l	2004-2014	4.17 ± 1.40	Remote, fertilizer, livestock	Dammers et al. (2015)



190 **Figure 2:** Time series of retrieved FTIR-NH₃ data over (a) Altzomoni and (b) UNAM, with a fitted Fourier series (red) to reproduce seasonality. Note the differences in magnitude.

Figure 2 also shows the fit of a Fourier series (Baylon et al., 2017) to reproduce seasonality in both stations. A clear cycle is seen at both stations, with a maximum between mid and late April, and a minimum in late December. However, the difference between the minimum and the maximum is larger at Altzomoni, with UNAM having greater NH₃ background concentrations. The average annual increase in the NH₃ columns obtained from the Fourier fit are $92 \pm 3.9 \times 10^{13}$ molecules/cm² yr at UNAM and $8.4 \pm 1.4 \times 10^{13}$ molecules/cm² yr at Altzomoni. Van Damme et al. (2021) reported a trend from 2008 to 2018 of $2.5 \pm 1.5 \times 10^{13}$ molecules/cm² yr for all of Mexico, which is closer to the Altzomoni value. The difference in magnitude can be attributed to the datasets and methodology as the present study uses ground-based FTIR measurements from two sites with higher values in 2019 and 2020, while Van Damme et al. (2021) used IASI satellite data over a wider region between 2008 to 2018.

The average diurnal variability of the FTIR NH₃ total columns at both stations is displayed in Figure 3. The largest average NH₃ columns at the urban station are on the order of 1.50×10^{16} molecules/cm² and were observed during the morning and the evening. Although the diurnal pattern is not as evident as in other cities where motor vehicles have been found to be a dominant source of urban NH₃ (e.g., Osada et al., 2019; Kotnala et al., 2020), traffic emissions in Mexico City still might play a role in conjunction with other urban sources of atmospheric NH₃. The average NH₃ columns at UNAM have a minimum of 1.35×10^{16} molecules/cm² at 13h, which can be attributed to the conversion to ammonium as was observed by Moya et al. (2004) that reported the surface gas phase NH₃ and PM NH₄⁺ evolution at an urban site in Mexico City.



210 **Figure 3:** Average diurnal evolution of NH_3 total columns over Mexico City at (a) Altzomoni and (b) UNAM. Different years are shown in different colours, the thick white line is the average for all years, and the blue shading indicates $\pm 1\sigma$.

The diurnal cycle at the remote station (Figure 3a) is noticeably different, with NH_3 columns that increase systematically as the day progresses, with the largest variability in the afternoon hours. Altzomoni is located within a natural protected area with few local sources of NH_3 , and even less so during the morning hours when values are around 0.10×10^{16} molecules/cm², when cooler temperatures do not favour the volatilization of NH_3 . The columns increase throughout the day, 215 having the largest average values of 0.76×10^{16} molecules/cm² in the evening, probably transported from lower altitudes by the dynamics of the regional boundary layer (Baumgardner et al., 2009). This is supported by the large variability observed in the afternoon, since the probability that NH_3 is transported $> 1,700$ m a.g.l. (above ground level) up to this site strongly depends on the meteorological conditions, which vary from day to day. Comparisons between daily average NH_3 columns and the daily averages of some meteorological variables from the RUOA Network (Red Universitaria de Observatorios 220 Atmosféricos) such as temperature, relative humidity (RH), precipitation, and solar radiation, resulted in weak correlations (r between 0.1-0.3). However, these correlations were positive with temperature and solar radiation, and negative with RH and



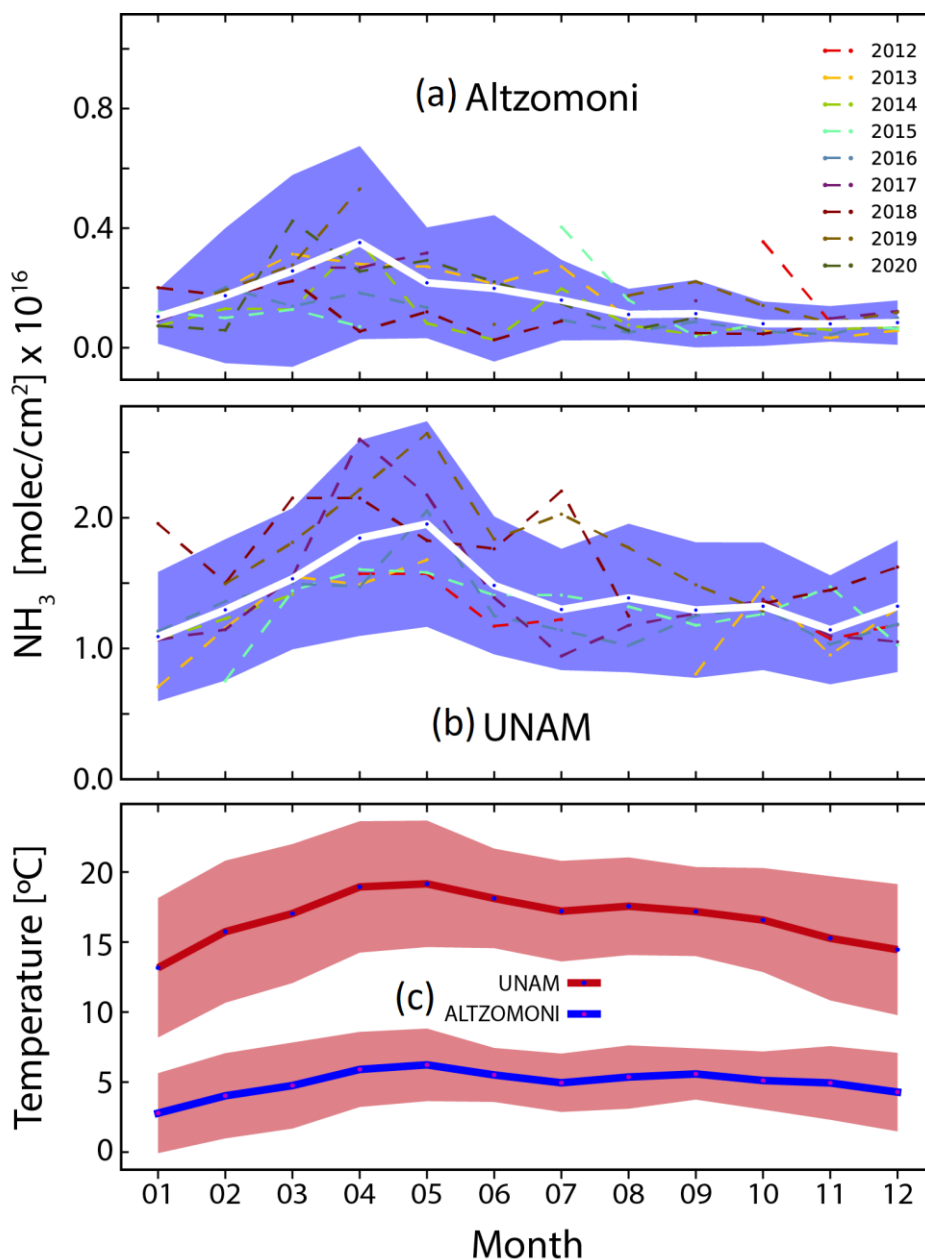
precipitation. The average wind speed for Altzomoni is 4.5 m/s, with dominant winds from the east-southeast and west-northwest, while the average wind speed for UNAM is 1.6 m/s, with dominant winds from the north and the north-northwest.

The seasonal variability of the FTIR NH_3 total columns is shown in Figure 4. In general, the pattern is similar at both stations, showing the NH_3 temperature dependence with larger NH_3 columns in the months of March, April, and May which correspond to the warm-dry season; this season usually has days with clear skies, weak winds, high pressure systems, and biomass burning events (Molina et al., 2020), and also corresponds to the most critical part of the fire season in Mexico City (CENAPRED, 2021; Yokelson et al., 2007). In addition, there are two agricultural seasons in the country, the first one from April to September and the second one from October to March. The fertilizer application combined with meteorological conditions could favour NH_3 volatilization from the agricultural sources contributing to the higher NH_3 spring columns observed in Figure 4. Smaller columns are clearly observed during the wet season (June to October), due to the increase in wet deposition, and during the cold-dry season from November to February, due to less favorable conditions for NH_3 volatilization. This is in agreement with Viatte et al., (2022). The annual cycle of NH_3 columns at the urban UNAM station is similar to that observed at the background Altzomoni station but has a larger amplitude. A study by Sun et al. (2017) observed that the growing efficiency of three-way catalysts in motor vehicles is responsible for large NH_3 emissions detected in urban locations in the USA and China. These emissions are strongly dependent on traffic volume and thus should not have a strong seasonality. On the other hand, emissions originating from agricultural activity usually have a distinct seasonality that depends on the fertilizer application and temperature (Sun et al., 2017; Van Damme et al., 2015, Viatte et al., 2022). In the current study, the annual cycles follows the pattern of temperature (Figure 4c), indicating that emissions from other sources, such as fires, waste treatment, human or pets emissions, may be contributing significantly to the NH_3 detected over the MCMA.

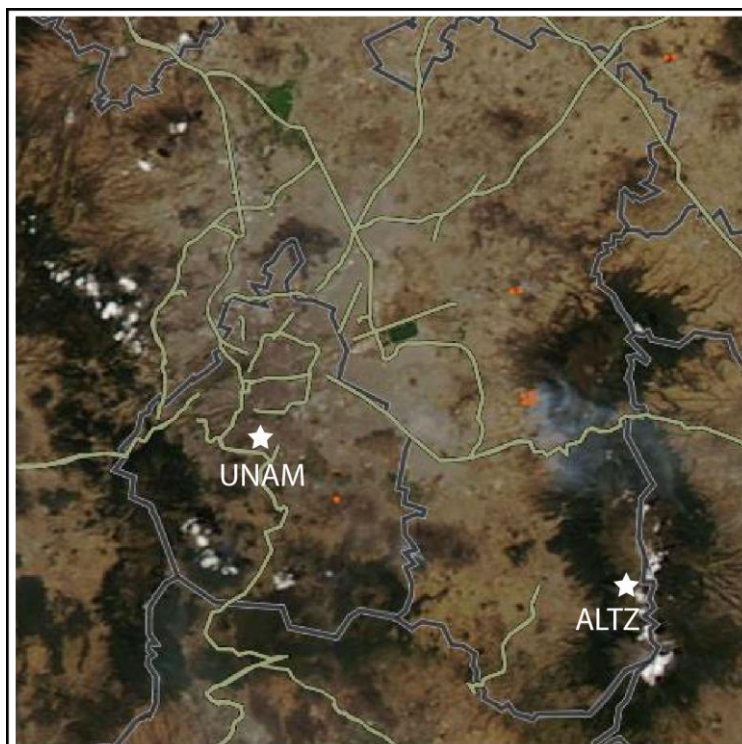
There are more features to note in Figure 4. While Altzomoni and UNAM NH_3 columns have similar annual cycles, those at Altzomoni have greater variability throughout the different years during the warm-dry season than during the rest of the year. This might be due to the strong relationship between pollutants reaching the high-altitude station and the boundary layer dynamics and wind conditions, which are more variable during the warm-dry season. However, another contribution to this variability may be biomass burning activity, which has a maximum during the warm-dry months as has been shown by Cady-Pereira et al. (2017). The 2013 pollution events presented by Cady-Pereira et al. (2017) are seen on April 23, May 9, and May 25 in Figure 2, with May 9 having the largest enhancements at Altzomoni; unfortunately, there are no coincident measurements for UNAM. At Altzomoni, the average NH_3 column for May 9, 2013 was $2.39 \pm 0.53 \times 10^{15}$ molecules/cm², which is 28% greater than the average column for the entire period (Table 1). However, in 2013, the largest NH_3 column measured at Altzomoni was on the evening of February 27 with an average value of $17.4 \pm 0.58 \times 10^{15}$ molecules/cm², almost ten times higher than the average column presented in Table 1. This enhancement on February 27, 2013 seems to be local and of short duration, most likely due to a nearby biomass burning event. This is supported by the detection of active



fires northwest of the site on that date by the MODIS instrument on Aqua as shown on Figure 5. With its high altitude and
255 few local sources, Altzomoni seems to be more sensitive for the detection of pollution events than UNAM. Even if the fires
are not occurring nearby, the increased lifetimes of emitted pollutants at these altitudes may favour transport over longer
distances to Altzomoni.



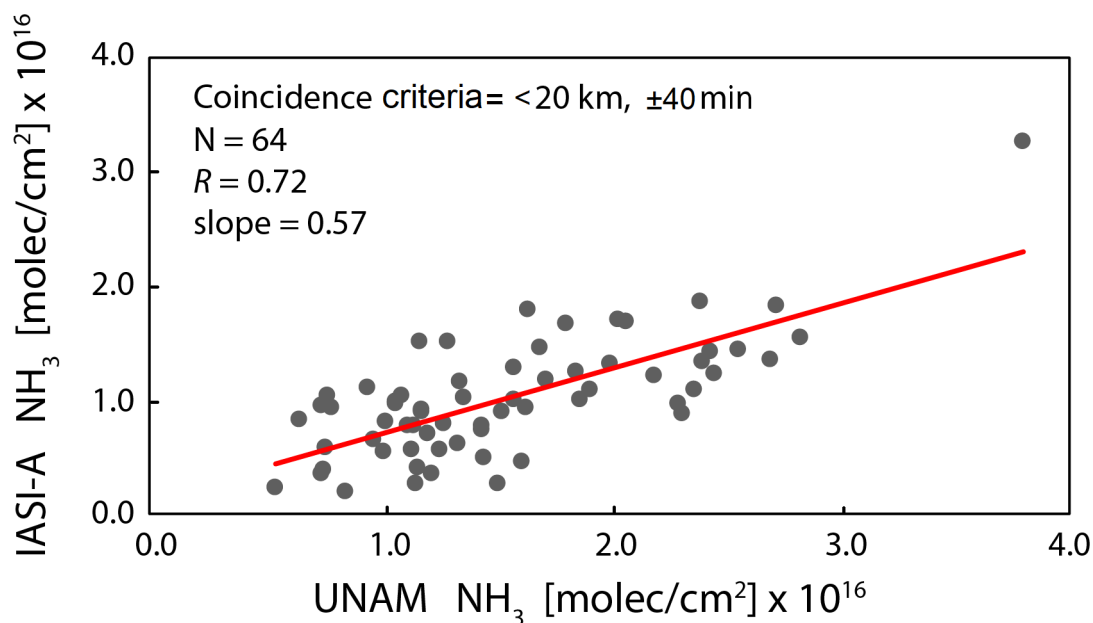
260 **Figure 4:** Monthly averages showing annual cycle of NH_3 over Mexico City at (a) Altzomoni and (b) UNAM. The thick white line is the average for all years and the shading indicates $\pm 1\sigma$. (c) Monthly averages of temperature at both stations between 2014-2018 for Altzomoni and 2012-2018 for UNAM. The shaded area indicates $\pm 1\sigma$.



265 **Figure 5:** Snapshot of Mexico's City fire events on February 27, 2013, from the Aqua MODIS instrument with true colour corrected reflectance and resolution of 250 m, obtained from NASA Worldview Snapshots (<https://earthdata.nasa.gov>). The red dots show the fire events. The stars indicate the location of the UNAM and Alzomoni stations.

3.2 Satellite observations: comparison with ground-based measurements and spatial distribution

The correlation between IASI-NH₃ and the ground-based FTIR-NH₃ total columns at UNAM from Nov 2013 to Dec 2018 is shown in Figure 6. The coincidence criteria are described in Sect. 2.2, and are based on values used in previous validations of IASI products using ground-based FTIR data (Dammers et al., 2016), including an elevation correction using the Space Shuttle Radar Topography Mission Global Product at 3 arcsec resolution over Mexico City (SRTMGL3, Farr et al., 2007). A total of 64 coincident data pairs were found, from which a correlation coefficient $R = 0.72$ and a mean relative difference (MRD) of $-32.2 \pm 27.5 \%$ were obtained ($\pm 1\sigma$). These results are consistent with $R = 0.64$ and $\text{MRD} = -30.8 \pm 43.9 \%$ reported by Dammers et al. (2016) for this region using an older version of the IASI-NH₃ product. The correlation is also similar to that of Tournadre et al. (2020), who obtained $R = 0.79$, when comparing IASI-NH₃ to FTIR-NH₃ columns using a similar instrument (Vertex 80) in Paris, and to the $R = 0.80$ and $\text{MRD} = -32.4 \pm 56.3 \%$ reported for 547 coincidences from several ground-based FTIR stations and IASI-NH₃ (Dammers et al., 2016). The IASI ANNI-NH₃-v3 product is thus in agreement with the ground-based data and even presents an improved correlation compared to the previous result. However, an underestimation in the IASI-NH₃ total columns of approximately 32% over Mexico City persists, for reasons that need to be investigated further.



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Figure 6: Correlation plot for IASI-A NH_3 vs. UNAM FTIR- NH_3 total columns, with coincidence criteria of < 20 km, \pm 40 minutes, elevation (FTIR station – IASI observation) < 300 m, IASI- NH_3 retrieval error < 100% between Nov 2013 and Dec 2018.

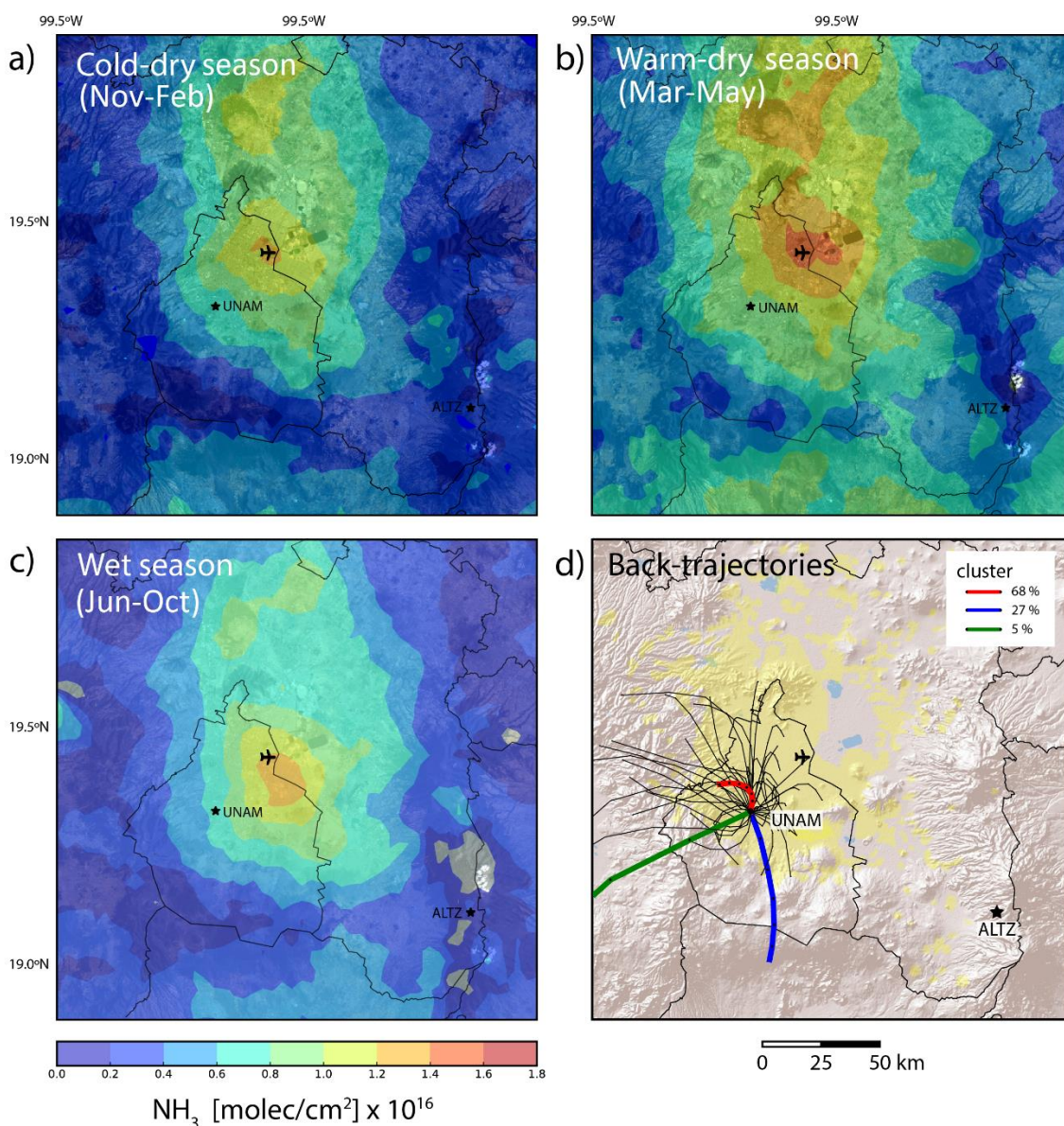
The spatial distribution of NH_3 over MCMA as observed by IASI is presented in Figure 7. The distribution shows a clear NH_3 enhancement in the northeast section of Mexico City and in part of the Estado de México region. There are several potentially important sources located in this area: Mexico City International Airport, an area of continuous traffic emissions; the Bordo Poniente compost plant, which treats around 1500 tons of daily organic waste from the city; wastewater discharge and treatment bodies with nearby bird colonies such as the regulation lagoon Cola de Pato; and the agricultural area at Texcoco. The combination of these factors, along with the high population density of this area, are likely to be cause of the NH_3 enhancements observed in this part of the city. This enhancement is partially in agreement with the location of the larger NH_3 emissions reported in the Mexico City Emissions Inventory of 2016 (SEDEMA, 2018) shown in Figure 1 in the northern part of the city, which is mainly associated with population activities and domestic animals' excreta. Figure 7d will be discussed in Section 3.3.

Figures 7a-c show the variations of NH_3 over the year, with the largest columns measured during the warm-dry season and to the northeast of UNAM. In contrast, the NH_3 columns are reduced in the wet season when wet deposition can occur, and are smallest during the cold-dry season, when there are lower temperatures and less NH_3 volatilization. To investigate the influence of local topography on the NH_3 distribution, Figure 8 compares the average IASI- NH_3 total column spatial distribution (a) with altitude (b). The figure illustrates that the highest columns are located at the lowest altitudes while the lowest columns are at higher altitudes, reflecting the source locations and the boundary layer dynamics. The figure shows that the main NH_3 sources in MCMA are located in the most urbanized areas in Mexico City and Estado de Mexico at an altitude of around 2250 m. These urban emissions agree with the statement of Li et. al. (2020) that human NH_3 emissions

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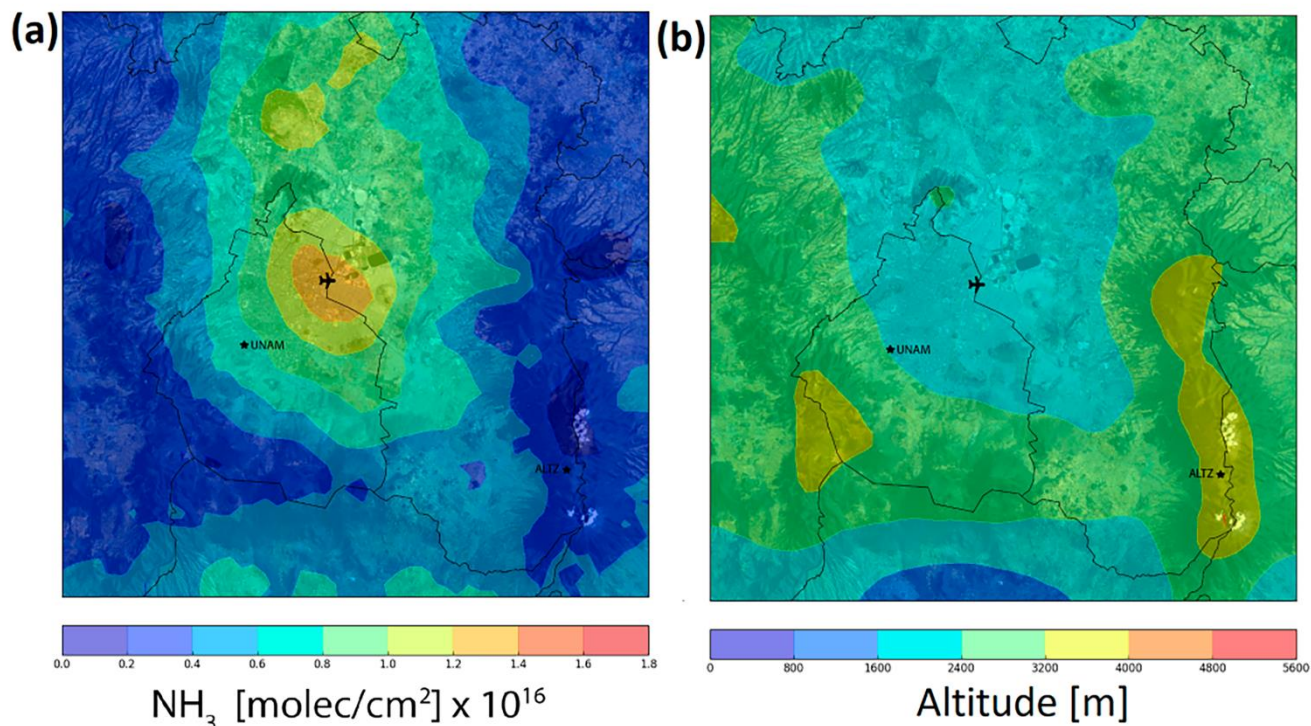


contributing significantly to the total NH_3 emissions in hot and highly populated urban areas such as Mexico City. A rough estimation using 25 °C as an average diurnal temperature for Mexico City and the 0.4 mg of NH_3 per hour at 25 °C from Li et. al. (2020) resulted in an estimate of 34 tonnes of NH_3 per year, a contribution of the same order of magnitude as all the “point sources” and “urban waste” combined according to the Mexico City Emissions Inventory for 2016 (SEDEMA, 2018).



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Figure 7: Spatial distribution of IASI-A NH_3 total columns for the morning overpass of MetOp-A over Mexico City, averaged over 2008–2018 for: (a) the cold-dry season (November – February), (b) the warm-dry season (March–May), and (c) the wet season (June–October). HYSPLIT back-trajectories for the UNAM site are shown in panel (d). The black stars indicate the locations of both stations, and Mexico City International Airport is shown for reference.

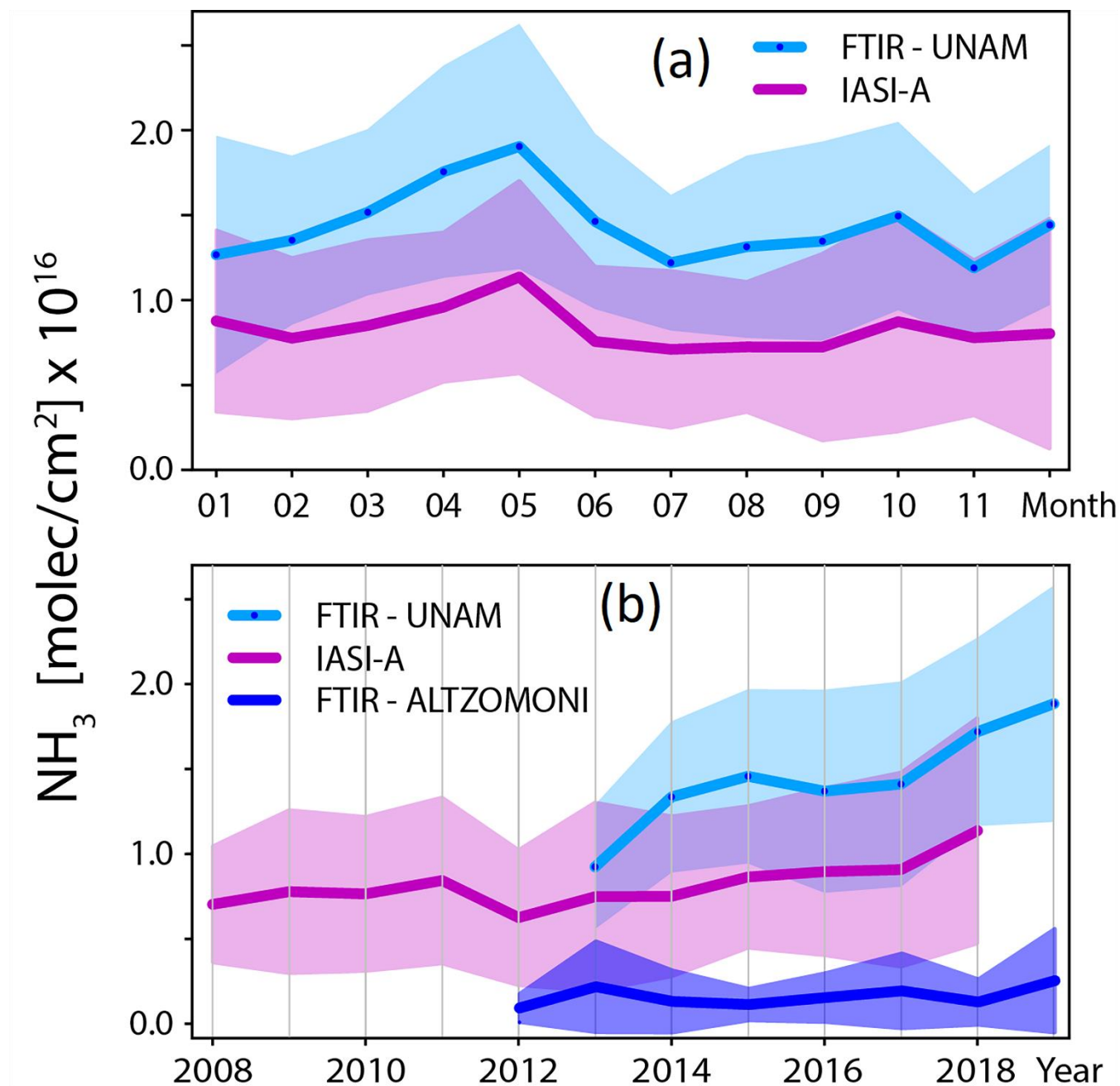


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Figure 8: Spatial distribution of (a) IASI-A NH₃ total columns for the morning overpass of MetOp-A over Mexico City, averaged over 2008-2018 (b) altitudes in Mexico City from the Space Shuttle Radar Topography Mission Global product City (SRTMGL3, Farr et al., 2007). The black stars indicate the location of ground-based stations, and Mexico City International Airport is shown for reference.

Comparisons between the NH₃ seasonal variability and time evolution over the UNAM station in Mexico City were performed using morning (9-11 h) FTIR-NH₃ columns and IASI-NH₃ columns with a spatial criterion of < 20 km from the UNAM station (Figure 9a). The NH₃ seasonal variability over Mexico City in Figure 7a, is similar for both the IASI and ground-based FTIR NH₃ columns and is in agreement with Figure 4. However, the IASI-NH₃ shown a consistent negative bias. The time evolution is represented with the IASI-NH₃ and FTIR-NH₃ annual averages in Figure 9b. The datasets suggest an increasing trend in the annual averages of the NH₃ total columns, with larger columns observed in the most recent years, even in Altzomoni except for 2013, which was affected by the February 27 event as discussed previously. Comparing the average IASI-NH₃ columns (using the < 20 km spatial criteria) for 2008 ($7.03 \times 10^{15} \pm 3.41 \times 10^{15}$ molecules/cm²) vs. 2018 ($11.4 \times 10^{15} \pm 6.64 \times 10^{15}$ molecules/cm²), there is an increment of 62 % over a decade for Mexico City. This positive increment agrees with the trend of $8.4 \pm 5.2 \%$ 10 yr⁻¹ reported by Van Damme et al. (2021) for all of Mexico.

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325 **Figure 9:** IASI and FTIR NH_3 total columns with coincidence criteria of < 20 km and < 2 hr: (a) monthly averages at UNAM, (b) diurnal annual averages at UNAM and Altzomoni. The shaded area indicates $\pm 1\sigma$.



3.3 Back-trajectory analysis and origin of observed NH₃ in Mexico City

A cluster analysis was applied using 8-hour back-trajectories 100 m above UNAM station to identify the main transport pathways for air masses arriving at UNAM station that correspond to the highest average hourly NH₃ total columns (Figure 7d). The Total Spatial Variance (TSV) method (Draxler et al., 2021) was used to fit the number of clusters, which was set to three in order to represent the primary trajectories. It was found that 68% of the trajectories originate from the north (red line with black dots), 27% from the west-southwest (green line), and 5 % from the south (blue line). However, by looking at the individual back-trajectories of the red cluster (the black-thin lines in Figure 7d), it is seen that most of the NH₃ detected at UNAM comes from a variety of local sources and does not suggest that NH₃-enriched air masses are being transported to the urban station only from the enhancement region to the northeast observed in Figures 7a to 7c. This is in agreement with Viatte et al. (2022). The relationship between the back-trajectories and measured NH₃ columns can be explained by the fact that Mexico City is located in a basin; the wind fields are constricted in this basin and in general they are breeze winds (6 km/h). Under these conditions, small locally distributed NH₃ urban emissions seem to be the main cause of the high column values of this pollutant measured at the UNAM station, this agrees with Figure 8 where the main NH₃ sources in MCMA are seen to be urban.

3 Conclusions

This work presented the temporal and spatial distribution of NH₃ total columns over the Mexico City Metropolitan Area derived from two ground-based FTIR spectrometers and IASI satellite observations. The average NH₃ total column at the urban UNAM site ($1.46 \pm 0.64 \times 10^{16}$ molecules/cm²) is considerably higher than that at the remote station Altzomoni ($1.87 \pm 2.40 \times 10^{15}$ molecules/cm²), with a clear difference in the diurnal cycle but similar seasonal variability. NH₃ spatial distribution from IASI shows the highest NH₃ columns in the northeast part of the city, an area surrounded by water bodies, a landfill, a compost plant for the treatment of all the organic waste, and the airport. The IASI ANNI-NH₃-v3 data product underestimates the NH₃ total columns over Mexico City, with a mean relative difference of 32%, over the period 2008-2018 but showed a similar temporal variability and a good correlation with FTIR measurements ($R=0.72$). The analysis of back-trajectories for the largest NH₃ enhancement events suggests that most of the NH₃ measured at the urban station is coming from local sources. The NH₃ observed at the remote site is most likely transported from the surroundings and it is influenced by biomass burning events. These results present evidence that sources other than from agriculture, such as motor vehicles, fires, human emissions, domestic animals, water discharge, and waste, have a significant contribution to the total NH₃ budget in the city. In general, an average annual increase is observed in Mexico City from both ground-based stations ($92 \pm 3.9 \times 10^{13}$ molecules/cm² yr at UNAM, $8.4 \pm 1.4 \times 10^{13}$ molecules/cm² yr at Altzomoni) and IASI (62 % / 10 yr⁻¹). A complementary study using surface NH₃ and PM concentrations from passive samplers and microsensors around this region is in progress. These observations, together with model data, will examine the role of reactive nitrogen in the pollution of Mexico City. A reevaluation of NH₃ emission sources contribution in the Mexico City inventory is suggested. Measures to



mitigate NH₃ emissions and reduce these positive trends are important, given that NH₃ is closely linked to secondary aerosol
360 formation and the deterioration of ecosystems.

Data availability: The UNAM and Alzomoni FTIR data used in this study are available from the correspondent author upon
request (beatriz.herrera@mail.utoronto.ca). The meteorological data for both FTIR stations are available at
<https://www.ruoa.unam.mx/>. The IASI ANNI-NH₃-v3 L2 data can be access at <https://iasi.aeris-data.fr/NH3/>. MODIS active
fire snapshots are available at <https://wvs.earthdata.nasa.gov/>. The code of the HYSPLIT model can be obtained from
365 <https://www.arl.noaa.gov/hysplit/getrun-hysplit/>. Last access to all URLs: 11 March 2022.

Competing interests: The authors declare that they have no conflict of interest.

Author contributions

BH is the main author of the paper, analyzed the data, made most of the figures, and wrote the text. WS contributed to the
data analysis. MG contributed to create some figures. AM contributed with the back-trajectory analysis. MG, KS, CR, FH,
370 TB, CV, ED, LC, and MVD contributed to the manuscript writing and provided support. AB provided technical support. ED
provided the Space Shuttle Radar Topography Mission Global product and support with the NH₃ retrievals. LC and MVD
developed the IASI-NH₃ product. CV and MVD provided the IASI data. All authors reviewed the manuscript.

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