10–year satellite–constrained fluxes of ammonia improve performance of chemistry transport models

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Abstract

In recent years, ammonia emissions have been continuously increasing being almost four times higher than in the 20th century. Although an important species as its use as a fertilized sustains human living, ammonia has major consequences both for humans and the environment, because of its reactive gas phase chemistry that makes it easily convertible to particles. Despite its pronounced importance, yet, ammonia emissions are highly uncertain in most emission inventories. However, the great development of satellite remote sensing nowadays provides the opportunity for more targeting research in constraining ammonia emissions. Here, we used satellite measurements to calculate global ammonia emissions over the period 2008–2017. Then, the calculated ammonia emissions were fed to a chemistry transport model and ammonia concentrations were simulated for the period 2008–2017.

The simulated concentrations of ammonia were compared with ground measurements from Europe, North America and Southeastern Asia, as well as with satellite measurements. The satellite-constrained ammonia emissions represent global concentrations more accurately than state-of-the-art emissions. Calculated fluxes in the North China Plain were seen more increased after 2015, not due to emission changes, but due to changes in sulfate emissions that resulted in less ammonia neutralization and hence in larger atmospheric loads. Emissions over Europe were also twice as much as those in traditional datasets with dominant sources to be industrial and agricultural applications. Four hot-spot regions of high ammonia emissions were seen in North America characterized by large agricultural activity, animal breeding, animal farms and animal breeding and agricultural practices. South America is dominated by ammonia emissions from biomass burning, which cause a strong seasonality. In Southeastern Asia, ammonia emissions from fertilizer plants in China, Pakistan, India and Indonesia are the most important, while a strong seasonality was observed with a spring and late summer peak due to rice and wheat cultivation. Measurements of ammonia surface concentrations were better reproduced with satellite-constrained emissions, so as measurements from CrIS (Cross-track Infrared Sounder).

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1 Introduction

Ammonia (NH_3) has received a lot of attention nowadays due to its major implications for the population and the environment (Erisman, 2004; Erisman et al., 2007). These include eutrophication of semi-natural ecosystems and acidification of soils (Stevens et al., 2010), secondary formation of particulate matter in the atmosphere (Anderson et al., 2003), and alteration of the global greenhouse balance (De Vries et al., 2011). More specifically in the troposphere, ammonia reacts with the abundant sulfuric and nitric acids (Malm, 2004) contributing 30 % to 50 % of the total aerosol mass of PM2.5 and PM10 (Anderson et al., 2003). Ammonium aerosols are therefore a very important component in regional and global aerosols processes (Xu and Penner, 2012) also having significant implications for human health (Aneja et al., 2009). Ammonia alters human health indirectly mainly through formation of PM2.5 (Gu et al., 2014) that penetrate the human respiratory systems and deposit in the lungs and alveolar regions (Pope III et al., 2002) causing premature mortality (Lelieveld et al., 2015). As regards to the climate impact, the same ammonium aerosol particles affect Earth's radiative balance, both directly by scattering incoming radiation (Henze et al., 2012) and indirectly as cloud condensation nuclei (Abbatt et al., 2006). They may also cause visibility problems and contribute to haze effect due to secondary PM formation.

Sources of ammonia include wild animals (Sutton et al., 2000), ammonia-containing watersheds (Sørensen et al., 2003), traffic (Kean et al., 2009), sewage systems (Reche et al., 2012), humans (Sutton et al., 2000), biomass burning (Sutton et al., 2008) and domestic coal combustion (Fowler et al., 2004), volcanic eruptions (Sutton et al., 2008) and agriculture (Erisman et al., 2007). The latter is responsible for the majority of ammonia global atmospheric emissions. Specifically, in the United States and Europe about 80% of all emissions is related to agriculture (Leip et al., 2015). Emissions have increased considerably since pre-industrial times and are unlikely to decrease due to the growing demand for food and feed (Aneja et al., 2008).

The growing attention in ammonia levels has enabled many monitoring actions in Europe (European Monitoring and Evaluation Programme, EMEP), in Southeastern Asia (East Asia acid deposition NETwork) and in the North America (Ammonia Monitoring Network in the US, AMoN-US; National Air Pollution Surveillance Program (NAPS) sites in Canada) to record surface concentrations of ammonia continuously. Recently, several satellite products have been also developed in an effort to identify global levels of ammonia considering that the

relatively sparse existing monitoring network has an insufficient coverage for this purpose. These are derived from satellite sounders as the Infrared Atmospheric Sounding Interferometer (IASI) (Van Damme et al., 2017), the Atmospheric Infrared Sounder (AIRS) (Warner et al., 2017), the Cross-track Infrared Sounder (CrIS) (Shephard and Cady-Pereira, 2015), the Tropospheric Emission Spectrometer (TES) (Shephard et al., 2015), and Greenhouse Gases Observing Satellite (Someya et al., 2020). Both IASI and CrIS ammonia products are being continuously compared and evaluated against other observations and products. Relevant analyses include comparison against column-integrated levels measured by Fourier transform infrared spectroscopy (FTIR) (Dammers et al., 2016, 2017), ground-based measurements (Van Damme et al., 2015; Kharol et al., 2018), bottom-up emissions (Van Damme et al., 2018; Dammers et al., 2019) and atmospheric chemistry transport models (CTMs) (Shephard et al., 2020; Whitburn et al., 2016a).

Despite its importance, ammonia is a poorly quantified trace gas, with uncertainties over 50% on the global emission budget and even higher on temporal and local scales (Dentener and Crutzen, 1994; Faulkner and Shaw, 2008; Reis et al., 2009) and up to 300% for the agricultural sector in Europe (European Environment Agency, 2019). In the present paper, we grid 10 years (2008–2017) of satellite measurements of ammonia retrieved from IASI to calculate monthly surface emissions (hereafter named NE) (see section 2). The same is done using the gridded IASI ammonia column concentrations from Van Damme et al. (2018) (named as VD0.5 and VDgrlf) (see section 2). The three different emission inventories together with a state–of–the–art one, which is more often used by models (named as EGG), are then imported in a CTM to simulate ammonia for the same 10–year period. More details of the different emissions used here are shown in sections 2.4 and 2.1. Finally, an evaluation of simulated surface concentrations against ground–based measurements from different monitoring stations and satellite products allow to quantify the improvements in ammonia emissions.

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2 Methods

2.1 LMDz-OR-INCA chemistry transport model

The Eulerian global CTM LMDz-OR-INCA was used to calculate ammonia lifetime, as well as to simulate ammonia concentrations from the emission fluxes calculated from IASI satellite products. The model couples the LMDz (Laboratoire de Météorologie Dynamique) General Circulation Model (GCM) (Hourdin et al., 2006) with the INCA (INteraction with Chemistry and Aerosols) model (Folberth et al., 2006; Hauglustaine et al., 2004) and with the

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land surface dynamical vegetation model ORCHIDEE (ORganizing Carbon and Hydrology In Dynamic Ecosystems) (Krinner et al., 2005). In the present configuration, the model has a horizontal resolution of $2.5° \times 1.3°$, the vertical dimension is divided into 39 hybrid vertical levels extending to the stratosphere. Large-scale advection of tracers is calculated from a monotonic finite-volume second-order scheme (Hourdin and Armengaud, 1999), deep convection is parameterized according to the scheme of Emanuel, (1991), while turbulent mixing in the planetary boundary layer (PBL) is based on a local second-order closure formalism. More information and a detailed evaluation of the GCM can be found in Hourdin et al. (2006).

The model simulates atmospheric transport of natural and anthropogenic aerosols recording both the number and the mass of aerosols. The aerosol size distribution is represented using a modal approach that consists of the superposition of 5 log-normal modes that represent both the size spectrum and whether the aerosol is soluble or insoluble (Schulz, 2007). The aerosols are treated in three particle modes, sub-micronic (diameter < 1 μm) corresponding to the accumulation mode, micronic (diameter 1–10 μm) corresponding to coarse particles, and super-micronic or super coarse particles (diameter > 10 μm). LMDz-OR-INCA accounts for emissions, transport (resolved and sub-grid scale), and dry and wet (in-cloud/below-cloud scavenging) deposition of chemical species and aerosols interactively. LMDz-OR-INCA includes a full chemical scheme for the ammonia cycle and nitrate particle formation, as well as a state-of-the-art $CH_4/NO_x/CO/NMHC/O_3$ tropospheric photochemistry. Further details about specific reactions, reaction rates and other information entering into the description of the ammonia cycle can be found in Hauglustaine et al. (2014).

The global transport of ammonia was simulated from 2007 to 2017 (2007 was the spin-up period) by nudging the winds of the 6-hourly ERA Interim Reanalysis data (Dee et al., 2011) with a relaxation time of 10 days (Hourdin et al., 2006). For the calculation of ammonia's lifetime, the model ran with traditional emissions for anthropogenic, biomass burning and oceanic emission sources using emissions from ECLIPSEv5 (Evaluating the CLimate and Air Quality ImPacts of Short-livEd Pollutants), GFED4 (Global Fire Emission Dataset) and GEIA (Global Emissions InitiAtive) (hereafter called EGG) (Bouwman et al., 1997; Giglio et al., 2013; Klimont et al., 2017).

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2.2 Satellite ammonia

2.2.1 IASI ammonia

The Infrared Atmospheric Sounding Interferometer (IASI) onboard the MetOp-A satellite measures Earth's infrared radiation twice a day in a spectral range of 645–2,760 cm^{-1} with an elliptical footprint with a diameter of 12 km at nadir (Clerbaux et al., 2009). Due to the larger thermal conditions that lead to smaller uncertainties, only morning data were used in the present assessment (Clarisse et al., 2010). Van Damme et al. (2018) reported limited impact of the IASI overpasses of 4%±8% on ammonia. The 10–year dataset used here is ANNI-NH3-v2.1R-I product (Van Damme et al., 2017) and relies on ERA-Interim ECMWF meteorological input data (Dee et al., 2011). The Artificial Neural Network for IASI (ANNI) algorithm converts the hyperspectral range index to an column–integrated NH_3 value (Whitburn et al., 2016a). The latter relies on the fact that the indices can be converted to a column by taking into account the spectral sensitivity to the ammonia abundance in the observed scene. The hyperspectral range indexes are derived from linear retrievals using a constant gain matrix which includes a generalized error covariance matrix (Van Damme et al., 2014b; Whitburn et al., 2016a). The dataset also provides cloud coverage for each measurement (August et al., 2012). Only measurements with a cloud fraction below 10% were processed in consistency with Van Damme et al. (2018). Cloud coverage was not provided for all measurements until March 2010 resulting in smaller data availability before that date. Van Damme et al. (2014a) reported that IASI better measures ammonia in spring and summer months, due to the strong dependence on thermal contrast (error below 50%). For an individual observation, an IASI-retrieved column is considered detectable when the vertical column density exceeds 9.68×10^{15} molecules cm^{-2} (surface concentration > 1.74 µg m^{-3}) at a thermal contrast of 20 K, while the vertical column density should be larger than 1.69×10^{16} molecules cm^{-2} (3.05 µg m^{-3}) at 10 K (Van Damme et al., 2014a). Although the retrieval algorithm uses a fixed vertical profile, extended validation of the resulting dataset has verified small uncertainties (Van Damme et al., 2015, 2018; Dammers et al., 2016; Whitburn et al., 2016b). For instance, Van Damme et al. (2018) reported a difference of 2%±24% (global average) in column–integrated ammonia using different vertical profiles in the retrieval algorithm.

2.2.2 CrIS ammonia

The Cross-Track Infrared Sounder (CrIS) was first launched on the NASA Suomi National Polar-orbiting Partnership (S-NPP) satellite on 28 October 2011 in a sun-synchronous low Earth orbit. The CrIS sensor provides soundings of the atmosphere with a spectral

190 resolution of 0.625 cm^{-1} (Shephard et al., 2015). One of the main advantages of CrIS is its

191 improved vertical sensitivity of ammonia closer to the surface due to the low spectral noise of

192 ~0.04K at 280K in the NH$_3$ spectral region (Zavyalov et al., 2013) and the early afternoon

193 overpass that typically coincides with high thermal contrast, which is optimal for thermal

194 infrared sensitivity. The CrIS Fast Physical Retrieval (CFPR) (Shephard and Cady-Pereira,

195 2015) retrieves an ammonia profile (14 levels) using a physics-based optimal estimation

196 retrieval, which also provides the vertical sensitivity (averaging kernels) and an estimate of the

197 retrieval errors (error covariance matrices) for each measurement. As peak sensitivity is

198 typically in the boundary layer between 900 and 700 hPa (~ 1 to 3 km) (Shephard et al., 2020),

199 the surface and total column concentrations are both highly correlated with the retrieved levels

200 in the boundary layer. Shephard et al. (2020) reports estimated total column random

201 measurement errors of 10–15%, with estimated total random errors of ~30%. The individual

202 profile retrieval levels have estimated random measurement errors of ~10 to 30 %, with

203 estimated total random errors increasing to 60 to 100% due to the limited vertical resolution.

204 These vertical sensitivity and error output parameters are also useful for using CrIS

205 observations in applications (e.g. data fusion, data assimilation; model-based emission

206 inversions (e.g., Cao et al., 2020; Li et al., 2019) as a satellite observational operator can be

207 generated in a robust manner. The detection limit of CrIS measurements has been calculated

208 down to 0.3–0.5 ppbv (Shephard et al., 2020). CrIS ammonia has been evaluated against other

209 observations over North America with the Ammonia Monitoring Network (AMoN) (Kharol et

210 al., 2018) and against ground-based Fourier transform infrared (FTIR) spectroscopy

211 observations (Dammers et al., 2017) showing small differences and high correlations.

212 **2.3 Inverse Distance Weighting (IDW) interpolation**

213   To process large amounts of measurements in a 2-dimensional grid of high resolution,

214 oversampling methods (Streets et al., 2013) can be used (Van Damme et al., 2018). However,

215 considering that the resolution of the CTM is 2.5°×1.3° (see section 2.4), there is no need to

216 process the measurements on such a high-resolution grid and therefore an interpolation method

217 was used. The method has been extensively used after the Chernobyl accident in 1986 to

218 process more than 500 thousand deposition measurements over Europe (De Cort et al., 1998;

219 Evangeliou et al., 2016).

220   IASI total column ammonia measurements were interpolated onto a grid of 0.5°×0.5°

221 using a modified Inverse Distance Weighting (IDW) algorithm described by (Renka, 1988).

222 This method is preferred due to its ease of use and to its high quality of interpolation. The IDW
223 interpolation is defined by:

224
$$\hat{v}(x,y) = \frac{\sum_{i=1}^{n} w_i v_i}{\sum_{i=1}^{n} w_i} \qquad \textbf{Eq. 1}$$

225 where $\hat{v}(x,y)$ is the interpolated value at point (x,y), $w_1, \dots, w_i$ are the relative weights and
226 $v_1, \dots, v_n$ are the observation values. The weights are defined by the inverse distance functions:

227
$$w_i = \left(\frac{(r_w - d_i)}{r_w d_i}\right)^2 \qquad \textbf{Eq. 2}$$

228
$$\text{for } (r_w - d_i) = \begin{cases} r_w - d_i \, if \, d_k < r_w, \\ 0 \, if \, d_k \geq r_w. \end{cases}$$

229 where r_w denotes the radius of influence of the point (x_i, y_i), d_i the Euclidean distance
230 between point (x,y) and (x_i, y_i), and d_k is the threshold distance. We used a threshold
231 distance (d_k) of 50 km, which is similar to the size of each grid cell; different d_k values were
232 included in a sensitivity study (see section 4.2). The Euclidean distance is calculated using

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233 Vincenty's formulae (Vincenty, 1975). Finally, the gridded IASI total column ammonia was re-
234 gridding to the model resolution (2.5°×1.3°) using bilinear interpolation.

2.4   Emission flux calculation of ammonia

236   The emission fluxes of ammonia were calculated using a 1–dimensional box model that
237 assumes first-order loss terms for ammonia and has been already used previously (Van Damme
238 et al., 2018; Whitburn et al., 2016b). It takes into account the gridded column concentrations of
239 ammonia that were calculated with the IDW interpolation method and all the potential removal
240 processes of ammonia occurring in a hypothetical atmospheric box according to the following
241 equation:

242
$$E_{NH3} = {M_{NH3}}/{\tau} \qquad \textbf{Eq. 3}$$

243 where M_{NH3} is the mass of ammonia in each atmospheric box (grid-cell) in molecules cm^{-2} and
244 τ is the lifetime of ammonia in the box (given in seconds).

245   Van Damme et al. (2018) assumed a constant lifetime for ammonia, admitting that this is
246 a limiting factor of their study on the basis that chemical loss and deposition are highly variable
247 processes that can change the lifetime drastically. To tackle the large variability of the lifetime
248 of ammonia, we used monthly gridded lifetime calculated from a CTM. This gives robustness
249 in the calculated emissions fluxes considering that at regions where sulfuric and nitric acids are
250 abundant, the chemical loss will be more intensive and, thus, lifetime will be much shorter
251 affecting emissions dramatically.

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253   The lifetime (τ) of ammonia in each grid-box results from the three processes affecting
254   ammonia concentrations: transport (t_{trans}) in and out of the grid-cell, chemical loss (t_{chem})
255   and deposition (t_{depo}):

256
$$\frac{1}{\tau} = \frac{1}{t_{trans}} + \frac{1}{t_{chem}} + \frac{1}{t_{depo}}$$ **Eq. 4**

257   In a CTM, the lifetime can be easily calculated from the species mass balance equation (Croft
258   et al., 2014):

259
$$\frac{dC(t)}{dt} = S(t) - \frac{C(t)}{\tau(t)}$$ **Eq. 5**

260   where $C(t)$ is the atmospheric burden of ammonia at time t, $S(t)$ is the time-dependent source
261   emission fluxes and $\tau(t)$ is the removal timescale. Assuming steady-state conditions and
262   considering that emission fluxes of ammonia are continuous, there is a quasi-equilibrium
263   between sources and removals of ammonia (Dentener and Crutzen, 1994), and the modeled
264   lifetime of ammonia τ_{mod} can be defined as:

265
$$\tau_{mod} = \frac{C_{NH3}}{L_{NH3}^{trans,chem,depo}}$$ **Eq. 6**

266   where C_{NH3} is the atmospheric burden of ammonia and $L_{NH3}^{trans,chem,depo}$ is the total loss due to
267   any process affecting ammonia in the model (transport, chemical reactions, deposition).

268   We calculate ammonia emission fluxes using IASI satellite measurements that we
269   interpolated (see section 2.3) to the model resolution (2.5°×1.3°) and applying a variable
270   lifetime taken from a CTM (hereafter NE emissions). We also calculate ammonia emissions
271   from the oversampled IASI data of Van Damme et al. (2018), after bilinear re-gridding to the
272   model resolution (2.5°×1.3°), applying a constant lifetime for ammonia of 12 hours (hereafter
273   VD0.5 emissions) and the same variable lifetime from a CTM as in the NE emissions (hereafter
274   VDgrlf emissions).

275   # 3   Results

276   In this section, the main results of the monthly emissions (NE) are presented for the 10-
277   year period (2008–2017) of IASI observations. We first describe the monthly modelled
278   ammonia lifetimes (section 3.1). Then, we explain the main characteristics of the obtained
279   emissions (section 3.2) and compare them with those calculated using the IASI gridded
280   products from Van Damme et al. (2018) (VD0.5 and VDgrlf), as well as the ones from the state-
281   of-the-art inventories of EGG and EDGARv4.3.1-GFED4 (Crippa et al., 2016; Giglio et al.,

282 2013) that are often used in CTMs (section 3.3). We finally turn our focus to emissions at
283 continental regions and document their seasonal variation in emissions (section 3.4).

3.1   Modelled lifetime of ammonia

285   The lifetime of ammonia has been reported to range from a few hours to a few days
286 (Behera et al., 2013; Pinder et al., 2008) so ammonia can only be transported over relatively
287 short distances. This short spread of ammonia is also due to the fact that (a) the majority of its
288 emissions are surface ones (major source is agricultural activity), and (b) its surface deposition
289 velocities are high for most surfaces (Hov et al., 1994). The atmospheric lifetimes of ammonia
290 were summarized in Van Damme et al. (2018). Specifically, Quinn et al. (1990) and more
291 recently Norman and Leck (2005) reported lifetimes of a few hours in the West Pacific, South
292 Atlantic and Indian Oceans, which is in agreement with Flechard and Fowler (1998), who
293 reported a 2-hour lifetime in an area of Scotland where most sources are of agricultural origin.
294 Similar to them, Dammers et al. (2019) recently reported a lifetime estimated from satellite
295 measurements of 2.35±1.16 hours for large point sources based on satellite measurements. The
296 majority of ammonia lifetimes reported regionally or globally fall within 10 and 24 hours
297 independently of the different approaches (Hauglustaine et al., 2014; Hertel et al., 2012; Möller
298 and Schieferdecker, 1985; Sutton et al., 1993; Whitburn et al., 2016b), while Dentener and
299 Crutzen (1994) reported slightly higher lifetimes within a range between 0.9 and 2.1 days
300 depending on ammonia emission fraction of natural origin. Monthly averaged atmospheric
301 ammonia lifetimes in the present study were derived using the version of the LMDz-OR-INCA
302 that includes non-methane hydrocarbons (Hauglustaine et al., 2004).

303   Ammonia lifetime depends on numerous factors such as the presence of ammonia's
304 reactants (sulfuric and nitric acids, through SO_2 and NO_x emissions), meteorological parameters
305 (atmospheric water vapour, and temperature, atmospheric mixing and advection) and ammonia
306 emissions. In ammonia–poor conditions, all ammonia is rapidly removed by neutralising
307 sulfuric acid with an intermediate production of bisulfate. If ammonia increases further
308 (ammonia–rich conditions), then reaction with nitric acid occurs forming nitric ammonium. At
309 this point, the ammonia/sulfuric acid/nitric acid equilibrium becomes very fragile. If sulfate
310 concentrations decrease, then free ammonia is produced, which gradually reacts with nitric acid
311 resulting in production of aerosol phase nitric ammonium. But if particles are aqueous, then
312 sulfate ions in solution increase the equilibrium vapour pressure of ammonia with nitric acid
313 reversing the reaction towards gaseous phase reactants. So, sulfate reductions are linked with

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314 non-linear increases of aerosol nitrates and decreases of aerosol ammonium and water (Seinfeld

315 and Pandis, 2000).

316   The calculated ammonia lifetime is shown in Figure 1a averaged for the whole study

317 period. The average lifetime was calculated to be 11.6±0.6 hours, which is in the range of the

318 previously reported values. Lower values (~10 hours) were observed in clean remote areas

319 characterized by low ammonia emissions (e.g., Amazon forest, Sahara and Australia), while in

320 the rest of the globe the lifetime was closer to the average value. The highest lifetimes (~16

321 hours) occur over Southern Brazil and Venezuela, which are both areas with relatively high

322 ammonia emissions and low sulfuric and nitric acid concentrations (Figure 1c). These

323 conditions are characterized by a low atmospheric sulfuric and nitric acids availability to

324 remove ammonia rapidly, hence causing an increase in lifetime.

3.2 Satellite-constrained emissions

326   The average ammonia emissions calculated from the 10-year IASI observations are

327 shown in Figure 1b (also in Figure S 1a), the reactants' atmospheric burden in Figure 1c and

328 their seasonal variability in Figure 1d together with monthly modelled lifetimes. The year-by-

329 year total ammonia emissions are depicted in Figure S 1 with a monthly temporal resolution.

330 Emissions decline from 242 Tg yr^{-1} in 2008 to 212 Tg yr^{-1} in 2011. In 2012 – 2014, emissions

331 show little variation (194, 204 and 195 Tg yr^{-1}, respectively), before they increase steeply to

332 248 Tg yr^{-1} in 2015. Finally, in 2016 and 2017 they remain at the same high level (197 and 227

333 Tg yr^{-1}, respectively).

334   The global average annual emission calculated from VD0.5 amounts to 189 Tg (9-year

335 average), which is comparable to the average of the 10-year period that we have calculated in

336 the present study (average±sd: 213±18.1 Tg yr^{-1}). The increase in the emissions we calculate

337 during 2015 and 2017 stand out. The explanation for these increases could be twofold. If sulfur

338 dioxide (a precursor of sulfates) emissions decreased over time, less sulfates are available to

339 neutralize ammonia, hence resulting in higher ammonia column concentrations seen by IASI

340 that could be attributed to new emissions erroneously (see section 2.4). This has been already

341 reported for the North China Plain. To improve air quality, the Chinese government

342 implemented new emission regulations aimed at decreasing the national total NO_x emissions

343 by 10% between 2011 and 2015 (Liu et al., 2017). Several recent studies (Duncan et al., 2016;

344 Krotkov et al., 2016) have highlighted the effectiveness of the air quality policy, as evidenced

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352   by a decreasing trend in nitrogen dioxide columns over China since 2012. The same has been

353   reported for the sulfur dioxide emissions (Koukouli et al., 2018; Krotkov et al., 2016; Wang et

354   al., 2013). If sulfur dioxide and sulfates presented a constant year-by-year pattern or even

355   increased, then the calculated ammonia emissions would be likely realistic.

356   To sort out between these two possibilities, we used sulfur dioxide measurements from

357   NASA's Ozone Monitoring Instrument (OMI, Yang et al., 2007) instrument, whereas sulfate

358   column concentrations were taken from the Modern-Era Retrospective Analysis for Research

359   and Applications, Version 2 (MERRA2, Gelaro et al., 2017) reanalysis data from NASA's

360   Global Modeling and Assimilation Office (GMAO). Figure S 2 shows timeseries of column

361   concentrations of sulfur dioxide and sulfates from OMI and MERRA2 averaged globally, for

362   continental regions (Europe, North America, South America, Africa), as well as for regions

363   where ammonia emissions are particularly high (India and Southeastern Asia, North China

364   Plain). Although column concentrations of both sulfur dioxide and sulfates present strong

365   interannual variability (Figure S 2), their global concentrations show a strong decreasing trend

366   after 2015. The observed decrease indicates that sulfate amounts that neutralize ammonia and

367   form ammonium sulfate, thus it is likely that the higher ammonia concentrations seen from

368   IASI after 2015 are not necessarily a result of emission increases. This is not seen from the

369   respective precursor of the atmospheric nitric acid, nitrogen dioxide (Figure S 2).

370   Looking closely into regions with large changes in ammonias reactants and/or their

371   precursors after 2015 (Figure 2), we immediately see that a region of interest is the North China

372   Plain. The North China Plain has been identified as an ammonia hotspot mainly due to extensive

373   agricultural activities (Clarisse et al., 2009; Pan et al., 2018). Liu et al. (2018) reported a sulfur

374   dioxide reduction of about 60% over the recent few years in the North China Plain, sulfates

375   decreased by 50%, while ammonia emissions declined by only 7% due to change in agricultural

376   practices. The suggested decrease in ammonia reactants over the North China Plain is illustrated

377   by the calculated sulfur dioxide column concentration anomaly from OMI (Figure 2) and by

378   the sulfate concentration anomaly from MERRA-2 after 2015 (the highest calculated one)

379   (Figure S 3). Nitrogen dioxide concentration do not show any noticeable annual change, despite

380   their strong seasonal cycle (Figure S 2). The IASI-constrained ammonia emissions calculated

381   here show only a tiny increase of 0.19 ± 0.04 kt y^{-1} after 2015 in the North China Plain and of

382   10 ± 3.1 Tg y^{-1} globally with respect to the 10-year average (Figure 2). This is due to the change

383   of sulfur dioxide and nitrogen oxide emission regulations in China, which in turn led to reduced

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394 inorganic matter (sulfates, nitrates and ammonium) resulting in regional increases of gaseous
395 ammonia (Lachatre et al., 2019).

396 It should be noted here that decreases in sulfur dioxide and nitrogen dioxide have been
397 reported to have occurred since 2005, at least in Eastern USA and to a lesser extent in Eastern
398 Europe (Krotkov et al., 2016). At the same time, sulfur dioxide and nitrogen dioxide
399 concentrations had started increasing after 2005 in India, a country that shows the largest
400 agricultural activity in the world. The latter has balanced the global sulfur dioxide and nitrogen
401 dioxide budget, explaining that the decreasing trend after 2015 that we report has been affected
402 by our choice to present global averages.

3.3 Comparison with traditional emission datasets

404 In this section, we quantify the main differences of our IASI-constrained emission dataset
405 with other state-of-the-art inventories used in global models and for different applications (air
406 quality, climate change etc…). Aside from comparing our emissions with those calculated using
407 Van Damme et al. (2018) data with a constant lifetime (hereafter called VD0.5), we extend our
408 comparison to more traditional datasets such as those of ECLIPSEv5-GFED4-GEIA (EGG) for
409 2008–2017, and EDGARv4.3.1-GFED4 (Crippa et al., 2016; Giglio et al., 2013) for 2008–2012
410 period. Finally, the ammonia emissions presented in this study (NE emissions) are compared
411 to emissions calculated from Van Damme et al. (2018) gridded IASI column data applying a
412 variable (modelled) ammonia lifetime presented in Figure 1b (hereafter referred as VDgrlf).

413 The 10-year comparison of our calculated emissions with VD0.5 is shown in Figure 3.
414 The 10-year average difference amounts to 29±15 Tg yr^{-1} (average±sd). In all years, the largest
415 differences could be seen over Latin America and over tropical Africa. Our emissions (NE)
416 show a different structure in the Indo-Gangetic Plain and situated slightly more northerly than
417 those in VD0.5. The difference might be due to the IDW interpolation used to process the IASI
418 ammonia in the NE emissions compared with the oversampling method used in VD0.5 (see
419 section 2.3). Nevertheless, Northern India has been identified as a hot-spot region for ammonia,
420 mainly due the importance of agricultural activities in the region (Kuttippurath et al., 2020;
421 Tanvir et al., 2019).

422 Figure S 4 and Figure S 5 present a comparison of our calculated emissions (NE) with
423 the basic state-of-the-art datasets of EGG and EDGARv4.3.1-GFED4, respectively. In both
424 datasets, ammonia emissions remain almost constant over time (average±sd: 65±2.8 Tg yr^{-1}

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429 and 103±5.5 Tg yr⁻¹, respectively). The total calculated ammonia emissions in EGG and

430 EDGARv4.3.1-GFED4 are up to three times lower than those calculated from NE (average±sd:

431 213±18.1 Tg yr⁻¹) or from VD0.5 (9-year average: 189 Tg yr⁻¹). This results in 10-year annual

432 differences that are very significant (average±sd: 150±19.3 Tg yr⁻¹ and 111±19.2 Tg yr⁻¹,

433 respectively); the largest differences appear over South America (EGG: 7.1±0.3 Tg yr⁻¹, VD0.5:

434 22 Tg yr⁻¹, NE: 28±3.0 Tg yr⁻¹, VDgrlf: 24±1.3 Tg yr⁻¹), while European emissions are

435 practically identical in all datasets except EGG (EGG: 6.9±1.1 Tg yr⁻¹, VD0.5: 11 Tg yr⁻¹, NE:

436 15±2.2 Tg yr⁻¹, VDgrlf: 11±1.0 Tg yr⁻¹). Emissions from South China Plain are much higher in

437 the two traditional datasets that those presented in this paper (EGG: 25±1.2 Tg yr⁻¹, VD0.5: 36

438 Tg yr⁻¹, NE: 38±2.8 Tg yr⁻¹, VDgrlf: 39±1.8 Tg yr⁻¹). Ammonia emissions derived over China

439 in this work (NE) are among the highest worldwide (Figure S 1), which agrees well with the 9-

440 year average emissions calculated in VD0.5 inventory over China (see Figure 3). To assess to

441 which extent emissions from EGG and EDGARv4.3.1-GFED4 are underestimated can only be

442 done by comparing ammonia with ground or satellite observations.

443 The comparison of the annual ammonia emissions in the NE dataset to the modified

444 VDgrlf emissions is shown in Figure S 6. The latter showed a better agreement to the emissions

445 presented in this study with mean annual different of 14±19 Tg yr⁻¹ (average±sd). Previously

446 observed emission differences in the two state-of-the-art inventories over South America and

447 Africa have been now minimized, as well as the displacement north of the Indo-Gangetic Plain

448 emissions remains important. Nevertheless, the smaller differences of our emissions (NE) from

449 those of VDgrlf as compared with the respective difference from the VD0.5 emissions, show

450 the large impact that a more realistic variable lifetime might have in emission calculations with

451 this methodology in these regions.

3.4 Site-specific ammonia emissions and seasonal variation

453 **Figure 4** illustrates specific regions that show the largest ammonia emissions (Europe,

454 North America, South America and Southeastern Asia). These emissions correspond to the

455 IASI-constrained emissions calculated in this study (NE) and are presented as total annual

456 emissions averaged over the 10-year period of study. At the bottom panels of the same figure,

457 the seasonal variation of the emissions is shown for each of the four hot-spot regions and each

458 of the 10 years of the study.

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European total ammonia emissions were estimated to be 15 ± 2.2 Tg yr^{-1} (average$\pm$sd), more than double compared with those reported in EGG (6.9 ± 1.1 Tg yr^{-1}) and similar to those in VD0.5 (11 Tg yr^{-1}) or those in VDgrlf (11 ± 1.0 Tg yr^{-1}). The greatest emissions were calculated for Belgium, the Netherlands and the Po Valley in Italy (Figure 4). High emissions are also found in North and Northwestern Germany and over Denmark. In contrast, very low emissions are found in Norway, Sweden and parts of the Alps. It is not possible to quantitatively distinguish between different sources of ammonia. It has been reported that approximately 75% of ammonia emissions in Europe originate from livestock production (Webb et al., 2005), and 90% from agriculture in general (Leip et al., 2015). More specifically, ammonia is emitted from all stages of manure management, from livestock buildings during manure storage and application to land, as well as from livestock urine. These emissions are strong over most of Northwestern European countries, although sources like fertilization and non-agricultural activities (traffic and urban emissions) can be also important. An example is Tange in Germany, which shows a late summer peak due to growing crops application. No obvious seasonality in the emissions can be seen for Europe as a whole, as the hot-spot regions are rather few compared to the overall surface of Europe. An exception to this stable emission situation over the year occurs during 2010 and during 2015, years for which a late summer peak. In 2010, large wildfires in Russia resulted in high ammonia emissions (R'Honi et al., 2013), while year 2015 has been also characterized as an intense fire year (though not like 2010), with fires occurring in Eurasia (Min Hao et al., 2016).

North America and in particular the US (Figure 4) has been characterized by four hot-spot regions. First, a small region in Colorado, Central US, which is the location of a large agricultural region that traditionally releases large ammonia emissions (Malm et al., 2013). Another example is the state of Iowa (home to more than 20 million swine, 54 million chickens, and 4 million cattle), northern Texas and Kansas (beef cattle), and southern Idaho (dairy cattle) (McQuilling, 2016). Furthermore, the three major valleys in Salt Lake, in Cache, and in Utah in the midwestern US show an evident, but lower intensity hot-spot, as they are occupied by massive pig farms associated to open waste pits. The largest emissions were calculated for the San Joaquin Valley in California (vegetables, dairy, beef cattle and chickens) and further to the South (Tulare and Bakersfield), an area characterized by feedlots (Van Damme et al., 2018; McQuilling, 2016). North American annual ammonia emissions over the 10-year period were averaged 1.1 ± 0.1 Tg yr^{-1} (average$\pm$sd). These values are over two orders of magnitude higher than those in EGG (0.062 ± 0.0013 Tg yr^{-1}). Note that his estimate is three times lower than those

498 reported in VD0.5 (3.1 Tg yr^{-1}) or in VDgrlf (3.4±0.5 Tg yr^{-1}). The 2008–2017 interannual

499 variability (Figure 4) all show a minimum in winter. Maximum emissions were observed in late

500 spring, due to the contribution from mineral fertilizer and manure application, in summer, due

501 to influence of livestock housing emissions, and some years both in spring and summer (Makar

502 et al., 2009; Zhu et al., 2013, 2015). A topographical dependence was also seen in midwest

503 emissions that peaked in April, whereas over the rest of the US maximum emissions were

504 appeared in summer (Paulot et al., 2014).

505   Ammonia emissions have different characteristics in South America and in Western

506 Africa as both are fire-dominated regions. For simplicity we only present South America in

507 Figure 4. This region is dominated by natural ammonia emissions mainly from forest, savanna

508 and agricultural fires (Whitburn et al., 2014, 2016b) and volcanoes (Kajino et al., 2004;

509 Uematsu et al., 2004). This causes a strong seasonal variability in the ammonia emissions with

510 the largest fluxes observed from August to October in all years (Figure 4). This strong

511 dependence of South America from biomass burning emissions was first highlighted by Chen

512 et al. (2013) and by van Marle et al. (2017). It also became particularly pronounced during the

513 large wildfires in the Amazon rainforest in summer 2019 (Escobar, 2019). We estimated the

514 10-year average ammonia emissions to be 28±3.0 Tg yr^{-1} (average±sd) in agreement with

515 VD0.5 (22 Tg yr^{-1}) and VDgrlf (24±1.3 Tg yr^{-1}). The respective emissions in EGG are four

516 times lower than these estimates (7.1±0.3 Tg yr^{-1}).

517   The last column to the right of Figure 4 presents the 10-year average annual ammonia

518 emissions and their respective interannual variability in Southeastern Asia. We define this

519 region spanning from 70°E–130°E in longitude and from 0°N–45°N in latitude. Ammonia

520 emissions were estimated to be 38±2.8 Tg yr^{-1} (average±sd) similar to VD0.5 (36 Tg yr^{-1}) and

521 VDgrlf (39±1.8 Tg yr^{-1}) and slightly higher than those presented in EGG (25±1.2 Tg yr^{-1}). They

522 comprise ammonia fertilizer plants, such as in Pingsongxiang, Shizuishan, Zezhou-Gaoping,

523 Chaerhan Salt Lake, Delingha, Midong-Fukang and Wucaiwan (China), Indo-Gangetic Plain

524 (Pakistan and India), Gresik (Indonesia). China and India contribute more than half of total

525 global ammonia emissions since the 1980s with the majority of these emissions to originate

526 from rice cultivation followed by corn and wheat (crop-specific emissions). More specifically,

527 emissions from these crops due to synthetic fertilizer and livestock manure applications are

528 concentrated in North China Plain (Xu et al., 2018). Considering that Southeastern Asia is the

529 largest agricultural contributor in the global ammonia budget, a strong seasonality in the

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534 emissions was observed. Temporal ammonia emissions peak in late summer of most years,
535 when emissions from rice cultivation, synthetic fertilizer application and livestock manure
536 spreading (Xu et al., 2016) are important, and in spring when wheat cultivation dominates
537 (Datta et al., 2012). Of course, the respective emissions from biomass burning should also be
538 mentioned. However, these are difficult to be distinguish and are expected to be a relatively
539 small source compared to agricultural emissions.

4 Discussion

541   In this section, we conduct simulations over the 10-year period (2008–2017, 1-year spin-
542 up), with all the emissions derived and compare the NH$_3$ concentrations with ground-based
543 observations over Europe, North America, Southeastern Asia (section 4.1), and observations
544 from CrIS (section 4.1). These simulations consist in: (i) a simulation using traditional
545 emissions using EGG; (ii) a simulation using emissions calculated from IASI data from Van
546 Damme et al. (2018) applying a constant lifetime of 12 hours for ammonia (VD0.5); (iii) a
547 simulation using gridded emissions presented in the present paper (NE) calculated as described
548 in section 2; and (iv) a simulation using emissions calculated from IASI data from Van Damme
549 et al. (2018) applying a variable (modelled) lifetime (VDgrlf). Finally, we perform a sensitivity
550 analysis in order to define the levels of uncertainty of our emissions in section 4.2 and discuss
551 potential limitation of the present study in section 4.3.

4.1 Validation against ground-based observations and satellite products

553   **Figure 5** shows a comparison between modelled surface concentrations of ammonia with
554 ground measurements from Europe (EMEP, https://emep.int/mscw/), North America (AMoN,
555 http://nadp.slh.wisc.edu/data/AMoN/) and Southeastern Asia (EANET,
556 https://www.eanet.asia). To avoid overplotting, the Gaussian kernel density estimation (KDE)
557 was used, which is a non-parametric way to estimate the probability density function (PDF) of
558 a random variable (Parzen, 1962):

$$f(x) = \frac{1}{Nh}\sum_{i=1}^{N} K\left(\frac{x-x_i}{h}\right) \qquad \textbf{Eq. 7}$$

560 where K is the kernel, x_i the univariate independent and identically distributed point of the
561 relationship between modelled and measured ammonia and h is a smoothing parameter called
562 the bandwidth. KDE is a fundamental data smoothing tool that attempts to infer characteristics
563 of a population, based on a finite dataset. It weighs the distance of all points in each specific
564 location along the distribution. If there are more points grouped locally, the estimation is higher
565 as the probability of seeing a point at that location increases. The kernel function is the specific

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mechanism used to weigh the points across the data set and it uses the bandwidth to limit the scope of the function. The latter is computed using the Scott's factor (Scott, 2015). We also provide the mean fractional bias (MFB) for modelled and measured concentrations of ammonia as follows:

$$MFB = \frac{1}{N}\frac{\sum_{i=1}^{N}(C_m - C_o)}{\sum_{i=1}^{N}(\frac{C_m + C_o}{2})} \times 100\% \qquad \textbf{Eq. 8}$$

where C_m and C_o are the modelled and measured ammonia concentrations and N is the total number of observations. MFB is a symmetric performance indicator that gives equal weights to under- or over-estimated concentrations (minimum to maximum values range from -200% to 200%). Furthermore, we assess the deviation of the data from the line of best fit using the root mean square error (RMSE) defined as:

$$RMSE = \sqrt{\sum_{i=1}^{N}\frac{(C_m - C_o)^2}{N}} \qquad \textbf{Eq. 9}$$

From 134 European stations, nearly 300,000 measurements made at a daily to weekly temporal resolution over the period of study (2007–2018) are presented on **Figure 5**. All emission datasets underestimate ammonia surface concentration over Europe. The most accurate prediction of concentrations was achieved using the traditional EGG emissions that underestimated observations by 67%, also being the least scattered from the best fit ($RMSE_{EGG} = 4.06\,\mu g\,N\,m^{-3}$), followed by the emissions presented in this paper ($MFB_{NE} = -72\%$, $RMSE_{NE} = 4.65\,\mu g\,N\,m^{-3}$), although they were more variable. VD0.5 or VDgrlf emissions further underestimated observations, though they were less sparse (**Figure 5**d). About 12% of the modelled concentrations using EGG were outside of the 10-fold limit from the observations, in contrast to only 17% and 15% in VD0.5 and VDgrlt, and 20% in NE. With regards to the spatial comparison with the observed concentrations, all datasets cause overestimations in the ammonia concentrations predicted in Western Europe. EGG appears to be the most accurate in Central Europe (all stations with suffix DE00), NE emissions in all Spanish stations (suffix ES00) and VD0.5 and VDgrlf emissions in Italian stations (**Figure S 7**).

The comparison of simulated ammonia concentrations to observations over North America includes 119 stations, which represent nearly 27,000 observations (Figure 6) with a weekly, bi-weekly or monthly resolution. The only emission dataset that lead to an underestimation of ammonia concentrations was EGG (**$MFB_{EGG} = -28\%$**). Two others, VD0.5 and VDgrlf caused ammonia observations to be strongly overestimated (**$MFB_{VD0.5} =$**

608 52% $and\ MFB_{VDgrlf} = 54$%), while NE slightly ($MFB_{NE} = 32$%). All inventories resulted
609 in about the same variability in ammonia concentrations with RMSEs between 4.15 and 4.17
610 μg N m-3 (Figure 6). About 10% of the predicted concentrations using EGG emissions were at
611 least 10 times off from the measured ones, more than twice the number of measurements
612 compared to the other dataset. NE emissions better capture levels in the easternmost stations of
613 the US (AL99, AR15, CT15, IL37, IN22, MI52, NY56, ON26) and in California (CA83) and
614 Oklahoma (OK98), which are close to hot-spot regions (see section 3.4). EGG emissions
615 perform better in Northwestern (ID03), Central (KS03) and several stations located over the
616 Eastern United States (KY03, KY98, OH09, AR03, IL46, KS03, GA41). The emission
617 inventory VD0.5 leads to a very good agreement in ammonia concentrations over all stations
618 of the North American continent (AL99, GA40, ID03, GA41, IL37, IL46, IN20, IN22, KS97,
619 PA00, MD99, MI52, TN04, NM99, NY96, OH99, OK98) (Figure S 8).

620 In Southeastern Asia 62 stations from 13 countries were included in the comparison from
621 the EANET monitoring network (Figure 7). These included about 8,000 surface measurements
622 in monthly or 2-weekly resolution. As a whole, all emission inventories underestimate station
623 concentrations of EANET with MFBs between -102% (EGG) and -61% (VD0.5 and VDgrlf).
624 The least spread model concentrations were those simulated using VD0.5 and VDgrlf
625 ($RMSE = 4.61 - 4.65\ \mu g\ N\ m^{-3}$). Around 19% of model concentrations using EGG were
626 outside the 10-fold limit of the 1×1 line with observations, 12% using NE emissions and only
627 5% and 6% using VD0.5 and VDgrlf, respectively. VD0.5 and VDgrlf emissions capture well
628 the Japanese (suffix JPA) and Taiwanese stations (suffix THA). Given the short lifetime and
629 the relatively coarse spatial scales, the model fails to capture the variability that exists within
630 each gridbox (Figure S 9).

631 To give an overview of the comparison of the modelled surface concentrations of
632 ammonia from the four different simulations, each with different emissions (EGG, VD0.5, NE
633 and VDgrlf), we present station-by-station calculated MFB values in Figure 8. Although the
634 traditional EGG emissions capture many stations very well, there are large MFB values
635 observed in Eastern and Western USA (AMoN), Northern Europe (EMEP), whereas large
636 overestimations are observed in most of the Southeastern Asian stations (EANET). The large
637 bias at several AMoN stations decrease when using satellite-derived emissions. All datasets
638 miscalculated surface concentrations in Southeastern Asia, although some stations present
639 lower MFBs when using IASI constrained emissions. Note that large differences when

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comparing bias from all measurements versus station-by-station bias have been calculated as a result of the different frequency of measurements in each station.

To further show whether the satellite-derived emissions presented here (NE) capture surface concentrations of ammonia or not, we used surface ammonia concentrations from CrIS from 1st May 2012 to 31st December 2017. The comparison is shown as PDF of surface modelled against CrIS concentrations of ammonia calculated with the Gaussian KDE for North America, Europe and Southeastern Asia in **Figure 9**. NE emissions slightly overestimate ammonia ($MFB = 0.09 - 0.10$). NE emissions generally result in higher surface concentrations, also showing large $RMSEs$ $(3.28 - 3.51 \ \mu g \ N \ m^{-3})$. However, 90% of the modelled concentrations were within a factor of 10 from the CrIS observation.

4.2 Uncertainty analysis

A sensitivity analysis in order to calculate the level of uncertainty that each of the parameter gives to the modelled surface concentrations of ammonia was also performed. The relative uncertainty was calculated as the standard deviation of ammonia's surface concentrations from a model ensemble of 10 members (**Table 1**) divided by the average. The first six members are the surface concentrations that resulted from simulations of ammonia emissions after perturbation of the Euclidian distance d_k in the parameters of the IDW interpolation. The remaining four members are simulated concentrations using the previously reported emissions datasets (EGG, VD0.5, NE and VDgrlf). The results are shown as a 10-year (2008–2017) annual average relative uncertainty in **Figure 10** and as annual average relative uncertainty of surface concentrations for every year of the 10-year period in **Figure S 10**.

The surface concentrations resulting from the different calculated emissions mainly affects oceanic regions, with values reaching 100%. The reason for this could be threefold. First, the IDW interpolation shows to be affected by severe outlier values, which are found in several oceanic regions (**Figure S 11**); this creates high gridded column ammonia concentrations and, in turn, fluxes at regions that are not supported by previous findings or measurements. Second, the methodology with which ammonia concentrations are retrieved in IASI has certain limitation, with respect to (i) the use of constant vertical profiles for ammonia, (ii) potential dependencies of total column ammonia and temperature that are not taken into account, and (iii) instrumental noise that can cause bias (Whitburn et al., 2016a). Third, there is much less ammonia over the Ocean, hence the relative error bars are much larger. Large uncertainties in surface ammonia concentrations were observed in regions characterized by

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710   large anthropogenic contribution, such as North India, North China Plain and Central USA.
711   Smaller uncertainties were found in Central Africa and in Amazonia, regions that are linked
712   with episodic biomass burning emissions (Figure 4).

713   **4.3   Limitations of the present study**

714   We discuss the importance of certain limitations in the methodology of the present study
715   and in the validation of the results. These limitations will also be commented upon in the overall
716   conclusion of the paper.

717   Regarding the methodology, emissions of short-lived species are determined, among
718   other methods, using top-down approaches. When only satellite measurements are available,
719   they are usually averaged over a particular location and surface emissions are calculated using
720   a mass balance approach (Lin et al., 2010; Zhao and Wang, 2009). This is done by assuming a
721   1-dimensional box-model, where atmospheric transport between grids is assumed to be
722   negligible and loss due to deposition or chemical reactions very fast. The solution to this
723   problem is the use of Kernels (Boersma et al., 2008), which makes the computation of the
724   emissions very intense. It has been reported that for resolutions, such as those used in the
725   present paper ($2.5° \times 1.3°$), non-local contributions to the ammonia emissions are relatively
726   small (Turner et al., 2012). Although, the use of Kernels is the proper way to account for non-
727   local contributions, we believe that negligible transport here is a fair assumption, due to the
728   small lifetimes of ammonia calculated from the CTM (11.6 ± 0.6 hours); therefore,
729   transportation from the adjacent grid-cells should be small. Note that although this method has
730   been suggested for short lived climate pollutants, it is not suitable for species with lifetime from
731   days to weeks (e.g. black carbon, Bond et al., 2013).

732   Another limitation of the present study is that the same model is used for the calculation
733   of the modelled lifetimes and for the validation of the emissions that were calculated using
734   these lifetimes (NE and VDgrlf). A more accurate validation would require an independent
735   model for the simulations of surface concentrations using these emissions. Nevertheless, the
736   IASI-constrained emissions of ammonia presented here are publicly available for use in global
737   models.

738   # 5   Conclusions

739   In the present paper, satellite measurements from IASI were used to constrain global
740   ammonia emissions over the period 2008–2017. The data were firstly processed to monthly
741   ammonia column concentrations with a spatial resolution of $2.5° \times 1.3°$. Then, using gridded

743 lifetime for ammonia calculated with a CTM, monthly fluxes were derived. This contrasts with
744 previously reported methods that used a single constant lifetime. This enables a more accurate
745 calculation in regions where different abundances of atmospheric sulfuric and nitric acid, as
746 well as in their precursors (sulfur and nitrogen dioxide, respectively) can neutralize ammonia
747 through heterogeneous chemical reactions to sulfate and nitrate aerosols. The calculated
748 ammonia emission fluxes were then used to simulate ammonia concentrations for the period
749 2008–2017 (referred to as NE). The same simulations were repeated using baseline emissions
750 from ECLIPSEv5-GFED4-GEIA (referred to as EGG), emissions constrained by Van Damme
751 et al. (2018) IASI data using a constant lifetime for ammonia (named as VD0.5) and emissions
752 based on Van Damme et al. (2018) retrievals using a modelled lifetime from a CTM (named as
753 VDgrlf). The simulated surface concentrations of ammonia were compared with ground
754 measurements over Europe (EMEP), North America (AMoN) and Southeastern Asia (EANET),
755 as well as with global satellite measurements from CrIS. The main conclusions can be
756 summarized as follows:

757 • The 10-year average annual ammonia emissions calculated here (NE) were estimated to be
758   213 ± 18.1 Tg yr^{-1}, which is 15% higher than those in VD0.5 (189 Tg yr^{-1}), and 6% higher
759   than those in VDglrf (201 ± 10.4 Tg yr^{-1}). These emission values amount to twice the
760   published from datasets, such as EGG (65 ± 2.8 Tg yr^{-1}) and EDGARv4.3.1-GFED4,
761   (103 ± 5.5 Tg yr^{-1}).

762 • In the North China Plain, a region characterized by intensive agricultural activities, a small
763   increase of ammonia emissions is simulated after 2015. This is attributed to decreases in
764   sulfur species, as revealed from OMI and MERRA-2 measurements. Less sulfates in the
765   atmosphere leads to less ammonia neutralization and hence to larger loads in the
766   atmospheric column as measured by IASI.

767 • In Europe, the 10-year average of ammonia emissions were estimated at 15 ± 2.2 Tg yr^{-1}
768   (NE), twice as much as those in EGG (6.9 ± 1.1 Tg yr^{-1}) and similar to those in VD0.5 (11
769   Tg yr^{-1}) or VDgrlf (11 ± 1.0 Tg yr^{-1}). The strongest emission fluxes were calculated over
770   Belgium, Netherlands, Italy (Po Valley), Northwestern Germany and Denmark. These
771   regions are known for industrial and agricultural applications, animal breeding activities,
772   manure/slurry storage facilities and manure/slurry application to soils.

773 • Some hot-spot regions with high ammonia emissions were distinguished in North America:
774   (i) in Colorado, due to large agricultural activity, (ii) in Iowa, northern Texas and Kansas,
775   due to animal breeding, (iii) in Salt Lake, Cache, and Utah, due to animal farms associated

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with open waste pits and (iv) in California, due to animal breeding and agricultural practices. Ammonia emissions in North America were 1.1±0.1 Tg yr^{-1} or two orders of magnitude higher than in EGG (6.2±0.1 kt yr^{-1}) and three times lower than those in VD0.5 (3.1 Tg yr^{-1}) or in VDgrlf (3.4±0.5 Tg yr^{-1}), with maxima observed in late spring, due to fertilization and manure application and summer, due to livestock emissions.

- South America is dominated by natural ammonia emissions mainly from forest, savanna and agricultural fires causing a strong seasonality with the largest fluxes between August and October. The 10-year average ammonia emissions were as high as 28±3.0 Tg yr^{-1} similar to VD0.5 (22 Tg yr^{-1}) and VDgrlf (24±1.3 Tg yr^{-1}) and four times higher than EGG (7.1±0.3 Tg yr^{-1}).

- In Southeastern Asia, the 10-year average ammonia emissions were 38±2.8 Tg yr^{-1}, in agreement with VD0.5 (36 Tg yr^{-1}) and VDgrlf (39±1.8 Tg yr^{-1}) and slightly higher than those in EGG (25±1.2 Tg yr^{-1}). The main sources were from fertilizer plants in China, Pakistan, India and Indonesia. China and India hold the largest share in the ammonia emissions mainly due to rice, corn and wheat cultivation. A strong seasonality in the emissions was observed with a late summer peak in most years, due to rice cultivation, synthetic fertilizer and livestock manure applications and in spring due to wheat cultivation.

- Large bias was calculated in several ground-based stations when using the state-of-the-art emissions EGG. The bias decreased substantially when satellite-derived emissions were used to simulate surface concentrations of ammonia.

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Deleted: About 88% of the modelled concentrations over Europe using EGG were inside the 10-fold limit from the observations, higher than those with VD0.5 (83%), VDgrlf (85%) and NE (80%). All emission datasets overestimate of ammonia in Eastern Europe, EGG captures better Central Europe, NE emissions predict concentrations in Spain and VD0.5 with VDgrlf emissions in Italy.¶
In North America, 90% of the modelled concentrations using EGG emissions were less than 10 times different from the measured ones; more than 95% of the modelled concentrations in North American stations were in the same range using NE, VD0.5 and VDgrlf emissions. NE emissions better capture levels in the easternmost stations of the US closer to the respective hot-spot regions, whereas EGG emissions perform better in Northwestern and Central USA. VD0.5 and VDgrlf emissions perform well in most of the North American stations.¶
All emissions underestimate station concentrations in Southeastern Asia. The least spread model concentrations were those simulated using VD0.5 and VDgrlf. About 81% of modelled concentrations using EGG were in the 10-fold limit of the 1×1 line with observations, 88% using NE and only 95% and 94% using VD0.5 and VDgrlf, respectively. VD0.5 and VDgrlf emissions capture well the Japanese and Taiwanese stations.¶
The comparison of the modelled ammonia with satellite observations from CrIS globally showed that the best agreement was achieved using the VDgrlf emissions in 2012–2014. After 2015, all satellite retrieved emissions show a better agreement with CrIS concentrations.¶
Overall, the satellite-constrained ammonia emissions calculated using a variable lifetime appear to give more realistic concentrations, with respect to station and satellite measurements. Accordingly, state-of-the-art emissions appear to underestimate ammonia significantly.

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FIGURE LEGENDS
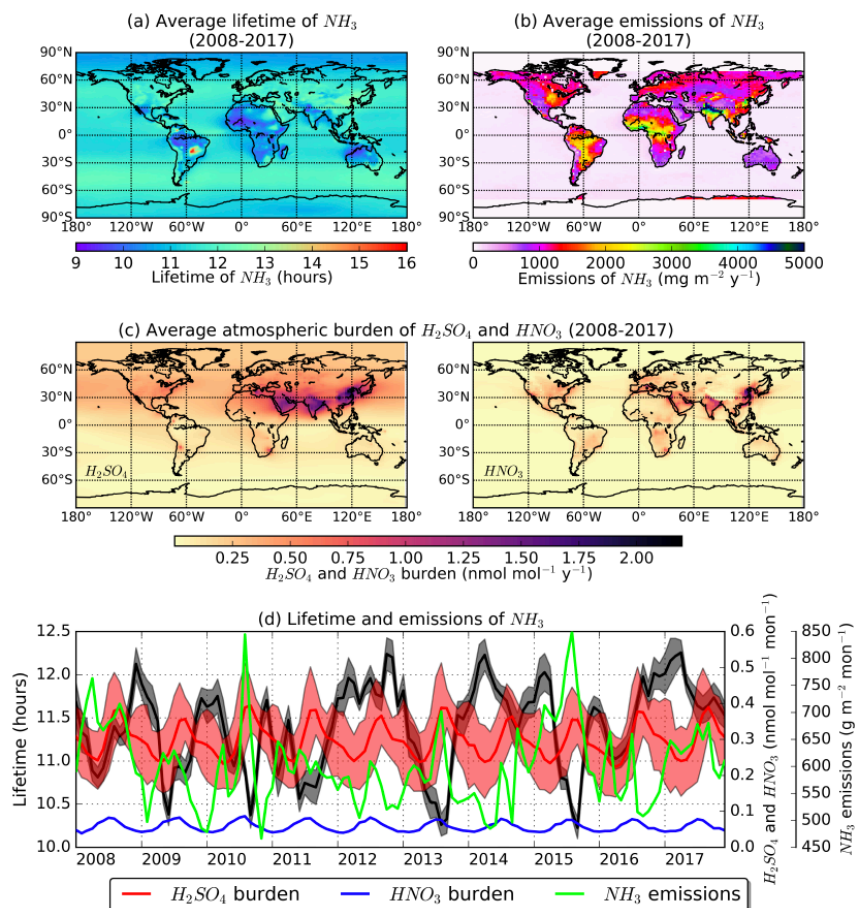
1298
1299 Figure 1. (a) 10-year average model lifetime of ammonia calculated from the LMDz-OR-INCA,
1300 (b) total annual emissions averaged over the 10-year period (NE emissions), (c) atmospheric
1301 burden of the reactants sulfuric and nitric acid calculated in the model, and (d) monthly
1302 timeseries of lifetime (black), ammonia emissions (green), sulfuric (red) and nitric acid column
1303 concentrations (blue) for the whole 10-year period.

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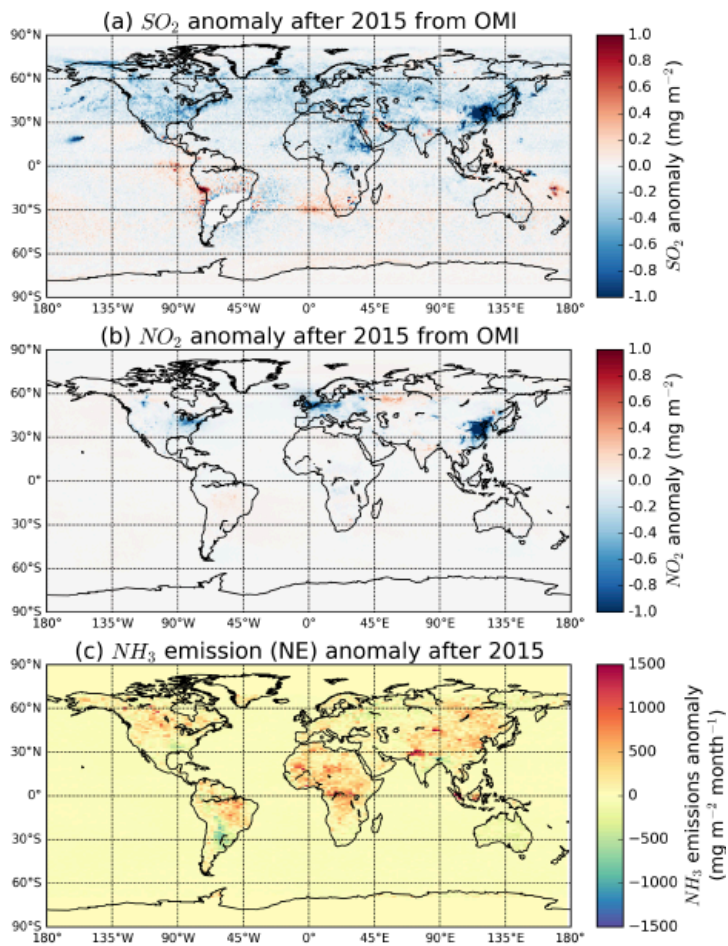
Figure 2. Annual average total column (a) sulfur dioxide and (b) nitrogen dioxide anomaly after 2015 from OMI, and (c) annual average emission anomaly of ammonia calculated from IASI in the present study (NE).

GLOBAL EMISSION DIFFERENCES OF NH_3
FROM VD0.5 (10 YEAR AVERAGE)

+29.4 Tg
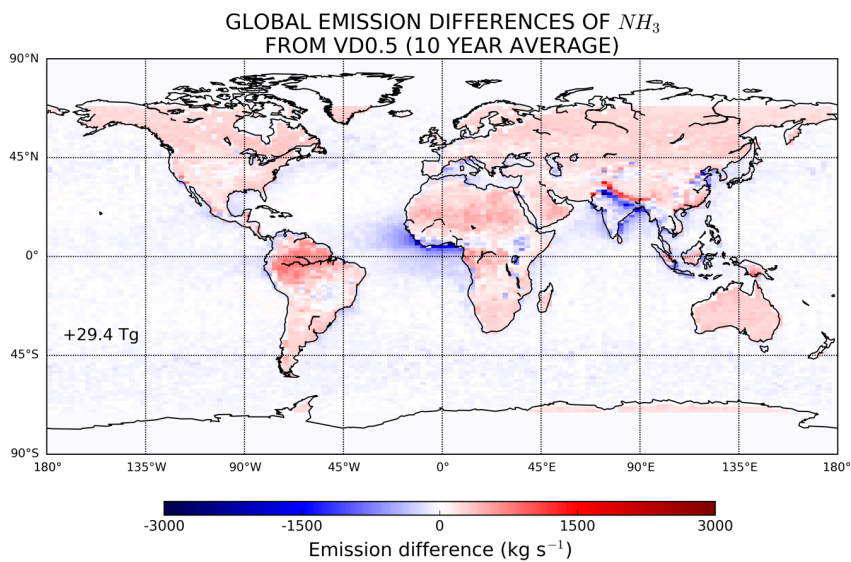
Emission difference (kg s^{-1})

Figure 3. Global differences of ammonia emissions calculated in the present study (NE) from those calculated using Van Damme et al. (2018) gridded concentrations applying a constant lifetime of 0.5 days (VD0.5). The results are given as 10-year average (2008–2017) and the number denotes the annual difference in the emissions.

HOT-SPOT REGIONS AND SEASONALITY OF NH_3 EMISSIONS
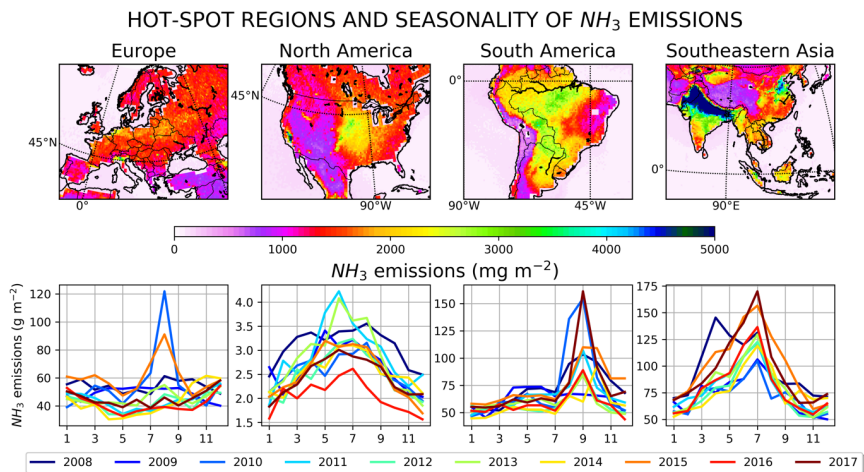
Figure 4. Total annual emissions of ammonia averaged over the 10-year period (2008–2017) in Europe, North and South America and Southeastern Asia, which are regions characterized by the largest contribution to global ammonia budget. In the bottom panels the monthly variation of the emissions is shown for each year of the study period.

COMPARISON WITH OBSERVATIONS FROM EMEP (N=299075)
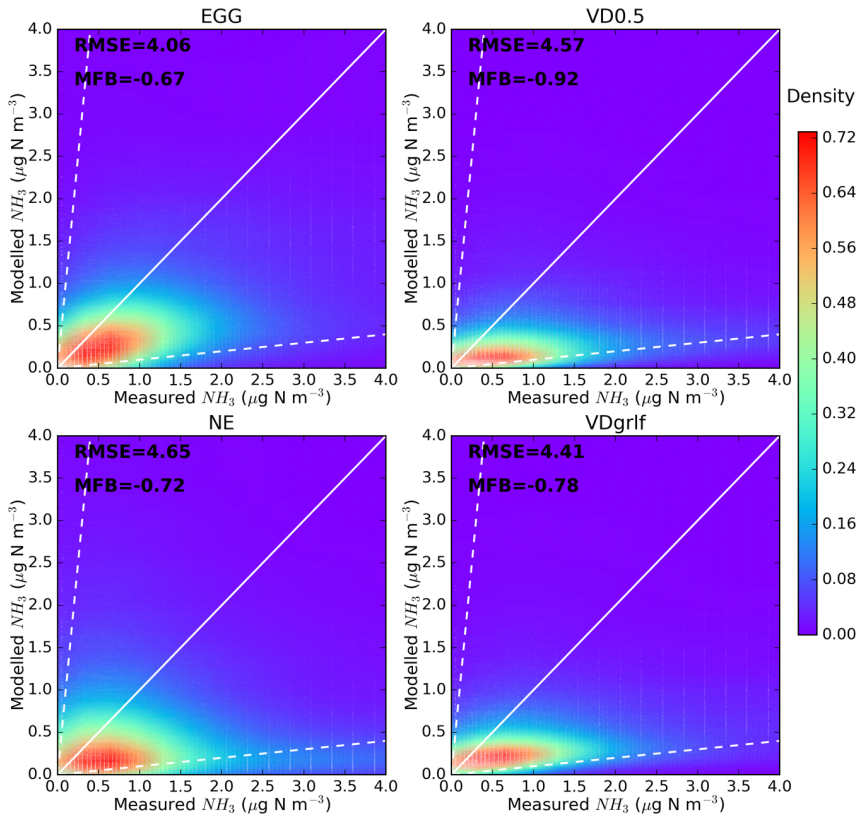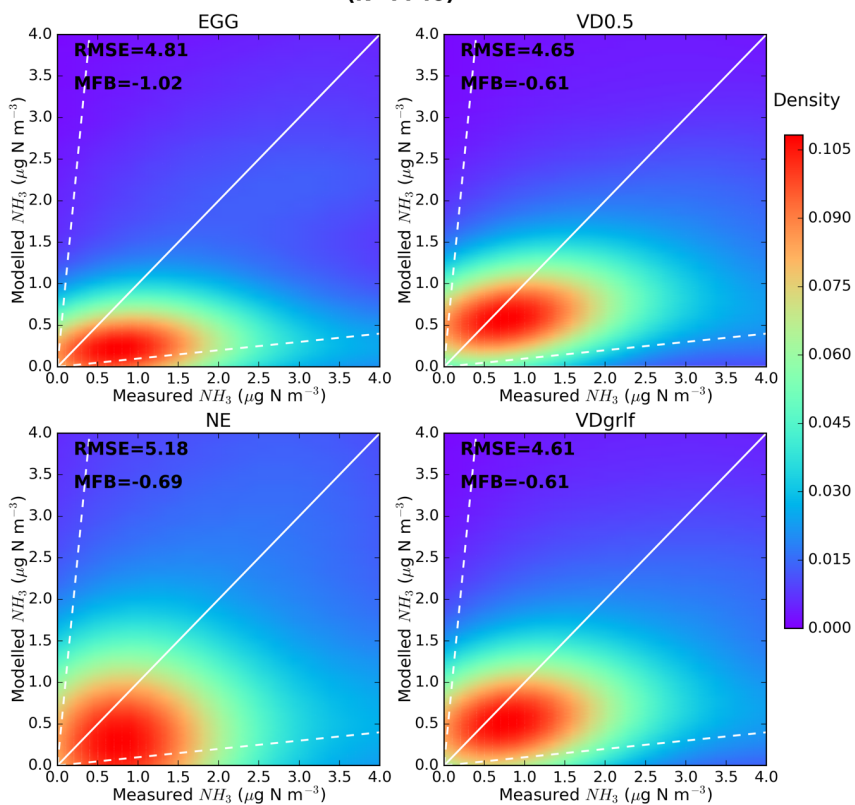
Figure 5. Validation of modelled concentrations of ammonia for different emissions datasets (EGG, VD0.5, NE and VDgrlf) against ground-based measurements from EMEP for the 10-year (2008–2017) study period. Scatterplots of modelled against measured concentrations for the aforementioned emission inventories were plotted with the Kernel density estimation, which is a way to estimate the probability density function (PDF) of a random variable in a non-parametric way.
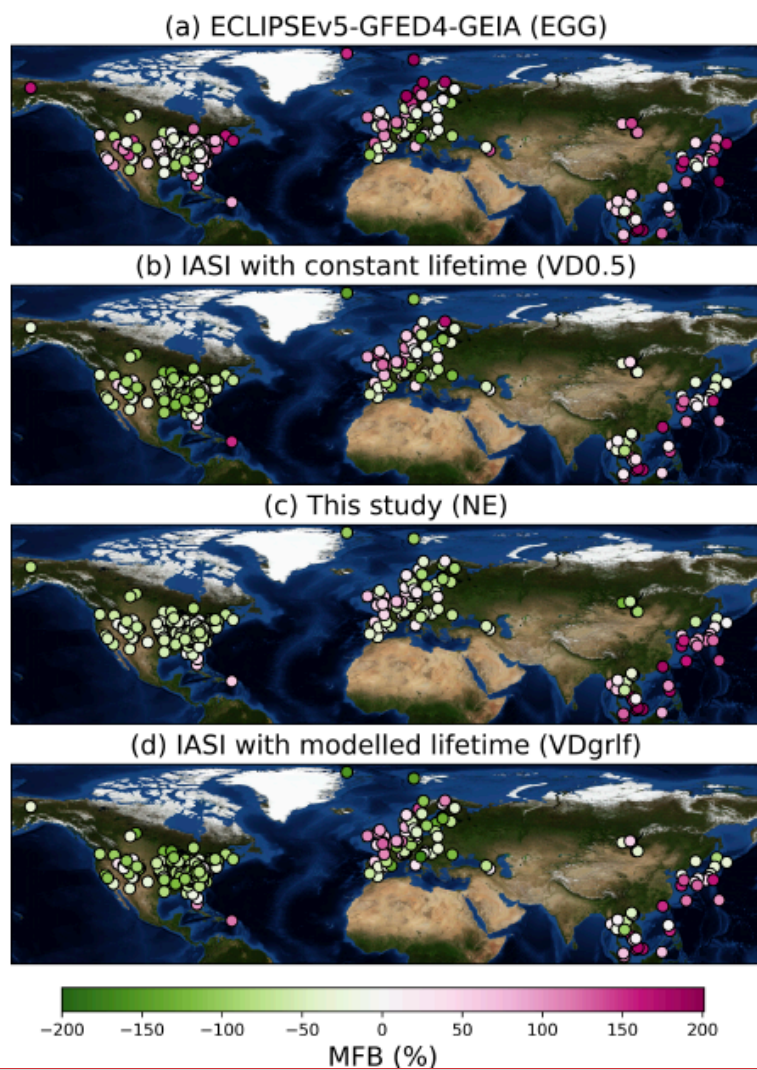
COMPARISON WITH OBSERVATIONS FROM AMON
(N=27096)
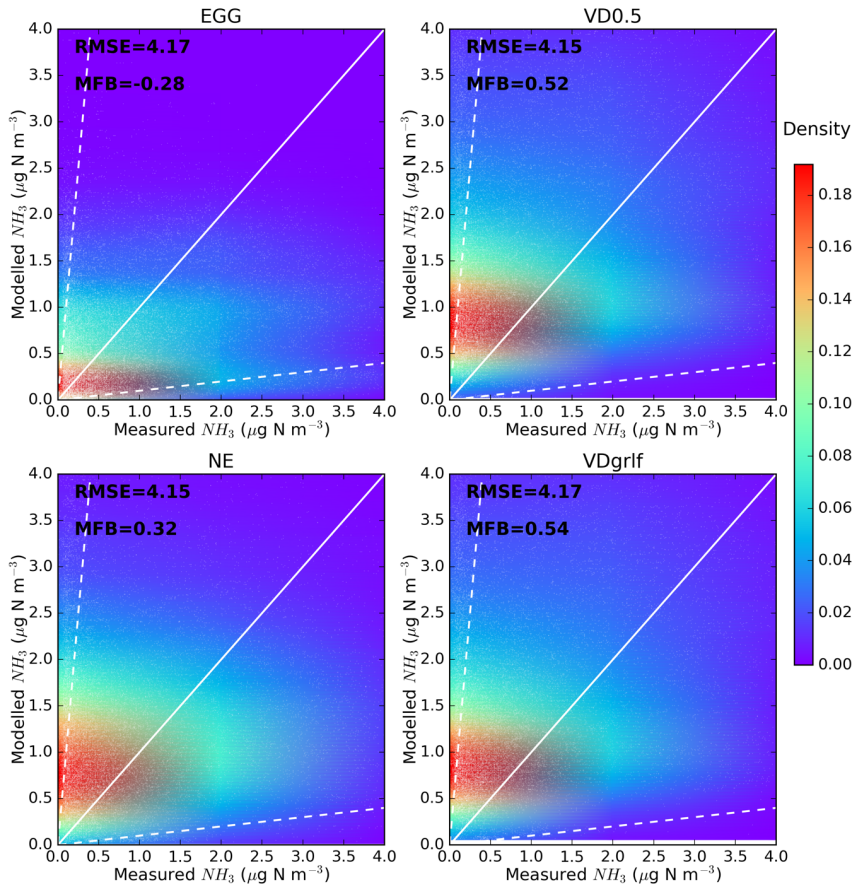
Figure 6. Validation of modelled concentrations of ammonia for different emissions datasets (EGG, VD0.5, NE and VDgrlf) against ground-based measurements from AMON for the 10-year (2008–2017) study period. Scatterplots of modelled against measured concentrations for the aforementioned emission inventories were plotted with the Kernel density estimation, which is a way to estimate the probability density function (PDF) of a random variable in a non-parametric way.

COMPARISON WITH OBSERVATIONS FROM EANET
(N=7740)

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Figure 7. Validation of modelled concentrations of ammonia for different emissions datasets (EGG, VD0.5, NE and VDgrlf) against ground-based measurements from EANET for the 10-year (2008–2017) study period. Scatterplots of modelled against measured concentrations for the aforementioned emission inventories were plotted with the Kernel density estimation, which is a way to estimate the probability density function (PDF) of a random variable in a non-parametric way.

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(a) ECLIPSEv5-GFED4-GEIA (EGG)

(b) IASI with constant lifetime (VD0.5)

(c) This study (NE)

(d) IASI with modelled lifetime (VDgrlf)

MFB (%)

Figure 8. Overview of the comparison with ground-based measurements of ammonia. MFB for each of the stations from AMoN, EMEP and EANET monitoring stations calculated after running LMDz-OR-INCA with the emissions of EGG, VD0.5, NE and VDgrlf for the period 2008–2017.
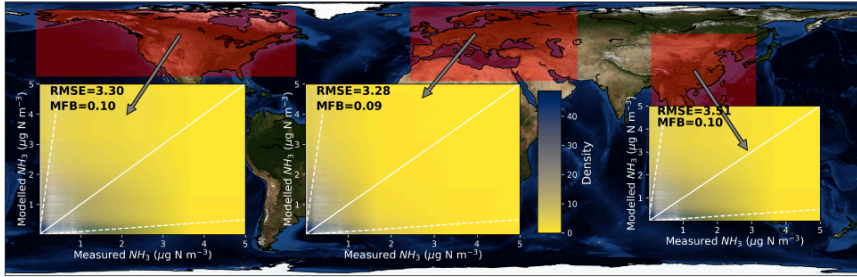
Figure 9. Kernel density estimation (KDE) of the probability density function (PDF) of modelled versus CrIS concentrations of ammonia in a non-parametric way. Modelled concentrations are results of simulations using NE emissions datasets for the period 2012–2017, for which CrIS data were available. The comparison is shown for North America, Europe and Southeastern Asia.
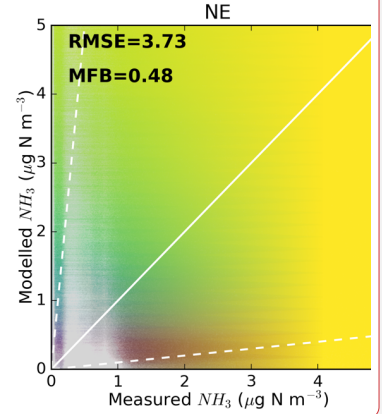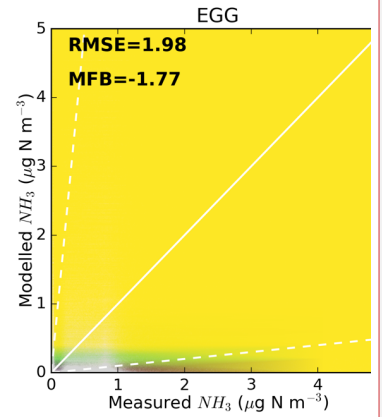
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GLOBAL AVERAGE UNCERTAINTY OF NH_3
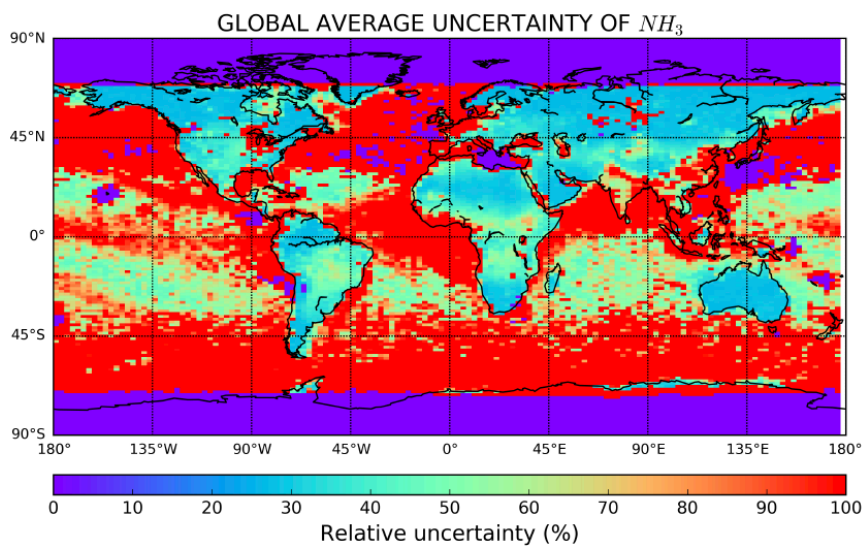
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1364 Figure 10, 10-year average relative uncertainty of modelled surface concentrations expressed

1365 as the standard deviation of surface concentrations from a model ensemble (Table 1) divided

1366 by the average.

1367

1370 Table 1. Model ensemble simulations using different emissions for ammonia that were used in
1371 the calculations of uncertainty. Uncertainties were calculated as the standard deviation of the
1372 surface concentrations of ammonia from the 10 ensemble members for the 10-year period
1373 (2008–2017).

	Parameter perturbed	10-year average emissions (Tg yr^{-1})
Ensemble 1	$d_k = 0$ in Eq. 2	121±50.6
Ensemble 2	$d_k = 10$ in Eq. 2	175±33.3
Ensemble 3	$d_k = 20$ in Eq. 2	189±28.7
Ensemble 4	$d_k = 60$ in Eq. 2	218±15.5
Ensemble 5	$d_k = 100$ in Eq. 2	208±51.8
Ensemble 6	$d_k = 500$ in Eq. 2	223±26.5
Ensemble 7	EGG	65±2.8
Ensemble 8	VD0.5	189
Ensemble 9	NE	213±18.1
Ensemble 10	VDgrlf	201±10.4

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1376 **SUPPLEMENTARY FIGURE LEGENDS**

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1378 Figure S 1.

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1380 Figure S 2.

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