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Global and regional model simulations of atmospheric ammonia

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Abstract

Ammonia (NH₃) is a basic gas of significant atmospheric interest because of its role in the possible formation of fine particulates and because it is a source of fixed nitrogen in soils and plants. NH₃ processing in the atmosphere has been simulated using two 3-D models: the global chemistry transport model, STOCHEM-CRI and the regional coupled meteorological-chemical model, WRF-Chem-CRI. From analysis of STOCHEM-CRI simulations, NH₃ removal fluxes of dry deposition (24.6 Tg(N)/yr), wet deposition (20.8 Tg(N)/yr), NH₄⁺ formation (25.6 Tg(N)/yr) and reaction with OH (1.7 Tg(N)/yr) have been calculated, making a global annual average burden of 0.22 Tg(N) and life-time of 1.1 days. The gas-phase loss by OH, NO₃ and stabilized Criegee intermediates contribute 3%, <1% and <1%, respectively to the total global loss of tropospheric NH₃. The highest concentrations of NH₃ are found to be in the region of South and East Asia, which are associated mostly with agricultural NH₃ emissions. Loss of surface NH₃ by reaction with OH increases by up to 25% along the equator because of the abundances of ozone. Comparison of satellite observations and model results give a better understanding of the temporal and spatial variations of atmospheric NH₃ on a global and regional scales. Using the anthropogenic seasonal NH₃ emission class in the model gives a poor representation of seasonal NH₃. The positive bias in Africa and South America for all seasons is likely due to undetermined sources in the model such as underestimated biomass burning emissions of NH₃ adopted in the model. The regional model

results over North-West Europe during summer months are biased low compared with the measurements- suggesting either missing sources, or too efficient loss processes in the region.

Keywords: Atmospheric ammonia; aerosol; agricultural emissions, global loss; global burden; atmospheric life-time; satellite measurement

1. Introduction

NH₃ is the most abundant alkaline gaseous species in the troposphere and can neutralise H₂SO₄, HNO₃, and HCl to form ammonium salts leading to aerosols (Bigg, 2004; McMurry et al., 2005; Gaydos et al., 2005; Baek and Aneja, 2005; Aneja et al., 2009), which can deteriorate the regional air quality and atmospheric visibility (Erisman and Schaap, 2004; Pinder et al., 2008; Gu et al., 2014; Wang et al., 2015) and influence the global radiation budget (Charlson et al., 1991; Forster et al., 2007; Shindell et al., 2009). The major sources of NH₃ include the bacterial decomposition of animal excreta, large scale fertilizer application on soil, crops, oceans, biomass burning and other combustion processes (Bouwman et al., 1997; Asman et al., 1998; Olivier et al., 1998; Kean et al., 2000; Davison and Cape, 2003; Gilliland et al., 2003; Yamaji, 2004; Aneja et al., 2012; Whitburn et al., 2015). Dry and wet deposition are the most relevant removal pathways for atmospheric NH₃ (Asman et al., 1998; Adams et al., 1999), which have been identified as one of the most rapidly growing sources of anthropogenic nitrogen entering estuarine, coastal, and oceanic waters, with estimates suggesting that atmospheric deposition contributes 20-40% of biologically available new nitrogen entering coastal waters (Duce et al., 1991; Paerl, 1995; Paerl and Whitall, 1999; Paerl et al., 2002). High atmospheric nitrogen deposition rates are coincident with regions experiencing harmful algal bloom expansion (Paerl and Whitall, 1999). Because of these important roles that NH₃ plays in air, soil and water pollution, it is undoubtedly important to understand its sources, deposition and atmospheric behaviour (e.g. gas-particle system and new particle formation), and how these impact on the predictions of the global budget and spatial distribution of NH₃.

The global distribution and the global budget of the atmospheric NH₃ have considerable uncertainties (Clarisse et al., 2009; Sutton et al., 2013; Fowler et al., 2013) due to the coexistence of its various sinks (Galloway et al., 2008). The global budget and distribution of

NH₃ has been studied using different model simulations in previous studies (Schlesinger and Hartley, 1992; Dentener and Crutzen, 1994; Adams et al., 1999; Rodriguez and Dabdub, 2004; Feng and Penner, 2007; Xu and Penner, 2012; Hauglustaine et al., 2014). The gas phase oxidation of NH₃ can have important roles in tropospheric budgets and distributions of NH₃. The knowledge and understanding of these reactions on a global scale are essential to evaluate NH₃ oxidative effects in the atmosphere. The accurate representation of NH₃ chemistry is also required to obtain a good agreement between modelled and observed ammonium and nitrate aerosol concentrations.

The dynamical emission parameterisation, gas-particle partitioning, deposition and bi-directional exchange of NH₃ have previously been implemented and studied using a number of chemical transport models (CTMs). Many CTMs used in these studies have employed Eulerian spatial grids, which enable comprehensive coverage of the domain of interest, but the resulting chemical fields are subject to numerical diffusion and artificial dilution, e.g. EMEP model (Fagerli and Aas, 2008; Simpson et al., 2012), GEOS-Chem (Zhu et al., 2015; Schiferl et al., 2016; Paulot et al., 2014), LOTOS-EUROS (Wichink Kruit et al., 2012), WRF-Chem (Werner et al., 2017; Tuccella et al., 2012), DEHM (Brandt, et al., 2012) and AURAMS (Makar et al., 2009). In contrast, other CTMs have used Lagrangian spatial grids, these generally represent dynamical processes more accurately, with relatively lower computational costs, but suffer from numerical dispersion, necessitating the use of numerical solutions to ensure even spatial coverage, e.g. FRAME model (Kryza et al., 2011; Zhang et al., 2011; Aleksankina et al., 2018), TREND model (Asman, 2001), ACDEP model (Skjth et al., 2004; 2011), STILT-Chem model (Wen et al., 2013), OPS model (Van Pul et al., 2008; Wichink Kruit et al., 2017). In this study, a Lagrangian model, STOCHEM, and an Eulerian model, WRF-Chem-CRI, with the same chemistry scheme, CRI v2-R5, are used to simulate emissions, transport, transformation and removal of NH₃ by gas phase reactions along with heterogeneous and depositional loss, which provide a powerful tool to examine its global (STOCHEM) and regional (WRF-Chem-CRI) distribution and burden more accurately.

2. Model description

2.1. STOCHEM-CRI

STOCHEM-CRI is a global 3-D chemistry transport model (CTM), in which the troposphere is divided into 50,000 air parcels of constant mass. The air parcels are advected every three

hours using a 4th order Runge-Kutta scheme via a Lagrangian approach (Stevenson et al., 1998). It is an offline model with the transport and radiation driven by archived meteorological data (e.g. pressure, temperature, humidity, interpolated wind data, tropopause height, cloud amount, precipitation, boundary layer height, and surface parameters) from the UK Meteorological Office Unified Model, which operates at a grid resolution of 1.25° longitudes by 0.83° latitude and twelve unevenly spaced vertical levels, with an upper boundary up to 100 hPa. A detailed description of the dispersion processes including the vertical coordinate and advection scheme used in STOCHEM can be found in Collins et al. (1997) with updates described by Derwent et al. (2008). The chemical processes that occur within the parcel, together with emission, deposition (both dry and wet) and removal processes are generally uncoupled from transport processes to enable local determination of the chemistry timestep (Cooke et al., 2010; Utembe et al., 2010). The rate of dry deposition is dependent on whether the air parcel is over land or ocean with appropriate species dependent deposition velocities. The sea ice and Antarctica are treated as ‘oceans’ and all other land ice is treated as ‘land’.

Schrader and Brümmner (2014) reported a range of dry deposition velocities for NH_3 at different environments, e.g. 22 mm/s for coniferous forests, 15 mm/s for mixed forests, 11 mm/s for deciduous forests, 9 mm/s for semi-natural sites, 7 mm/s for urban sites, 7 mm/s for water surface, and 10 mm/s for agricultural sites. However, we used an average dry deposition velocity of 8.0 mm/s for all land and ocean, which was also used by Sorteberg and Hov (1996) for their numerical modelling study. The loss rate of NH_3 via wet deposition was determined by a combination of dynamic and convective precipitation rates, height dependent coefficients obtained from Penner et al. (1994) and scavenging profiles. Removal by wet scavenging is uniform amongst each air parcel within a given cell covered by the relevant precipitation information (Collins et al., 1997).

The gas phase losses of NH_3 are investigated in terms of the reactions with OH, NO_3 and stabilized Criegee intermediates. We used the Common Representative Intermediates mechanism version 2 and reduction 5 (CRI v2-R5) in STOCHEM, referred to as ‘STOCHEM-CRI’, which create the reasonable OH, NO_3 and stabilized Criegee intermediates fields. The detailed description of the CRI v2-R5 mechanism is given by Watson et al. (2008) with updates highlighted in Jenkin et al. (2008) and Utembe et al. (2009; 2010) and the full mechanism is available via the Master Chemical Mechanism (MCM) website (<http://mcm.leeds.ac.uk/CRI/>). The concentration of each chemical species is then

updated using a backward Euler integration with a time step of five minutes (Collins et al., 1997). The NH_3 that is emitted into STOCHEM-CRI has a major role in fixing the pH of cloud water and hence the oxidation rate of SO_2 to ammonium sulphate through the cloud-phase reactions. The ammonium sulphate then falls as NH_4^+ in rain or evaporates to form ammonium aerosol. More details about the implementation of ammonium sulphate formation through the cloud-phase reactions in STOCHEM-CRI can be found in Stevenson et al. (2003), Derwent et al. (2003) and Sanderson et al. (2006). In STOCHEM-CRI, the coarse mode nitrate aerosol is formed by the interaction of HNO_3 and N_2O_5 with coarse mode soil-dust and sea-salt aerosol (Derwent et al., 2003). Pierson and Brachaczek (1988) showed that NO_3^- in fine mode was NH_4NO_3 and NO_3^- in coarse mode was both NH_4NO_3 and NaNO_3 . We split coarse mode nitrate aerosol (NaNO_3 , formed from the sea-salt displacement reaction) from fine mode ammonium nitrate (NH_4NO_3 , formed from the reaction between NH_3 and HNO_3) in the updated STOCHEM-CRI model.

Table 1

The gas phase reactions of NH_3 used in the different simulations by the STOCHEM-CRI

Simulation	Reactions of NH_3 in the model	Rate coefficient (molecules ⁻¹ cm ³ s ⁻¹)	References
STOCHEM-Base	$\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3$ $\text{NH}_4\text{NO}_3 \rightarrow \text{HNO}_3 + \text{NH}_3$	2.5×10^{-14} $2.8 \times 10^{-4} \exp(118.87 - (24084/T) - 6.025 \ln T)^*$	a a
STOCHEM-Gas	$\text{O}(^1\text{D}) + \text{NH}_3 \rightarrow \text{OH} + \text{NH}_2$ $\text{OH} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_2$ $\text{NO}_2 + \text{NH}_2 \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O}$ $\text{NO}_2 + \text{NH}_2 \rightarrow \text{NH}_2\text{O} + \text{NO}$ $\text{O}_3 + \text{NH}_2 \rightarrow \text{NH}_2\text{O} + \text{O}_2$ $\text{O}_3 + \text{NH}_2\text{O} \rightarrow \text{NH}_2 + 2\text{O}_2$ $\text{NH}_2\text{O} + \text{OH} \rightarrow \text{HNO} + \text{H}_2\text{O}$ $\text{HNO} + \text{OH} \rightarrow \text{NO} + \text{H}_2\text{O}$ $\text{NO} + \text{NH}_2 \rightarrow \text{H}_2\text{O} + \text{N}_2$ $\text{O}(^1\text{D}) + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2$ $\text{NO}_3 + \text{NH}_3 \rightarrow \text{HNO}_3 + \text{NH}_2$ $\text{SCI} + \text{NH}_3 \rightarrow \text{Products}$	2.5×10^{-10} $1.7 \times 10^{-12} \exp^{(-710/T)}$ $4.3 \times 10^{-6} (T)^{-2.191} \exp^{(-229/T)}$ $1.5 \times 10^{-12} (T)^{0.032} \exp^{(761/T)}$ 1.5×10^{-13} 2.0×10^{-14} 1.8×10^{-10} 5.0×10^{-11} $4.0 \times 10^{-12} \exp^{(450/T)}$ 4.9×10^{-11} $3.0 \times 10^{-14} \exp^{(-1839/T)}$ $(3.1 \pm 0.5) \times 10^{-20} T^2 \exp^{(1011 \pm 48/T)}$	Sander et al. (2011) Sander et al. (2011) Klippenstein et al. (2013) Klippenstein et al. (2013) Sander et al. (2011) Bulatov et al. (1980) Sun et al. (2001) Sun et al. (2001) Sander et al. (2011) Sander et al. (2011) Anglada et al. (2014) Chhantyal-Pun et al. (2019)

*The unit is in s⁻¹. ^a These processes are described using a kinetic approach to represent constraints on the establishment of thermodynamic equilibria in the NH_4NO_3 – HNO_3 – NH_3 system as described in the text.

Extensions have been added to the gas-phase chemistry in STOCHEM-CRI to address ammonium nitrate (NH_4NO_3) formation. The approach adopted is highly simplistic and

utilises a chemical kinetic approach following the study of kinetic limitations in the NH_3 - HNO_3 - NH_4NO_3 system by Harrison and Mackenzie (1990), in the absence of the detailed physico-chemical and meteorological data that would be required for more detailed thermodynamic treatments (see, for example, Yu et al., 2005). A summary of the approach is given in Table 1. The formation of ammonium nitrate adopted a reversible reaction from NH_3 and HNO_3 vapour with the ratio of the forward and backward rate coefficients taken from Mozurkewich (1993). The forward rate coefficient was set to $2.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ so that for realistic ppb mixing ratios of NH_3 and HNO_3 , the formation of ammonium nitrate had a time constant of the order of one second or so.

The Base simulation (referred as STOCHEM-Base) based on the reference conditions used in the study of Utembe et al. (2011) in which the total global NH_3 emissions of 58.7 Tg N from industries, manure management, agricultural soils, agricultural waste burning, solid waste landfills, waste water handling, solid waste incineration, etc for 2012 were taken from global air pollutant emissions inventory EDGAR v4.3.2 (http://edgar.jrc.ec.europa.eu/overview.php?v=432_AP). The NH_3 emissions from this global database are used with some caveats. Crippa et al. (2018), reported that the uncertainty of NH_3 emissions in the EDGAR v4.3.2 inventory is in the range of 186-295% in 2012, highest among all pollutants in that database due to the high uncertainty of both agricultural statistics and emission factors. Previous studies have investigated in more detail the accuracy of the subsets of other EDGAR emissions datasets. Meng et al. (2017) recalculated the global emissions of NH_3 from combustion and industrial sources (which they determined contribute 11.8% of all NH_3 global emissions), using updated emission factors from China. In comparison with EDGAR v4.3.1, their total emissions for these sectors only, were 21.4% lower. Abdallah et al. (2016) showed large discrepancies between EDGAR-HTAP and 2 different regional emission inventories for Europe and Lebanon, with a 3-fold higher of EDGAR-HTAP in terms of emission estimates and spatial distribution. At the moment, however, these isolated developments have not been folded back into the available global emissions databases, and so we will use the EDGAR v4.3.2 dataset. The spatial distribution of each individual sources of NH_3 is extracted from the surface emission outlined in EDGAR. The biomass burning emissions of 5.9 Tg N, and oceanic emissions of 8.2 Tg N (Bouwman et al., 1997) were added in the global emissions of NH_3 . The surface emission class from biomass burning and oceans are distributed using monthly two-dimensional source maps at a

resolution of 5° longitude by 5° latitude (Olivier et al., 1996). A further simulation (referred as STOCHEM-Gas) was conducted after adding gas phase loss processes of NH_3 by OH, NO_3 , stabilized Criegee intermediates and $\text{O}(^1\text{D})$ outlined in Table 1. Both simulations were conducted with meteorology from 1998 for a period of 24 months with the first 12 months allowing the model to spin up. Analysis were performed on the subsequent 12 months of data.

2.2. WRF-Chem-CRI

WRF-Chem (version-3.8.1) referred to as WRF-Chem-CRI, is a regional 3-D meteorological Eulerian model with online chemistry (Grell et al., 2005). The model chemical setup follows that of Archer-Nicholls et al. (2015) and Khan et al. (2019), with modifications noted below. NH_3 (and SO_2 , NO_x) emissions are taken from the European TNO (Denier van der Gon et al., 2010) and UK NAEI (<http://naei.defra.gov.uk/>) databases, processed and combined as described in Archer-Nicholls et al. (2014), and have been updated to the years 2011 and 2015, respectively. TNO data used in this study is for the year 2011 and has a resolution of 0.125° longitude by 0.0625° latitude. The NAEI data used in this study is for the year 2015 and has a resolution of 1km by 1km. Chemical boundary conditions are taken from the MOZART global model (Emmons et al., 2010). Gas-phase chemistry is treated using the CRIv2R5 mechanism (Watson et al., 2008), while the aerosol scheme used is MOSAIC with 8 size bins (from $0.03\text{--}10\text{ }\mu\text{m}$) (Zaveri et al., 2008) and aqueous chemistry. NH_3 is treated as unreactive in the model, and so suffers no gas-phase chemical losses. Dry deposition of NH_3 , as well as of aerosol particles, as well as in- and below-cloud scavenging of gases and aerosol particles (and subsequent rain-out), all provide loss pathways for NH_3 . Gaseous dry deposition is treated using the Wesely model (Wesely, 1989; Erisman et al, 1994). Partitioning to the condensed-phase in parallel with acid gases (H_2SO_4 , HNO_3 , and HCl) is treated dynamically within the MOSAIC aerosol module, driven by the MESA-MTEM multi-component equilibrium solver (Zaveri et al., 2005a; 2005b). This calculates the equilibrium solution for a system consisting of H^+ , NH_4^+ , Na^+ , SO_4^{2-} , HSO_4^- , NO_3^- , and Cl^- ions, and has been evaluated against the rigorous thermodynamic solution calculated by the AIM III model (Clegg et al., 1998).

The model domain is that used in Archer-Nicholls et al. (2014) and Khan et al. (2019). It has a 15 km horizontal resolution, with 134 (E–W) by 146 (N–S) grid cells covering North-West Europe, and 41 vertical levels (with enhanced resolution within the planetary boundary

layer). Meteorology is driven using ECMWF ERA-Interim reanalysis data (Dee et al., 2011), with a 6 hourly time resolution, and surface data extracted on a N256 gaussian grid, while volume data was extracted at a lower resolution on a N128 gaussian grid. Simulations were performed for the period of July-Aug 2012, with model data output every hour.

2.3. Satellite instrumentation (IASI-ANNI-NH3-v2.1)

The measurement data for NH₃ are sparse and its measurement is difficult at relevant mixing ratios (<10 ppbv) (von Bobruzki et al., 2010) producing large uncertainties in the reported measurement data of NH₃. Thus, the Infrared Atmospheric Sounding Interferometer (IASI) satellite NH₃ column measurement data (IASI-ANNI-NH₃-v2.1, Van Damme et al., 2017) is used to validate STOCHEM data. IASI is a nadir-looking high-resolution Fourier transform spectrometer onboard the polar-orbiting sun-synchronous Metop (Meteorological Operational) satellites, which covers the entire globe twice a day (09:30 and 21:30 Local Solar Time Equator crossing, descending node). The IASI field of view is composed of 2×2 circular pixels each with an elliptical footprint on the ground varying from 12 km $\times$ 12 km (at nadir) up to 20 km $\times$ 39 km (off nadir), depending on the viewing angle. The availability of the measurements is mainly dependent on the cloud coverage. The retrieval of NH₃ is based on the calculation of a spectral hyperspectral range index (HRI) and subsequent conversion to a NH₃ total column (cm⁻²) using a neural network (Whitburn et al., 2016). The retrieval also includes a full uncertainty analysis, performed by perturbing the input parameters (temperature profile, HRI, NH₃ a priori profile, etc.) of the neural network. Van Damme et al. (2017) showed that the uncertainty of the satellite NH₃ measurements is mainly driven by the HRI and the temperature profile. We used Artificial Neural Network, ANNI-NH₃-v2R-I version of the retrieval technique, which relies on ERA-Interim ECMWF meteorological input data, along with built-in surface temperature (Van Damme et al., 2017) giving improved uncertainty of the satellite NH₃ data. More details about the NH₃ retrieval methods and the parameters used in the ANNI-NH₃-v2R-I dataset can be found in Whitburn et al. (2016) and Van Damme et al. (2017). The daily global NH₃ total columns (cm⁻²) for the entire 2016 year and July-August, 2012 from the measurements of IASI onboard Metop-A were collected from <https://iasi.aeris-data.fr/>. The STOCHEM-CRI model was driven by meteorology for the year 1998, which was a very strong El-Niño year, thus we selected the satellite data for another intense El-Niño year, 2016. For comparison with global modelling, the satellite and STOCHEM data within each model grid cell are averaged for the whole season being compared. For comparison with regional modelling, WRF-Chem-CRI is

sampled using the satellite measurement positional and temporal information (within a half hour of each of the model's hourly outputs); creating a set of co-located measurement and model data points. These data points are then grouped on to a $1^\circ \times 1^\circ$ grid, retaining temporal information, to enable investigation of the spatial correlation of the data.

3. Results and Discussion

3.1. Global budget of NH_3

Table 2 summarizes the global budget of NH_3 produced by the STOCHEM-Base and STOCHEM-Gas model simulations. In the model, the only source of atmospheric NH_3 is from the surface emissions of $72.9 \text{ Tg N yr}^{-1}$. In the STOCHEM-Base case, NH_3 is removed effectively by dry deposition (35%) and wet deposition (30%). The conversion of NH_3 to particulate NH_4^+ contributes 35% to the total loss of NH_3 . The global burden (291 Gg N) and life-time (4.1 days) of NH_4^+ are found to be higher than the global burden (232 Gg N) and life-time (1.16 days) of NH_3 , thus NH_4^+ can be transported longer distances downwind from the sources of NH_3 , which can impact on air quality and climate change. The global budget and lifetime of NH_3 are found to be higher than in the previous studies, significantly higher (two to three-fold) compared with the studies of Xu and Penner (2012) and Hauglustaine et al. (2014) (Table 2). The global total emission of NH_3 simulated by the STOCHEM-Base is $\sim 20 \text{ Tg N yr}^{-1}$ ($\sim 40\%$) higher than the emissions used in Adams et al. (1999), Xu and Penner (2012) and Hauglustaine et al. (2014), so it is not surprising to obtain a higher global burden in this study compared with other studies. The main loss of NH_3 , which is due to the formation of NH_4^+ is found to be ~ 1.5 -fold lower in STOCHEM than the studies of Dentener and Crutzen (1994), Adams et al. (1999) and Xu and Penner (2012), possibly as a result of the underestimation of NH_4NO_3 formation using the more simplistic chemical kinetic approach in STOCHEM. The underestimated loss due to the formation of NH_4^+ in this study reflects the increased global burden and lifetime of NH_3 in this study compared with the other studies (Table 2). The loss of NH_3 due to wet deposition is found to be larger than other studies. The increased deposition of NH_3 in the study reflects higher N deposition fluxes giving a significant nutrient input to the ecosystem. In the STOCHEM-Gas simulation, the loss of NH_3 through the reactions with OH, NO_3 and SCI contribute a non-negligible amount of 2%, <1% and <1%, respectively to its total loss resulting in a decrease of global burden (221 Gg N) and lifetime (1.11 days) of NH_3 . Moreover, the intermediate, NH_2 produced from the loss process by OH can provide a substantial amount of one of the strong greenhouse

gases, N₂O (0.5 Tg N yr⁻¹), which represents about 3% of the total global N₂O budget (Ciais et al., 2013). This number is comparable with the estimation of 0.6 Tg N yr⁻¹ by Dentener and Crutzen (1994) and Hauglustaine et al. (2014).

Table 2

Global budget and atmospheric life-time of simulated NH₃ in this study and their comparison with previous studies. The percentage contribution of the production and loss processes are shown in parenthesis.

	STOCH EM-Base	STOCH EM-Gas	Dentener and Crutzen (1994)	Adams et al. (1999)	Xu and Penner (2012)	Hauglustaine et al. (2014)
Production (Tg N/yr)						
Direct emission	72.9 (100)	72.9 (100)	45.0 (100)	53.6 (100)	53.6 (100)	50.5 (100)
Loss (Tg N/yr)						
Loss to NH ₄ ⁺	25.9 (35.6)	25.6 (35.2)	24.8 (55.1)	26.1 (48.7)	30.5 (56.9)	17.5 (34.6)
Loss by OH	n/a	1.7 (2.3)	1.8 (4.0)	1.1 (2.1)	0.7 (1.4)	0.6 (1.3)
Loss by NO ₃	n/a	0.1 (0.1)	n/a	n/a	n/a	n/a
Loss by SCI	n/a	0.1 (0.1)	n/a	n/a	n/a	n/a
Dry deposition	25.4 (34.9)	24.6 (33.8)	12.5 (27.8)	19.0 (35.5)	12.7 (23.7)	21.3 (42.3)
Wet deposition	21.5 (29.5)	20.8 (28.6)	5.9 (13.1)	7.4 (13.8)	9.6 (18.0)	11.1 (21.9)
Global Burden (Gg N)	232.5	221.3	260	140	70	90
Lifetime (τ) (days)	1.16	1.11	0.9	0.93	0.46	0.63

3.2. Global Surface and zonal distribution of NH₃

The surface concentrations of NH₃ are dependent on the partitioning between NH₃ and NH₄⁺, as controlled by particulate formation (Langford et al., 1992), as well as the loss due to dry and wet deposition, which is reflected in the surface distribution of NH₃. NH₃ concentrations (Figure 1a) exhibited a distinct surface distribution with peak values of up to 8.0 µg/m³ over South and East Asia. In the model, the fertilizer and domestic animals related activities

contribute most of the ammonia emissions (Bouwman et al., 1997), thus we found highest ammonia emissions in the agricultural regions (e.g. India, Bangladesh, China). A significant amount of NH_3 ($1\text{--}2\ \mu\text{g}/\text{m}^3$) is also found in North Africa, Central Africa and south America where biomass burning emissions are predominant. The distribution and the amount of global NH_3 is found to be consistent with Zhu et al. (2015) who used GEOS-Chem global chemical transport model with considering bidirectional air-surface exchange of NH_3 .

Figure 1 (a) Annual mean surface level distribution of NH_3 simulated by the STOCHEM-Base, (b) The percentage change of NH_3 distribution from STOCHEM-Base to STOCHEM-Gas simulation (after adding gas phase loss processes of NH_3 by NO_3 and OH in the model). Note that percentage change (%) = $((\text{STOCHEM-Gas} - \text{STOCHEM-Base}) \times 100) / \text{STOCHEM-Base}$

The inclusion of gas-phase loss processes of NH_3 through its reactions with OH and NO_3 decreases its concentrations over the tropics by up to 25% (Figure 1b). The loss flux of NH_3 by NO_3 is found to be more than one order of magnitude lower than the loss flux of NH_3 by OH (Table 2), thus the percentage loss of NH_3 shown in Figure 1b is mostly contributed by reaction with OH . OH is high in the tropics due to a combination of high water vapour and fast photochemistry, which results in greater decrease of NH_3 concentrations in the tropical regions. The seasonal variation of global OH has a direct implication on the percentage changes of NH_3 , with a significant reduction of up to 40% ($-0.70\ \mu\text{g}/\text{m}^3$) during J-J-A season over North Africa and Middle East countries compared with only up to 15% ($-0.20\ \mu\text{g}/\text{m}^3$) during D-J-F season over central Africa and south East Asia countries (see Supplementary Figures S1 and S2).

Figure 2 (a) Annual zonal mean distribution of NH₃ simulated by the STOCHEM-Base, (b) The percentage change of NH₃ distribution from STOCHEM-Base to STOCHEM-Gas simulation (after adding gas phase loss processes of NH₃ by NO₃ and OH in the model). Note that percentage change (%) = ((STOCHEM-Gas-STOCHEM-Base)*100)/STOCHEM-Base

NH₃ can exhibit strong vertical gradients in the boundary layer, which cannot be adequately resolved by the coarse model, STOCHEM-CRI. However, the zonal distribution of NH₃ from this study shows the peak at the surface between 20-35°N (Figure 2a). The concentration of NH₃ decreases with altitude due to its surface source, its removal by wet and dry deposition, and its conversion to NH₄⁺ particulate through the reaction with acidic substances (e.g. H₂SO₄, HNO₃). After adding the gas-phase loss reactions by OH and NO₃, the concentrations of NH₃ are reduced (3%) in the tropics at the top level of the troposphere. The OH concentration is highest above the surface of the tropics, but NH₃ and NO₃ levels are higher at the surface and decrease with altitude. These two combined effects resulted in reducing the concentration of NH₃ by up to 10% in the mid-altitudinal (700 hPa to 900 hPa) tropical region.

3.3. Impact of Reaction of NH₃ with Criegee intermediates

The reaction of NH₃ with stabilized Criegee intermediates is found to be insignificant (Jørgensen and Gross, 2009; Misiewicz et al., 2018, Chhantyal-Pun et al., 2019) compared with the other gas-phase oxidation reactions of NH₃. The co-location global surface plot of NH₃ and Criegee intermediate (Figure 3a) shows that there is a high degree of collocation in India, China, South America and central Africa. Integrating this loss process into STOCHEM-Gas, we found that the effect of Criegee loss on the NH₃ concentration is found to be minor, reducing surface NH₃ levels by only 1.5 pptv (equivalent to <1% loss of the total concentration) because of the very slow reaction. This small reduction is found in the intensive farming areas and the Amazonian rainforest areas. However, it is possible that

significant quantities of the $\text{NH}_3\cdot\text{H}_2\text{O}$ complex exists in the troposphere with high humidity and low temperature regions (Smolen et al., 1991; Wormald et al., 2001). The influence of $\text{NH}_3\cdot\text{H}_2\text{O}$ can be significant when we consider its reaction with stabilized Criegee intermediates. The water complexation of NH_3 can reduce the energy barrier of the transition state of the gas phase reaction of $\text{NH}_3 + \text{sCI}$, thereby increasing the reaction rate. Thus, the complexation could have a significant impact on the reaction of sCI and NH_3 in the troposphere. However, more studies, especially focusing on experimental measurements of the kinetics and product characterisation of these reactions are needed to quantify the impact of these reactions in the atmosphere.

Figure 3 (a) A co-location plot of NH_3 (coloured part) and Criegee intermediate (grey part), (b) the absolute reduction of NH_3 concentrations after adding its reaction with Criegee intermediate in the model assuming all Criegee intermediates react with the same rate as CH_2OO does. Note: Absolute change = (NH_3 field with Criegee loss- NH_3 field without Criegee loss)

3.4. Global Model-Satellite comparisons

The global STOCHEM and satellite observations of NH_3 for four seasons December-January-February (D-J-F), March-April-May (M-A-M), June-July-August (J-J-A) and September-October-November (S-O-N) (Figures 4 to 7, the data density for different seasons are shown in supplementary Figure S3), show that the measured NH_3 concentrations have a seasonal pattern with summer highs because of the transport of NH_3 downwind from agriculturally related sources and decomposition of NH_4NO_3 at higher temperature, but, the simulated NH_3 concentrations by the STOCHEM-Gas exhibited little seasonal pattern. The seasonal variation of measured NH_3 can be partly explained with the variable climate conditions in different seasons. The main emission sources of NH_3 (e.g. excreta from domestic animals, use of synthetic N fertilizers) vary seasonally depending on the crop production cycle and temperature, but using the seasonal anthropogenic emission class of NH_3 in the STOCHEM-

Gas could not give an accurate seasonal representation of NH_3 . Overall the IASI and STOCHEM-Gas NH_3 column give similar distributions for the main source areas e.g. India and China (Figure 4) which is consistent with the study of Whitburn et al. (2016) who compared IASI NH_3 column data with GEOS-Chem simulated NH_3 data.

The relationship between satellite and STOCHEM-Gas NH_3 is found to be very consistent with good to reasonable correlation ($r^2=0.29$ for D-J-F, $r^2=0.58$ for M-A-M, $r^2=0.42$ for J-J-A and $r^2=0.34$ for S-O-N) (Figures 4-7). The model-measurement deviation is pronounced with significantly higher NH_3 measured in North America (during J-J-A, S-O-N and M-A-M seasons), South America (during all seasons), Central and South Africa (during all seasons), South and East Asia (during J-J-A and M-A-M seasons) (Figures 4-7). The lack of agreement between satellite and STOCHEM-Gas in urban areas in North America is probably as a result of an underestimation of non-agricultural sources of NH_3 (e.g. traffic related sources) suggested by Whitehead et al. (2007), Perrino et al. (2002), Meng et al. (2011), Ianniello et al. (2010) and Hu et al. (2014). In the STOCHEM-Gas, traffic related emission is not included, which gives the underestimation of the model results compared with the measured data. In addition, the coarse grid resolution (5° latitude by 5° longitude) used for emissions, inter parcel exchange and data output mapping in STOCHEM make model-measurement comparison challenging, especially when emissions vary substantially over 5° latitude by 5° longitude (e.g. urban pollutions). The deviation of the model-measurement is also notable because the satellite measurement data of NH_3 has a very large variability in their associated uncertainty due to the variable sensitivity of the infrared outgoing radiation to the lower atmosphere as determined by thermal contrast (Clarisse et al., 2010; Bauduin et al., 2017).

The N fertilizer application to the rice fields and the volatilization of NH_3 from livestock farming and fertilizer (particularly urea) in South and East Asia can significantly increase the atmospheric concentration of NH_3 (Kumar et al., 2004; Biswas et al., 2008; Aneja et al., 2012; Bouwman et al., 1997). The higher concentrations of STOCHEM-Gas NH_3 (i.e. negative bias) during winter and lower concentrations (i.e. positive bias) during summer are found in these regions, which could be due to the use of the anthropogenic NH_3 seasonal emission distribution class in the model. However, in the satellite measurement, summertime is the best time to measure NH_3 by IASI and the uncertainty of the summer satellite NH_3 column is much lower than that of winter satellite NH_3 column (Van Damme et al., 2017). Moreover, the uncertainty distribution of NH_3 column analysis (Whitburn et al., 2016) shows that the uncertainties are 30-50% over the identified source regions and >150% over the low

NH₃ columns region, which can explain the deviation between measured and model NH₃ column.

Satellite data reveal that there is a significant amount of NH₃ emitted from the biomass burning regions. The largest emissions from biomass burning in the northern hemisphere are found during J-J-A over Eastern Russia. However, in the southern hemisphere the highest emissions are seen over Western and central Africa during December to May due to persistent burning of agricultural wastes (Haywood et al., 2008) and over South America during September to November due to extensive burning and minimum precipitation (Oliveras et al., 2014). The STOCHEM-Gas NH₃ is found to be much lower compared with measured NH₃ in these regions. The strong positive bias during D-J-F and M-A-M in Western and central Africa and during J-J-A in Eastern Russia and during S-O-N in South America could therefore be due to the possible low biomass burning emissions of NH₃ adopted in the STOCHEM-Gas or some undetermined sources of NH₃ not considered in the STOCHEM-Gas.

Figure 4. The model NH₃ values (a) and satellite derived column NH₃ values (b), the bias between satellite and model derived column NH₃ values (c) and the correlation between model-satellite derived column NH₃ values (d) for December-January-February (D-J-F) season. Note: Bias= (satellite NH₃- Model NH₃).

Figure 5. All panels are as in Figure 4 but for March-April-May (M-A-M) season

Figure 6. All panels are as in Figure 4 but for June-July-August (J-J-A) season

Figure 7. All panels are as in Figure 4 but for September-October-November (S-O-N) season

3.5. Regional modelling

The short atmospheric life-time of NH_3 and its strong vertical gradients in the boundary layer make it difficult to compare the measured NH_3 concentrations at different environmental and geographical conditions with the STOCHEM-CRI coarse model resolution ($5^\circ \times 5^\circ$) results. In order to address this limitation, we have simulated NH_3 over North-West Europe with a finer grid resolution ($15 \text{ km} \times 15 \text{ km}$) of the WRF-Chem-CRI regional model. Figure 8a and 8b represents the spatial distribution of NH_3 across Europe during August 2012 using an averaged regional model, WRF-Chem-CRI and satellite NH_3 column data, respectively. Both satellite and WRF-Chem-CRI show high concentrations of NH_3 over Northern Italy, Western France and Northern Germany. The average WRF-Chem-CRI data are lower in most continental regions (other than Northern Italy) than the satellite measurements, but the average WRF-Chem-CRI data are consistently higher over the North Sea (Supplementary Figure S4a). The lower WRF-Chem-CRI predictions could possibly be due to missing sources of NH_3 in the emission inventories (TNO, NAEI) used for these simulations. For example, uncertainties of $\pm 20\%$ (NAEI) and $\pm 29\%$ (TNO) for NH_3 emissions in these datasets are reported by Aleksankina et al. (2018) and Nielsen et al. (2014), respectively. The

satellite and WRF-Chem-CRI data across the whole domain show some correlation during this period; the Spearman's Rank coefficient for the whole dataset is 0.34. However, there are strong regional variations in this correlation, with coefficients generally over 0.3 across most continental regions, and up to 0.6 across Western France and Northern Germany. In contrast, the coefficient over the North Sea is around 0.1, and even becomes (weakly) anti-correlated over parts of the Atlantic and Scandinavia. These differences in correlation could be due to a number of factors – including availability of data (data density is highest over the continent, Supplementary Figure S4b), and differences in retrieval algorithms across land or sea. That correlation is highly significant over the continental hotspots (with Spearman p-values of <0.0001 in some regions, Supplementary Figure S4c), indicates that the spatial distribution of WRF-Chem-CRI emissions, and WRF-Chem-CRI transport processes, are reasonably accurate. However, the consistent underprediction of the magnitude of NH_3 column by the WRF-Chem-CRI also suggests that either the magnitude of these sources is on the low side, or that the WRF-Chem-CRI loss terms are too efficient.

Figure 8. Averaged NH_3 column data during August 2012 for (a) IASI satellite and (b) the WRF-Chem model. (c) The Spearman coefficient between satellite and model data within each 1×1 degree grid cell during this period, indicating the degree of correlation between the two.

4. Conclusion

A global 3-D chemistry and transport model, STOCHEM-CRI has been used to investigate the global annual NH_3 fluxes from sources to sinks, global distribution and seasonal variation of NH_3 throughout the troposphere. The gas phase reactions of NH_3 with OH, NO_3 and stabilized Criegee intermediates are found to be a minor contributor ($\sim 3\%$) to the removal of NH_3 in the troposphere, which was not fully accounted for in previous modelling studies. The

global burden and atmospheric life-time of NH_3 are found to be 0.22 Tg N and 1.1 days, respectively. The peak model NH_3 (up to $8.0 \mu\text{g}/\text{m}^3$) is found in South and East Asia because of emissions from livestock farming, mineral fertilizer (urea), and agricultural crops. A significant decrement of the NH_3 level (by up to 25%) is found in the tropics after including gas-phase loss processes of NH_3 by OH and NO_3 . The validation of model NH_3 from STOCHEM-CRI and WRF-Chem-CRI by satellite derived ground NH_3 concentrations from IASI NH_3 columns suggests there is reasonable accuracy in the spatial distribution of model emissions, and in the model transport processes, thus a combination of modelling and satellite measurements could be used to obtain a reliable ground NH_3 estimation globally and regionally. The STOCHEM-CRI and WRF-Chem-CRI model evaluation results show there is large under-prediction of NH_3 mostly in biomass burning regions and urban areas in North America. The underestimation of biomass burning sources of NH_3 and the absence of traffic in the STOCHEM-CRI resulted in an under-prediction of NH_3 for these regions. The weak seasonality of NH_3 because of using the anthropogenic seasonal NH_3 emission distribution class in the STOCHEM-CRI resulted in strong bias with satellite data, especially in South and East Asia where NH_3 emissions from domestic animals' excreta and synthetic N fertilizers are the highest.

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