https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics Discussions

Northwestward Cropland Expansion and Growing Urea-Based Fertilizer Use Enhanced NH_3 Emission Loss in the Contiguous United States

Peiyu Cao, Chaoqun Lu, Jien Zhang, Avani Khadilkar

Department of Ecology, Evolution, and Organismal Biology, Iowa State University, Ames, Iowa, USA

Correspondence to: Chaoqun Lu (clu@iastate.edu)

Abstract. The increasing demands of food and biofuel have promoted century-long cropland expansion and nitrogen (N) fertilizer enrichment in the United States. However, the role of such long-term human activities in influencing the spatiotemporal patterns of Ammonia (NH_3) emission remains poorly understood. Based on an empirical model including climate, soil properties, N fertilizer management, and cropland distribution history, we have quantified monthly fertilizer-induced NH_3 emission across the contiguous U.S from 1900 to 2015. Our results show that N fertilizer-induced NH_3 emission in the U.S. has increased from < 50 Gg N yr^{-1} before the 1960s to 640 Gg N yr^{-1} in 2015, for which corn and spring wheat planting is the dominant contributor. Meanwhile, urea-based fertilizers gradually grew to the largest NH_3 emitter and accounted for 78% of the total increase during 1960-2015. Geospatial analysis reveals that hotspots of NH_3 emission have shifted from the central U.S. to the northwestern U.S. from 1960 to 2015. The increasing NH_3 emissions in the northwestern U.S has been found to closely correlate to the elevated wet NH_4^+ deposition in this region over the last three decades. This study shows that April, May, and June account for the majority of NH_3 emission in a year. Interestingly, the peak emission month has shifted from June to April since the 1960s. Our results imply that the northwestward corn and spring wheat expansion and growing urea-based fertilizer uses have dramatically altered the spatial pattern and temporal dynamics of NH_3 emission, impacting air pollution and public health in the U.S.

1 Introduction

The tremendous increase in synthetic nitrogen (N) fertilizer uses has greatly promoted crop yields in the U.S. since the early 1900s (Cao et al., 2018; Erisman et al., 2008). The predictable rise in food demand may lead to greater N fertilizer consumption

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

in the coming decades (Alexandratos and Bruinsma, 2012; David et al., 1997). However, 5-9% of the N applied was lost to the atmosphere through ammonia (NH_3) volatilization (0.5-1 Tg N annually) in the U.S. at the beginning of this century, which lowered the N use efficiency (NUE) of crops and caused numerous environmental issues (Bouwman et al., 2002; Cassman and Walters, 2002; Lu et al., 2019; Tilman et al., 2002). In the U.S., synthetic N fertilizer-induced NH_3 volatilization, contributing to 15-30% of annual total NH_3 emission, has been identified as the second contributor to atmospheric NH_3 only next to livestock production (Park et al., 2004; Paulot et al., 2014; Reis et al., 2009; U.S. EPA, 2019). Atmospheric NH_3 plays a significant role in the formation of atmospheric particulate matters (PM) and is an important component of N deposition (Behera et al., 2013), which can degrade visibility, induce respiratory and cardiovascular disease, cause eutrophication of aquatic ecosystems, soil acidification, and reduce biodiversity (Bowman et al., 2008; Galloway et al., 2003). Thus, to quantify fertilizer-derived NH_3 emission over space and time is essential in assessing agricultural N budget and improving the accuracy of air quality modeling (Eickhout et al., 2006; Gilliland et al., 2006; van Grinsven et al., 2015).

However, it is challenging to quantify fertilizer-induced NH_3 emissions due to the paucity of information on spatially and temporally varied environmental conditions and various agricultural practices (Behera et al., 2013; Bouwman et al., 2002; Pinder et al., 2006; Sommer et al., 2004). Inverse modeling of atmospheric observations such as N deposition and satellite images has been developed as an indirect approach to estimate seasonal NH_3 emission at the regional and national scale (Gilliland et al., 2006; Liu et al., 2019)). However, this "top-down" approach has difficulty in separating contribution of each individual source of NH_3 emission due to the observations contain all sources of NH_3 emissions. Process-based modeling is a popular "bottom-up" approach for quantifying long-term spatially explicit of NH_3 emissions (Cooter et al., 2012; Riddick et al., 2016). These models require detailed information of local environmental conditions and farming practices that is generally not available. An alternate effective "bottom-up" approach to estimate single source of NH_3 emission is by emission factor (EF), which represents the proportion of NH_3 volatilization from N input. Compared to the constant EFs used to estimate annual NH_3 emissions in early studies, more recent empirical seasonal estimations have been improved based on environmental conditions and agricultural management practices (Bouwman et al., 2002; Goebes et al., 2003; Huang et al., 2012; Jiang et al., 2017; Kang et al., 2016). For example, by considering three fertilizer application timings and adopting EFs that consider differences among crop types, environmental factors, and fertilizer types, Paulot et al. (2014) estimated monthly NH_3 emission from N fertilizer uses in the U.S. during 2005-2008.

While more recent "top-down" and "bottom-up" estimations have elaborately quantified the seasonality and spatial heterogeneity of NH_3 emissions in the U.S. during a short period, few studies have assessed the spatiotemporal patterns of

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

NH3 emissions in the U.S. on a century scale. The lack of long-term assessment may limit our understanding and predictive capability in the dynamics of NH_3 emission under future changes in climate, land use, and agricultural management practices (Zhu et al., 2015). In the U.S., the hotspots of intensive agricultural cultivation and N fertilizer uses have shifted from the southeast U.S. to the Midwest and Northern Great Plains during the 20th Century (Cao et al., 2018; Johnston, 2014; Nickerson et al., 2011; Yu et al., 2018; Yu and Lu, 2018). It is reported that land sources of NH_3 play an important role in affecting the atmospheric N deposition and $PM_{2.5}$ (Du et al., 2014; Li et al., 2016; U.S. EPA, 2019), but it remains less known how land use change and N fertilizer management history have altered NH_3 emissions since 1900.

Based on spatially-explicit time-series of cropland distribution maps and N fertilizer management practices database, we adopted empirical modeling of EF to calculate monthly NH_3 emissions from synthetic N fertilizer uses in the contiguous U.S. at a resolution of 1 km × 1 km from 1900 to 2015. We examined the differences in the magnitude, spatiotemporal pattern, and seasonality of NH_3 emissions at national and regional scales under the impact of historical land use and N fertilizer management practices change. Our objects are to answer the following questions: (1) what roles did each crop type and each N fertilizer type play in historical NH_3 emission? (2) how did the fertilizer-induced NH_3 emission in the U.S. change over space and time? (3) how were the atmospheric NH_4^+ deposition dynamics associated with inter-annual variations in NH_3 emission?

2 Materials and Methods

In this study, a broadly applied residual maximum likelihood model (REML) derived emission factor was used to estimate synthetic N fertilizer-induced NH_3 emissions (Bouwman et al., 2002). We calculated the REML-emission factor based on spatial datasets of air temperature, soil properties, crop type, N fertilizer type and application method at a resolution of 1 km ×1 km. Our recent work has reconstructed state-level crop-specific N fertilizer management history in the U.S. with information of application timing, application method, and fertilizer types from 1900 to 2015 (Cao et al., 2018). In this study, we assigned N fertilizer use rates into exact days each year by linking fertilizer application timings with state-level survey of crop planting and harvesting dates. The daily fertilizer input rate was further aggregated to each month. We spatialized the monthly N fertilizer use data generated above to the U.S. 1-km gridded cropland distribution maps developed by Yu and Lu (2018). By multiplying N fertilizer use rates with emission factor, we obtained spatially explicit NH_3 emission at a monthly time step from 1900 to 2015. For display purposes, we resampled the spatial time-series of NH_3 emissions to 5 km × 5 km resolution with the average NH_3 emission depicted in each pixel. To represent the regional difference of NH_3 emission and its impact on N deposition, we partitioned the entire contiguous U.S. into seven regions: the Northwest (NW), the Southwest (SW), the Northern Great Plains (NGP), the Southern Great Plains (SGP), the Midwest (MW), the Southeast (SE), and the Northeast (NE) according to the U.S. Fourth National Climate Assessment (2019).

2.1 REML Model

Bouwman et al. (2002) summarized 1667 NH_3 volatilization measurements in 148 research papers to assess the effects of a variety of human management practices and environmental factors on NH_3 emission at global scale. Finally, six factors including air temperature, soil pH, and soil Cation Exchange Capacity (CEC), crop type, fertilizer type and application method, are considered in the REML model to determine the emission factor.

$$EF = exp(FV_{Tem} + FV_{pH} + FV_{CEC} + FV_{FT} + FV_{AM} + FV_{CT})$$

Where *EF* refers to Emission Factor, *FV* refers to Factor Value. The values of input data are grouped into broad classes. *Tem* refers to air Temperature and are grouped into two classes by 20 °C. *pH* refers to soil pH and has four classes. *CEC* refers to soil CEC and has four classes. *FT* refers to fertilizer type, including 12 types. *AM* refers to Application Method, including five ways such as broadcast, incorporate, solution, broadcast and then flood, and incorporate and then flood. *CT* refers to Crop Type and is classified as Upland crops, Grass, and Flooded crops. More detailed grouping information and the corresponding factor value can be found in the supplementary Table S1.

2.2 Input data preparation

2.2.1 Temperature

Daily temperature data was downloaded and resampled to 1km × 1km from high-resolution gridded met data products TS 2.1 from station observations by the Climatic Research Unit (CRU) of the University of East Anglia TS 2.1 and North America Regional Reanalysis (NARR) dataset from a combination of modeled and observed data (Mesinger et al., 2006; Mitchell and Jones, 2005). The daily temperature data were further aggregated to monthly average temperature.

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

2.2.2 Soil pH and CEC

We resampled the soil properties data (pH and CEC) of the U.S. obtained from Geospatial Data Gateway (gSSURGO, 2018) to 1 km ×1 km resolution. Among a variety of measurements, we adopted the soil pH from ph1to1h2o_r in the attribute table, which uses the negative logarithm at base 10 of the hydrogen ion activity in the soil using the 1:1 soil-water ratio method. Meanwhile, we chose cec7_r in the attribute table as our soil CEC indicator, which represents the amount of readily exchangeable cations that can be electrically absorbed to negative charges in the soil, soil constituent, or other material at pH 7.0, as estimated by the ammonium acetate method.

2.2.3 Crop land distribution maps

We adopted a newly developed 1 km × 1 km cropland dataset of the contiguous U.S. from 1900 to 2015 to drive the REML model and identify historical cropland expansion and abandon (Yu et al., 2018; Yu and Lu, 2018). The cropland maps were reconstructed to represent the area and distribution of cultivated land annually by harmonizing various sources of inventory data and remote sensing images. This dataset includes two components, crop type maps, and cropland density maps. The crop type maps indicate the crop type cultivated each year in each pixel. Whereas the density maps represent the percent of cropped land area while excluding summer idle/fallow areas of each grid cell correspondingly. Based on the data availability, multiple satellite products were used for five sub-periods to reconstruct the spatial distribution of principal crop types such as corn, soybean, and wheat. Meanwhile, the planting area of each crop type in each state is corrected by the state inventory. The cropland maps provide us the detailed distribution information of each crop type to allocate the crop-specific N fertilizer use rate, application timings, and application methods. More importantly, it delivers the cropland expansion and abandonment information of each crop type. More details about cropland maps can be found in (Yu et al., 2018; Yu and Lu, 2018).

2.2.4 Nitrogen fertilizer use dataset

The historical state-level crop-specific N fertilizer use dataset (N fertilizer use rate, N fertilizer types, and application timing) of the U.S. were produced from our previous study (Cao et al., 2018), which includes N fertilizer use rate for 10 major crop types during the period of 1900-2015. The 10 crops are corn, soybean, winter wheat, spring wheat, cotton, sorghum, rice, barley, durum wheat, and cropland pasture. All other crops were grouped into a category named others.

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

We calculated the proportion of 11 major single N fertilizers in total fertilizer consumption in each state each year. They include Anhydrous Ammonia (AnA), Aqua Ammonia (AqA), Ammonium Nitrate (AN), Ammonium Sulfate (AS), Nitrogen Solution (NS), Sodium Nitrate (SN), Urea, Calcium Nitrate (CN), Diammonium Phosphate (DAP), Monoammonium Phosphate (MAP), and Ammonium Phosphates (APs). All other N fertilizers were grouped into others. We assumed there is no difference in the share of fertilizer types among crop types within the same state. Thus we split state-level crop-specific N fertilizer use into 12 N fertilizer categories according to this share ratio.

We allocated annual N fertilizer use generated above to daily application by considering N fertilizer application timing (USDA-ERS, 2015) and crop phenology calendar (USDA-NASS, 2010). According to the USDA survey, we calculated the ratio of four application timings to annual fertilizer consumption of each crop in each state. Four application timings are fall (previous harvest), spring (before planting), at planting, and after planting. Thus, we further split annual N fertilizer use into four application timing by each crop type each fertilizer type each state. We assumed that fall application occurs one month after harvesting, whereas spring and after planting application occur one month before and after planting date, respectively. We obtained the surveyed planting and harvesting dates for each of nine major crops of each state from USDA-NASS (2010). Four key dates are reported for both planting and harvesting dates, respectively. These dates mirror the time points when 5%, 15%, 85%, and 95% of cropland acreage in each state are either planted or harvested, respectively. The period between the dates of 15% and 85% is the most active range. Therefore, we considered the most active period (15%-85%) accounts for 80% of N fertilizer use in each timing, whereas the periods of 5%-15% and 85%-95% contribute to 10%, respectively. We evenly allocated the N fertilizer use to every day in each period for four application timings. After that, we aggregated the daily application to monthly application. See example in Supplement table S2 and Fig. S1. We used the average monthly allocation ratio of eight major crops by excluding winter wheat to extract the monthly application rate of cropland pasture and other crops.

USDA-ERS (2015) also reported how N fertilizer was applied and the acreage percentage of each crop in the surveyed state receiving N fertilizer in this way. We regrouped the methods of USDA survey according to the categories of the REML model (Table S1). Specially, we assumed that broadcast and then flooded or incorporation and then flooded are only applied to rice. In addition, N fertilizer types AnA and AqA are only incorporated into soil and NS is only applied as solution. We calculated the planted area ratio of each application method of nine major crops of each state. We allocated N fertilizer use generated above to different application methods by using the area ratio. Thus, we generated monthly N fertilizer use rate under multiple application methods of each N fertilizer type of each crop type in each state.

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics
Open Access
Discussions

Based on the U.S. gridded crop type distribution maps developed by Yu and Lu (2018), we assigned the aforementioned monthly crop-specific N fertilizer use rate of each N fertilizer type at each timing and by each application method into each 1 km × 1 km grid cell from 1900 to 2015. In addition, we converted the N fertilizer use rate from planting area-based (g N m^{-2} cropland area per year) to grid area-based (g N m^{-2} land area per year) by timing the spatialized N fertilizer use rate with the corresponding cropland density maps.

2.3 Wet NH_4^+ deposition

We obtained 2338 m resolution annual wet NH_4^+ deposition data from 1985 to 2015 in the contiguous U.S. from National Atmospheric Deposition Program, which was derived from spatial interpolation of quality-controlled site observation data (NADP, 2019) (http://nadp.slh.wisc.edu/ntn/annualmapsByYear.aspx). We resampled the deposition database to 1 km resolution to make it comparable to our estimated NH_3 emission maps. The associations between fertilizer-induced NH_3 emission and wet NH_4^+ deposition during 1985-2015 at each grid cell were examined using Pearson correlation coefficients with statistical significance at $p < 0.01$ and $p < 0.001$.

3 Results

3.1 Historical NH_3 volatilization from crops and N fertilizers

Our estimation indicates that the ratio of national total NH_3 emission to total N fertilizer input declined from around 5.9% in the 1920s to below 4% in the 1970s, and then consistently rose back to 5.9% in the 2010s (Fig. 1a). We find that NH_3 emissions from synthetic N fertilizer in the U.S. remained less than 41 Gg N yr^{-1} before 1950 and then sharply increased to 465 Gg N yr^{-1} in 1981, followed by a slower rise to 640 Gg N yr^{-1} by 2015 (Fig. 1a). Regionally, NH_3 emissions have consistently increased since the 1960s in the Northern Great Plains and the Northwest. Whereas the NH_3 emissions in the remaining regions have leveled off or slightly declined after peaking in the 1980s (Fig. 2).

Among all major crop types, NH_3 volatilized from corn accounted for over 40% of total fertilizer-derived NH_3 emission after 1960. Moreover, the increase in NH_3 emissions from corn fields was the major driver of the NH3 emission growth in recent decades, contributing to 52% during 1980-2015, and 81% during 2000-2015 (Table S3). Although NH_3 emission from spring wheat accounted for less than 7% of total NH_3 emissions during 1980-2015, 15% of the fertilizer-NH_3 emission increase can be attributed to spring wheat production.

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

The contributions of N fertilizer types to total NH_3 volatilization varied in different periods (Fig. 1b). All other N fertilizer types, including single (i.e. Calcium ammonium nitrate) and mixed N fertilizers, are the dominant source of NH_3 emission before the 1960s (> 70%), during which the total NH_3 emissions were low. The contribution of urea-based fertilizers (Urea and Nitrogen solution) increased from 13.8% in 1960 to 68% in 2015, accounting for 78% of the fertilizer-induced NH_3 emission increase during this period (Fig. 1b, Table S4).

3.2 Spatiotemporal change in NH_3 volatilization

A large increase in NH_3 emissions was found across the U.S. from 1960 to 2015. Meanwhile, the hotspot of NH_3 emissions has shifted from the central U.S. to the Northern Great Plains and Minnesota (Fig. 3). Before 1960, most states in the US released less than 0.1 g NH_3-N m^{-2} yr^{-1}, except the west and east coasts and a few states in the Midwestern U.S., such as Indiana, and Ohio (Fig. 3a). Since 1980, a tremendous increase of NH_3 volatilization (0.2-0.4 g N m^{-2} yr^{-1}) occurred in the Midwest, the southern Great Plains, the Southeast, the Northwest, California, and Nebraska, with the highest NH3 emission centered in Indiana and Ohio (0.4-0.6 g N m^{-2} yr^{-1}) (Fig. 3b). NH_3 volatilization further enhanced in 2000, during which hotspots of NH_3 volatilization widely expanded in western Minnesota, Texas, and the western Southeast. (Fig. 3c). The most intensive NH_3 volatilization (> 0.6 g N m^{-2} yr^{-1}) occurred in the northern Great Plains, the Northwest, and Minnesota in 2015 (Fig. 3d).

We find that the NH_3 loss proportion to total N fertilizer use remained less than 6% in the eastern U.S. before the 1980s. However, 6%-9% loss ratios are found in vast areas in the western U.S., with some areas in South Dakota, Nevada, and Utah lost up to 12% of N fertilizer via NH_3 (Fig. 4). After the 1990s, the Northern Great Plains, the Northwest, and part of the Southwest gradually became major players with an NH_3 loss proportion greater than 12%.

3.3 Monthly NH_3 emissions

Our results indicate that, in 2015, NH_3 emission levels were reportedly high in April, May, and June (Fig. 5). In addition, the emission hotspots showed a large spatial variation over months (Fig. 5). Specifically, a vast amount of NH_3 (> 0.24 g N m^{-2} month^{-1}) volatilized from the Midwest, the Northern Great Plains, and parts of the Northwest in April, while the southern North Great Plains and the eastern Midwest served as a major NH_3 source (> 0.24 g N m^{-2} mont^{h-1}) in June. In contrast, NH_3 emissions in winter (Dec.-Feb.) and August were not only at a low level (< 0.04 g N m^{-2} month^{-1}) they were also spatially limited, such as the southern U.S. in February.

Monthly NH_3 emissions across the nation experienced a dramatic increase since 1960, especially during 1960-1980 (Fig. 6a). The NH_3 emissions in April have consistently increased by 85%, from 100 Gg N month^{-1} in 1980 to 185 Gg N month^{-1} in 2015, while the emissions in June and May slowly increased by 47% and 44%, from 78 Gg N month^{-1} and 71 Gg N month^{-1} to 115 Gg N month^{-1} and 102 Gg N month^{-1}, respectively. NH_3 volatilized in April, May, and June together account for 70% of annual emission (Fig. 6b). Before the 1950s, June dominated the annual emissions, followed by May and April. In this study, we find that maximum emissions have gradually shifted to earlier months and peaked in April since the 1950s. Interestingly, the reduction of emissions in June mainly occurred before the 1960s, whereas the rise of emissions in April mainly occurred after the 1970s (Fig. 6b).

Besides, our study indicates that the increment of April emission has widely distributed in the western U.S. since 1960, with the largest increase (> 20%) found in the Great Plains, the Northwest (Fig. S2). On the contrary, although large increases were found along the eastern coast of the U.S., minor decreases (< -5%) in June occurred in major agricultural regions, such as the corn-belt and the Northern Great Plains.

4 Discussion

4.1 Comparison with previous studies

We compared our estimates of annual NH_3 emissions across the contiguous U.S. with the previously published results (Fig. 7). The magnitudes of NH_3 emission estimates differ significantly, ranging from 460 Gg N yr^{1} to 756 Gg N yr^{-1}, among previous studies due to the difference of data sources (e.g. N fertilizer and cropland distribution) and estimation approaches (e.g. “bottom-up” and “top-down”) they adopted. our estimated NH_3 emissions are much lower than those estimated by two inventories, in which non-agricultural N fertilizer uses have been included (U.S. EPA, 2019) and emission factor is less constrained by environmental drivers (Goebes et al., 2003). For example, our estimate of NH_3 emission in 1995 is 40% lower than an early study (i.e., 756 Gg N yr^{-1} as estimated by Goebes et al. (2003) vs 504 Gg N yr^{-1} in this study). This may be because the EF Goebes et al. (2003) used was only based on N fertilizer type, while we considered the combined effects of temperature, soil properties, crop type, and N fertilizer management to modify the EF. Whereas our estimated NH_3 emission are very close to a “bottom-up” inventory (490 Gg N yr^{-1} from Park et al. (2004) vs 521 Gg N yr^{-1} from this study) and a “top-down” estimation (540 Gg N yr^{-1} from Gilliland et al. (2006) vs 512 Gg N yr^{-1} from this study). In contrast, Two studies, considering more constrains on EF such as canopy absorption and wind speed, had smaller NH_3 estimations (Bash et al., 2013;

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics Discussions

Paulot et al., 2014). For example, The NH_3 emission of 2002 by Bash et al. (2013), which considered the effect of canopy absorption and release additionally, is 20% lower than our estimate (460 Gg N yr^{-1} from Bash et al. (2013) vs 564 Gg N yr^{-1} from this study).

We also compared the spatial pattern of NH_3 emissions in 2011 estimated by our study with that from the U.S. National Emissions Inventory (U.S. EPA, 2019). The spatial patterns revealed by these two studies were similar: the hotspots of NH_3 emissions concentrated in the Northern Great Plains, parts of the Northwest, the Corn-Belt, and the Rice-Belt, and relatively lower NH_3 emissions were found along the eastern coast of the U.S. (Fig. S3).

We further explored the monthly variations in the estimated NH_3 emissions among studies (Fig. 8). All studies agreed that the majority of NH_3 is released in spring while winter is the minimum NH_3 emissions season (Gilliland et al., 2006; Goebes et al., 2003; Pinder et al., 2006). April was commonly identified as the peak NH_3 emission month by most of these studies, which is consistent with our estimate. An exception is that one study, considering canopy uptake and release of NH_3, found a delayed peak in summer (Bash et al., 2013). In addition, several studies found higher NH_3 emissions in March than our estimate, which may be caused by different N fertilizer allocation at N fertilizer application timing of winter wheat in these studies (Gilliland, 2003; Goebes et al., 2003; Pinder et al., 2006). Owing to the limited data of actual fertilizer use history, these studies used the recommendation from fertilizer experts to assume that a proportion of N fertilizer applied in fall (i.e., before planting for winter wheat) should be applied in early spring, before the green-up of winter wheat. Therefore, they estimated higher NH_3 emissions in March than ours. This different assumption in N fertilizer application timing of winter wheat may also introduce more disagreements to the secondary peak in fall (Fig. 8). Applying N fertilizer before winter wheat greening-up may reduce the risk of N leaching and denitrification. However, there is a lack of detailed sub-national information about the application rate and date for green-up of winter wheat. Therefore, we allocated N fertilizer by strictly following the crop planting and harvest schedule of winter wheat.

4.2 Spatiotemporal change in the NH_3 emissions

The "V" shape of historical national NH_3 emission factors mainly resulted from the changing preference in using different N fertilizer types. The decline in the early stage from the 1920s to the 1970s was due to the decrease in the use of Ammonium sulfate, while the rising emissions from the 1970s to present was caused by the popularity of Urea-based fertilizer (Fig 1b, Table S4). In addition, the N fertilizer use hotspots shifting to more alkaline areas (such as the Northern Great Plains) may contribute to this increasing trend. The NH_3 emission factor estimated by our study is close to 6% in the U.S. and is significantly

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics Discussions

lower than the estimated global EFs, ranging from 11% to 14% (Bouwman et al., 2002; Paulot et al., 2014; Vira et al., 2019). This indicates that agricultural management in the U.S. is more efficient in reducing NH_3 loss compared to other counties. However, NH_3 emission factor varied substantially across the U.S., ranging from 2.5% to 29% (Fig. 4). We find the highest loss proportion (> 12%) in the Northern Great Plains and the Northwest. We may be able to seek better N fertilizer management practices, such as adopting appropriate application timing and method, to reduce NH_3 emission in these high loss regions.

NH_3 emissions from synthetic N fertilizer in the U.S. increased rapidly during 1960-1980, which may be attributed to cropland expansion (Nickerson et al., 2011) and the dramatic increase in N fertilizer use rate in most crop types (Cao et al., 2018). However, the national increases in total NH_3 emissions from fertilizer use slowed down after 1980. Compared to the stable or declining trend in other five regions, the NH_3 emission of Northern Great Plains and the Northwest kept increasing to recent years, which contribute to the post-1980 increase of national NH_3 emissions (Fig. 2) (EPA, 2014). We recognized NH_3 emissions from corn and spring wheat dominated the increase in total NH_3 emissions after the 1980s (Fig 1a and Table S1). USDA Crop Production Historical Report shows that the largest increases in planted areas among all non-legume crop types from the period of 1960-1980 to the period of 1995-2015 were corn and spring wheat, increased by 12% and 22% respectively (Fig. S4). Specifically, the increases in corn and spring wheat planting area were mainly found in Kansas, Minnesota, and the states in the northern Great Plains and the Northwest (Fig. S4). In addition, the average N fertilizer use rates of corn and spring wheat have grown to be the second and third highest among other crop types since 2000 (Cao et al., 2018). Therefore, the rapid increase of corn and spring wheat cropland area combined with high N fertilizer use rate in the Northern Great Plains and the Northwest contribute to the increasing U.S. NH_3 emissions after the 1980s (Cao et al., 2018; Nickerson et al., 2011; Yu and Lu, 2018).

Urea-based fertilizer has been proven to trigger high NH_3 volatilization (Sommer et al., 2004). With two major urea-based fertilizer types, Urea and Nitrogen Solution, increased by over 4000% and 300% since 1980, respectively (Fig. S5), the northern Great Plains and the Northwest have grown to be the most urea-based fertilizer used regions since 1980 (Cao et al., 2018), which may contribute to the steep increase of NH_3 emission during this period (Fig. 2). Even worse, the alkaline soil in the Northern Great Plains and the Northwest leads to a high risk of NH_3 emission compared to other regions. For example, Iowa and Illinois in the Midwest received the most intensive N fertilizer in 2015 (Cao et al., 2018) but they did not show intensive NH_3 emissions, which might be due to the neutral to weak acidity soil. Under the enhanced effect of alkaline soil in the Northern Great Plains and the Northwest, the increasing urea-based N fertilizer use and the northwestward corn and spring wheat expansion together greatly boosted the NH_3 loss proportion, which may contribute to the decreasing crop NUE in these

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

regions (Lu et al., 2019) (Fig. 4). High NH_3 emission can significantly degrade air quality and largely decrease crop NUE. Therefore, more effective policies and agricultural management are still needed in those high NH_3 loss proportion regions. Applying urease inhibitor with urea-based fertilizer was proved an effective practice to decrease NH_3 loss (Pan et al., 2016; Soares et al., 2012; Tian et al., 2015). In addition, 4R management (Right fertilizer source, Right rate, Right timing, and Right place) is effective in mitigating high NH_3 emissions.

4.3 Monthly peak of NH_3 emissions shifting from 1900 to 2015

The application timings of N fertilizer differ dramatically across the U.S. (Cao et al., 2018), which highly influence the seasonality of NH_3 emissions in different regions (Paulot et al., 2014). Corn and spring wheat producers in the Midwest, the Northern Great Plains, and the Northwest apply most of N fertilizer in spring before planting, resulting in a sharp peak of NH_3 emission in April (Fig. 2). Whereas farmers in the Southern Great Plains prefer to apply most of N fertilizer after planting for cotton and split annual N fertilizer use into fall and after planting for winter wheat, resulting in peaks in summer and fall. As corn and spring wheat expanded into Minnesota, the Northern Great Plains, and the Northwest, as well as the increased use in urea-based fertilizer, NH_3 emissions from these areas rapidly gained the weight of total NH_3 emissions of the country. This change advanced the monthly NH_3 emission peak at the national scale (Fig. 6). In addition, the monthly peak shifting may be more prominent if we took long-term crop phenology change into consideration. We adopted the latest crop phenology date of 2010 in our study to calculate monthly NH_3 volatilization for the entire study period. However, due to the development of genotypes and improvement of agricultural management and equipment, corn-planting date became earlier by approximately four weeks from 1930 to 1980 (Duvick, 1989), and two weeks between the 1980s and the 2000s in the corn-belt (Kucharik, 2006). In addition, widespread springtime warming across much of North America has also pushed toward an earlier planting date since the 1940s (Hu et al., 2005; Schwartz et al., 2006). Therefore, the monthly peak shifting earlier would be more evident in the U.S.

4.4 Effects of increasing NH_3 emissions on wet NH_4^+ deposition

Although the intensive NH_4^+ in wet deposition concentrated in the central U.S., the largest increase in wet NH_4^+ deposition was found in the northern Great Plains and Minnesota from 1985 to 2015 (Du et al., 2014; Li et al., 2016). Atmospheric NH_3 has a very short lifetime and deposits close to the source quickly. Therefore, NH_4^+ deposition is highly affected by local NH_3 emissions. NH_3 emissions from increasing forest fire and livestock numbers in the northwestern U.S. may contribute to the

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics
Discussions

wet NH_4^+ deposition in recent decades (Abatzoglou and Williams, 2016). Our analysis indicated that the increase of NH_3 emissions from synthetic N fertilizer in the Northern Great Plains, the Northwest, and Kansas significantly contributed to the increase of NH_4^+ wet deposition during 1985-2015 (Fig. 9). Whereas with decreasing NH_3 emissions from N fertilizer in parts of Washington, Wisconsin, Florida, the Southeast and the Northeast since 1980 (Fig. 2), the wet NH_4^+ deposition promoted by increasing forest fire, rapid urbanization, and growing livestock population (Fenn et al., 2018) showed strong negative relations with NH_3 emissions from synthetic N fertilizer in these regions. In addition to wet NH_4^+ deposition, the PM2.5 also showed an increasing trend in Minnesota, the Northern Great Plains, and the Northwest during 2002 and 2013 (U.S. EPA, 2019). Since NH_3 in the atmosphere heavily involves in formatting $PM_{2.5}$, the increase of NH_3 may contribute to the increase of $PM_{2.5}$ in these regions. Therefore, the increase of NH_3 emissions induced by northwestward corn and spring wheat expansion and consequent urea-based fertilizer use might largely enhance the environmental stress in these regions.

4.5 Uncertainty

The major uncertainty sources in this study include the following aspects. (1) state-level N management data (rate, application timing, application method, and the fraction of each N fertilizer type) were used to calculate NH_3 emissions over the contiguous U.S. in our study because of the paucity of sub-state details. (2) The crop-specific N Application timing and method derived from the latest survey years were assumed to be unchanged over time due to the scarcity of inter-annual survey data. This assumption may cause bias in the monthly pattern of NH_3 emissions. For example, urea-based fertilizer, which is suitable for spring application, has been increasingly used to replace fall-applied anhydrous ammonia since 1960, we may underestimate NH_3 emissions in fall before 2000. (3) The ratio of each N fertilizer type was assumed to be constant across crop types in each state in a year. This may cause biases because farmers may apply different types of N fertilizers to different crops. (4) We allocated each N fertilizer type to the same application timing for each crop of each state based on state-level crop-specific application timing. However, farmers may only apply a certain N fertilizer at the time when its maximum profit can be achieved. For example, due to the high potential loss, Nitrogen Solution is seldom applied in fall after harvest. (5) Although we considered the effects of temperature, soil properties, crop type, and N fertilizer type and application method on NH_3 emission estimate, other factors such as wind speed, soil moisture, nitrification and urease inhibitors, and different N fertilizer use rate may also significantly influence NH_3 emissions (Behera et al., 2013; Jiang et al., 2017; Lam et al., 2017). Increasing evidence suggests that NH_3 emissions increase exponentially with increasing N fertilizer rate (Jiang et al., 2017). Thus, we may underestimate NH_3 emissions under a high N fertilizer use rate. Another example is the use of nitrification and urease

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

inhibitors. Nitrification inhibitors have been found to increase NH_3 loss while urease inhibitors can limit NH_3 volatilization (Lam et al., 2017). Therefore, the uncertainty of usage of nitrification or urease inhibitor is likely to misrepresent NH_3 emissions. In addition, considering bidirectional exchange process may improve the accuracy of seasonal NH_3 emission estimation (Bash et al., 2013).

5 Conclusion

This study comprehensively examined the spatiotemporal patterns of NH_3 emission owing to historical cropland expansion and N fertilizer management in the U.S. from 1900 to 2015. We also examined the relationship between NH_3 emission and wet NH_4^+ deposition over the last three decades. The gridded monthly time-series estimations of NH_3 emission, at a spatial resolution of 1 km × 1km, could serve as a solid database for national and regional air quality modeling and N budget assessment.

Our results indicate that NH_3 emission from synthetic N fertilizer uses in the U.S. rapidly increased from < 50 Gg N yr^{-1} before the 1960s to 640 Gg N yr^{-1} in 2015, among which corn and spring wheat are the major contributors. In addition, increasing use of urea-based fertilizers enhanced the N loss through NH_3 emission after 1960. Spatially, the intensive NH_3 emission spots have shifted from the central U.S. to the northwestern U.S. since 1960 due to the northwestward cropland expansion onto the alkaline soils. Cropland expansion and N fertilizer management practice changes also altered the seasonal pattern of NH_3 emission in the U.S., shifting the peak emission month from June to April since the 1960s. Moreover, our analyses reveal that the increasing wet NH_4^+ deposition in the Northern Great Plains could be greatly attributed to the increasing NH_3 emission in this region since 1985. In summary, our work highlights the importance of comprehensive assessment of environmental consequences of agricultural production. We call for proper fertilizer management practices in reducing NH_3 emission and improving nitrogen use efficiency.

Data availability. The estimated NH3 emission dataset derived from this study is publicly available via figshare at https://figshare.com/articles/Ammonia_emission_from_agricultural_synthetic_nitrogen_fertilizer_use_in_the_contiguous_U_S_during_1900-2015_a_set_of_gridded_time-series_data/11692038 (Cao et al., 2020).

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Author contributions. CL and PC designed the research. PC compiled the database and carried out the data analysis. PC drafted the manuscript, with the guidance of CL and JZ. All the co-authors contributed to and reviewed the manuscript.

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

Acknowledgements. This work was supported by the Iowa Nutrient Research Center, and NSF Dynamics of Coupled Natural and Human Systems (CNH) program (1924178).

Reference

Abatzoglou, J. T. and Williams, A. P.: Impact of anthropogenic climate change on wildfire across western US forests, Proc. Natl. Acad. Sci., 113(42), 11770 LP – 11775, doi:10.1073/pnas.1607171113, 2016.

Alexandratos, N. and Bruinsma, J.: World agriculture towards 2030/2050: the 2012 revision, Rome., 2012.

Bash, J. O., Cooter, E. J., Dennis, R. L., Walker, J. T. and Pleim, J. E.: Evaluation of a regional air-quality model with bidirectional NH_3 exchange coupled to an agroecosystem model, Biogeosciences, 10(3), 1635–1645, doi:10.5194/bg-10-1635-2013, 2013.

Behera, S. N., Sharma, M., Aneja, V. P. and Balasubramanian, R.: Ammonia in the atmosphere: A review on emission sources, atmospheric chemistry and deposition on terrestrial bodies, Environ. Sci. Pollut. Res., 20(11), 8092–8131, doi:10.1007/s11356-013-2051-9, 2013.

Bouwman, A. F., Boumans, L. J. M. and Batjes, N. H.: Estimation of global NH3 volatilization loss from synthetic fertilizers and animal manure applied to arable lands and grasslands, Global Biogeochem. Cycles, 16(2), 8–14, doi:10.1029/2000GB001389, 2002.

Bowman, W. D., Cleveland, C. C., Halada, Ĺ., Hreško, J. and Baron, J. S.: Negative impact of nitrogen deposition on soil buffering capacity, Nat. Geosci., 1, 767 [online] Available from: https://doi.org/10.1038/ngeo339, 2008.

Cao, P., Lu, C. and Yu, Z.: Historical nitrogen fertilizer use in agricultural ecosystems of the contiguous United States during 1850–2015: application rate, timing, and fertilizer types, Earth Syst. Sci. Data, 10(2), 969–984, doi:10.5194/essd-10-969-2018, 2018.

Cao, P., lu, C., Zhang, J. and Khadilkar, A.: Ammonia emission from agricultural synthetic nitrogen fertilizer use in the contiguous U.S. during 1900-2015: a set of gridded time-series data, , doi:10.6084/m9.figshare.11692038.v1, 2020.

Cassman, K. G. and Walters, D. T.: Agroecosystems , Nitrogen-use Efficiency , and Nitrogen Management Agroecosystems , Nitrogen-use Efficiency , 2002.

Cooter, E. J., Bash, J. O., Benson, V. and Ran, L.: Linking agricultural crop management and air quality models for regional to national-scale nitrogen assessments, Biogeosciences, 9(10), 4023–4035, doi:10.5194/bg-9-4023-2012, 2012.

David, M. M. B., Gentry, L. L. E., Kovacic, D. a. and Smith, K. M. K.: Nitrogen balance in and export from an agricultural watershed, J. Environ. Qual., 26(4), 1038–1048, doi:10.2134/jeq1997.00472425002600040015x, 1997.

Du, E., Vries, W. de, Galloway, J. N., Hu, X. and Fang, J.: Changes in wet nitrogen deposition in the United States between 1985 and 2012, Environ. Res. Lett., 9(9), 95004 [online] Available from: http://stacks.iop.org/1748-9326/9/i=9/a=095004, 2014.

Duvick, D. N.: Possible genetic causes of increased variability in US maize yield. p. 147–156. JR Anderson and PBR Hazel (ed.) Variability in grain yields: Implications for agricultural research and policy in developing countries. John Hopkins Univ. Press, Baltimore, MD, Possible Genet. causes increased Var. US maize yield. p. 147–156. JR Anderson PBR Hazel Var. grain yields Implic. Agric. Res. policy Dev. countries. John Hopkins Univ. Press. Balt., 1989.

Eickhout, B., Bouwman, A. F. and van Zeijts, H.: The role of nitrogen in world food production and environmental sustainability, Agric. Ecosyst. Environ., 116(1), 4–14, doi:https://doi.org/10.1016/j.agee.2006.03.009, 2006.

Erisman, J. W., Sutton, M. A., Galloway, J., Klimont, Z. and Winiwarter, W.: How a century of ammonia synthesis changed the world, Nat. Geosci., 1, 636 [online] Available from: https://doi.org/10.1038/ngeo325, 2008.

Fenn, M. E., Bytnerowicz, A., Schilling, S. L., Vallano, D. M., Zavaleta, E. S., Weiss, S. B., Morozumi, C., Geiser, L. H. and Hanks, K.: On-road emissions of ammonia: An underappreciated source of atmospheric nitrogen deposition, Sci. Total Environ., 625, 909–919, doi:https://doi.org/10.1016/j.scitotenv.2017.12.313, 2018.

Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B. and Cosby, B. J.: The Nitrogen Cascade, Bioscience, 53(4), 341–356 [online] Available from: http://dx.doi.org/10.1641/0006-3568(2003)053[0341:TNC]2.0.CO, 2003.

Gilliland, A. B.: Seasonal NH_3 emission estimates for the eastern United States based on ammonium wet concentrations and an inverse modeling method, J. Geophys. Res., 108(D15), 4477, doi:10.1029/2002JD003063, 2003.

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics
Discussions

Gilliland, A. B., Wyat Appel, K., Pinder, R. W. and Dennis, R. L.: Seasonal NH3 emissions for the continental united states: Inverse model estimation and evaluation, Atmos. Environ., 40(26), 4986–4998, doi:https://doi.org/10.1016/j.atmosenv.2005.12.066, 2006.

Goebes, M. D., Strader, R. and Davidson, C.: An ammonia emission inventory for fertilizer application in the United States, Atmos. Environ., 37(18), 2539–2550, doi:https://doi.org/10.1016/S1352-2310(03)00129-8, 2003.

van Grinsven, H. J. M., Bouwman, L., Cassman, K. G., van Es, H. M., McCrackin, M. L. and Beusen, A. H. W.: Losses of Ammonia and Nitrate from Agriculture and Their Effect on Nitrogen Recovery in the European Union and the United States between 1900 and 2050, J. Environ. Qual., 44, 356–367, doi:10.2134/jeq2014.03.0102, 2015.

gSSURGO: Gridded Soil Survey Geographic (gSSURGO) Database for the Conterminous United States, United States Dep. Agric. Nat. Resour. Conserv. Serv. [online] Available from: https://gdg.sc.egov.usda.gov/, 2018.

Hu, Q., Weiss, A., Feng, S. and Baenziger, P. S.: Earlier winter wheat heading dates and warmer spring in the U.S. Great Plains, Agric. For. Meteorol., 135(1), 284–290, doi:https://doi.org/10.1016/j.agrformet.2006.01.001, 2005.

Huang, X., Song, Y., Li, M., Li, J., Huo, Q., Cai, X., Zhu, T., Hu, M. and Zhang, H.: A high-resolution ammonia emission inventory in China, Global Biogeochem. Cycles, 26(1), 1–14, doi:10.1029/2011GB004161, 2012.

Jiang, Y., Deng, A., Bloszies, S., Huang, S. and Zhang, W.: Nonlinear response of soil ammonia emissions to fertilizer nitrogen, Biol. Fertil. Soils, 53(3), 269–274, doi:10.1007/s00374-017-1175-3, 2017.

Johnston, C. A.: Agricultural expansion: land use shell game in the U.S. Northern Plains, Landsc. Ecol., 29(1), 81–95, doi:10.1007/s10980-013-9947-0, 2014.

Kang, Y., Liu, M., Song, Y., Huang, X., Yao, H., Cai, X., Zhang, H., Kang, L., Liu, X., Yan, X., He, H., Zhang, Q., Shao, M. and Zhu, T.: High-resolution ammonia emissions inventories in China from 1980 to 2012, Atmos. Chem. Phys., 16(4), 2043–2058, doi:10.5194/acp-16-2043-2016, 2016.

Kucharik, C. J.: A Multidecadal Trend of Earlier Corn Planting in the Central USA, Agron. J., 98, 1544–1550, doi:10.2134/agronj2006.0156, 2006.

Lam, S. K., Suter, H., Mosier, A. R. and Chen, D.: Using nitrification inhibitors to mitigate agricultural N2O emission: a double-edged sword?, Glob. Chang. Biol., 23(2), 485–489, doi:10.1111/gcb.13338, 2017.

Li, Y., Schichtel, B. A., Walker, J. T., Schwede, D. B., Chen, X., Lehmann, C. M. B., Puchalski, M. A., Gay, D. A. and Collett, J. L.: Increasing importance of deposition of reduced nitrogen in the United States, Proc. Natl. Acad. Sci., 113(21), 5874 LP – 5879, doi:10.1073/pnas.1525736113, 2016.

Liu, L., Zhang, X., Wong, A. Y. H., Xu, W., Liu, X., Li, Y., Mi, H., Lu, X., Zhao, L., Wang, Z., Wu, X. and Wei, J.: Estimating global surface ammonia concentrations inferred from satellite retrievals, Atmos. Chem. Phys., 19(18), 12051–12066, doi:10.5194/acp-19-12051-2019, 2019.

Lu, C., Zhang, J., Cao, P. and Hatfield, J. L.: Are We Getting Better in Using Nitrogen?: Variations in Nitrogen Use Efficiency of Two Cereal Crops Across the United States, Earth's Futur., 7(8), 939–952, doi:10.1029/2019EF001155, 2019.

Mesinger, F., DiMego, G., Kalnay, E., Mitchell, K., Shafran, P. C., Ebisuzaki, W., Jović, D., Woollen, J., Rogers, E., Berbery, E. H., Ek, M. B., Fan, Y., Grumbine, R., Higgins, W., Li, H., Lin, Y., Manikin, G., Parrish, D. and Shi, W.: North American Regional Reanalysis, Bull. Am. Meteorol. Soc., 87(3), 343–360, doi:10.1175/BAMS-87-3-343, 2006.

Mitchell, T. D. and Jones, P. D.: An improved method of constructing a database of monthly climate observations and associated high-resolution grids, Int. J. Climatol., 25(6), 693–712, doi:10.1002/joc.1181, 2005.

NADP: (National Atomspheric Deposition Program). NADP Program Office, 465 Henry Mall, Madison, WI 53706. [online] Available from: http://nadp.slh.wisc.edu/ntn/annualmapsByYear.aspx, 2019.

Nickerson, C., Ebel, R., Borchers, A. and Carriazo, F.: Major Uses of Land in the United States, 2007. [online] Available from: https://www.ers.usda.gov/webdocs/publications/44625/11159_eib89_2_.pdf?v=41055, 2011.

Pan, B., Lam, S. K., Mosier, A., Luo, Y. and Chen, D.: Ammonia volatilization from synthetic fertilizers and its mitigation strategies: A global synthesis, Agric. Ecosyst. Environ., 232, 283–289, doi:10.1016/j.agee.2016.08.019, 2016.

Park, R. J., Jacob, D. J., Field, B. D., Yantosca, R. M. and Chin, M.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy, J. Geophys. Res. Atmos., 109(D15), doi:10.1029/2003JD004473, 2004.

Paulot, F., Jacob, D. J., Pinder, R. W., Bash, J. O., Travis, K. and Henze, D. K.: Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE_NH3), J. Geophys. Res. Atmos., 119(7), 4343–4364, doi:10.1002/2013JD021130, 2014.

Pinder, R. W., Adams, P. J., Pandis, S. N. and Gilliland, A. B.: Temporally resolved ammonia emission inventories: Current estimates, evaluation tools, and measurement needs, J. Geophys. Res. Atmos., 111(D16), doi:10.1029/2005JD006603, 2006.

Reis, S., Pinder, R. W., Zhang, M., Lijie, G. and Sutton, M. A.: Reactive nitrogen in atmospheric emission inventories, Atmos. Chem. Phys., 9(19), 7657–7677, 2009.

Riddick, S., Ward, D., Hess, P., Mahowald, N., Massad, R. and Holland, E.: Estimate of changes in agricultural terrestrial nitrogen pathways and ammonia emissions from 1850 to present in the Community Earth System Model, Biogeosciences, 13(11), 3397–3426, doi:10.5194/bg-13-3397-2016, 2016.

Schwartz, M. D., Ahas, R. and AASA, A.: Onset of spring starting earlier across the Northern Hemisphere, Glob. Chang. Biol., 12(2), 343–351, doi:10.1111/j.1365-2486.2005.01097.x, 2006.

Soares, J. R., Cantarella, H. and Menegale, M. L. de C.: Ammonia volatilization losses from surface-applied urea with urease and nitrification inhibitors, Soil Biol. Biochem., 52, 82–89, doi:https://doi.org/10.1016/j.soilbio.2012.04.019, 2012.

Sommer, S. G., Schjoerring, J. K. and Denmead, O. T.: Ammonia emission from mineral fertilizers and fertilized crops, Adv. Agron., 82(5577622), 82004–82008, 2004.

Tian, Z., Wang, J. J., Liu, S., Zhang, Z., Dodla, S. K. and Myers, G.: Application effects of coated urea and urease and nitrification inhibitors on ammonia and greenhouse gas emissions from a subtropical cotton field of the Mississippi delta region, Sci. Total Environ., 533, 329–338, doi:https://doi.org/10.1016/j.scitotenv.2015.06.147, 2015.

Tilman, D., Cassman, K. G., Matson, P. A., Naylor, R. and Polasky, S.: Agricultural sustainability and intensive production practices, Nature, 418, 671 [online] Available from: https://doi.org/10.1038/nature01014, 2002.

U.S. EPA: (Environmental Protection Agency). 2011 National Emissions Inventory Data. [online] Available from: https://www.epa.gov/air-emissions-inventories/2011-national-emissions-inventory-nei-data, 2019.

U.S. Fourth National Climate Assessment: No Title, [online] Available from: https://www.globalchange.gov/nca4, 2019.

USDA-ERS: (U.S. Department of Agriculture - Economic Research Service)Tailored Report: Crop Production Practices. [online] Available from: https://data.ers.usda.gov/reports.aspx?ID=17883, 2015.

USDA-NASS: U.S. Department of Agriculture - National Agricultural Statistics Service. Field Crops Usual Planting and Harvesting Dates., 2010.

Vira, J., Hess, P., Melkonian, J. and Wieder, W. R.: An improved mechanistic model for ammonia volatilization in Earth system models: Flow of Agricultural Nitrogen, version 2 (FANv2), Geosci. Model Dev. Discuss., 2019, 1–49, doi:10.5194/gmd-2019-233, 2019.

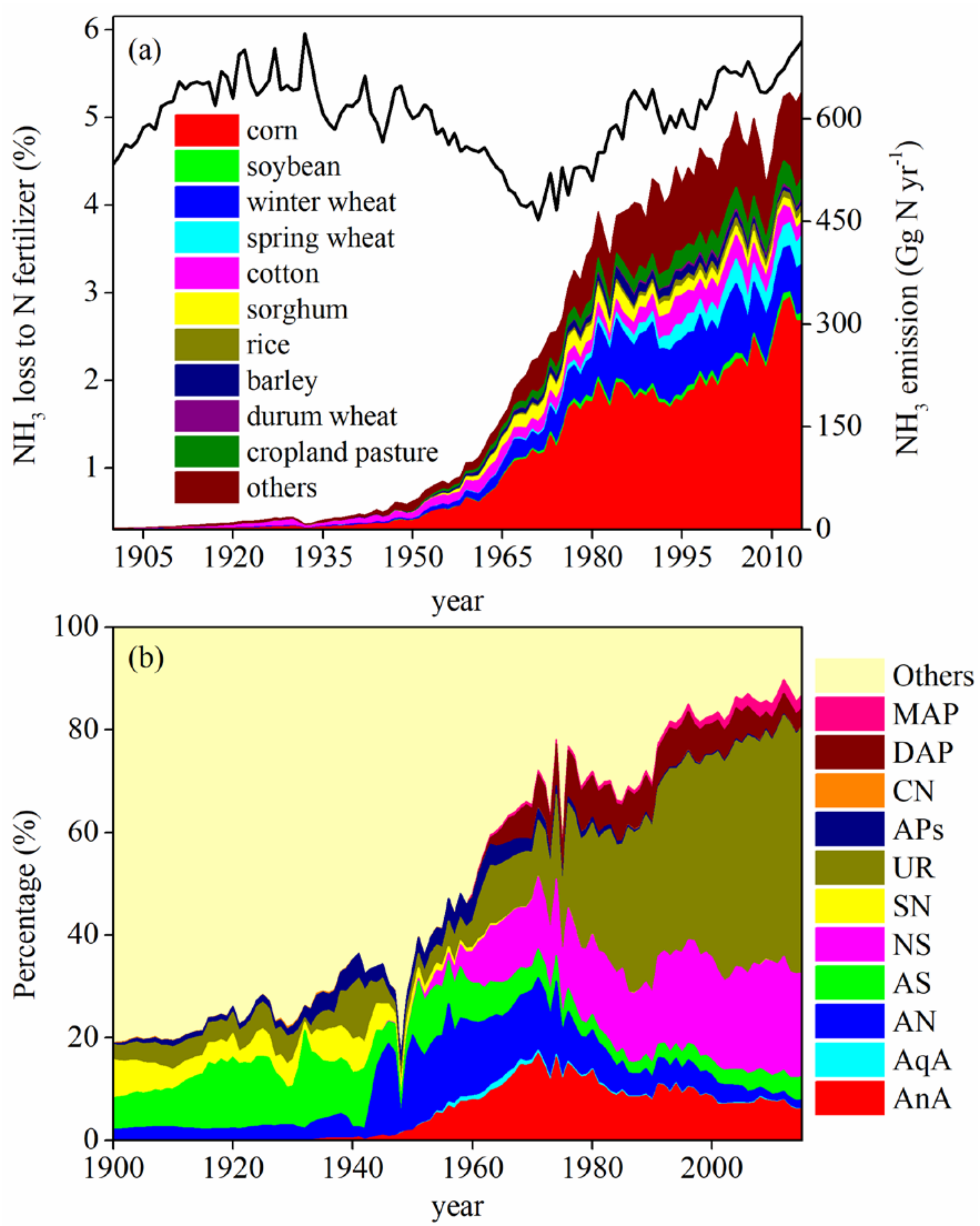
Yu, Z. and Lu, C.: Historical cropland expansion and abandonment in the continental U.S. during 1850 to 2016, Glob. Ecol. Biogeogr., 27(3), 322–333, doi:10.1111/geb.12697, 2018.

Yu, Z., Lu, C., Cao, P. and Tian, H.: Long-term terrestrial carbon dynamics in the Midwestern United States during 1850–2015: Roles of land use and cover change and agricultural management, Glob. Chang. Biol., 24(6), 2673–2690, doi:10.1111/gcb.14074, 2018.

Zhu, L., Henze, D. K., Bash, J. O., Cady-Pereira, K. E., Shephard, M. W., Luo, M. and Capps, S. L.: Sources and Impacts of Atmospheric NH 3 : Current Understanding and Frontiers for Modeling, Measurements, and Remote Sensing in North America, Curr. Pollut. Reports, 1(2), 95–116, doi:10.1007/s40726-015-0010-4, 2015.

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

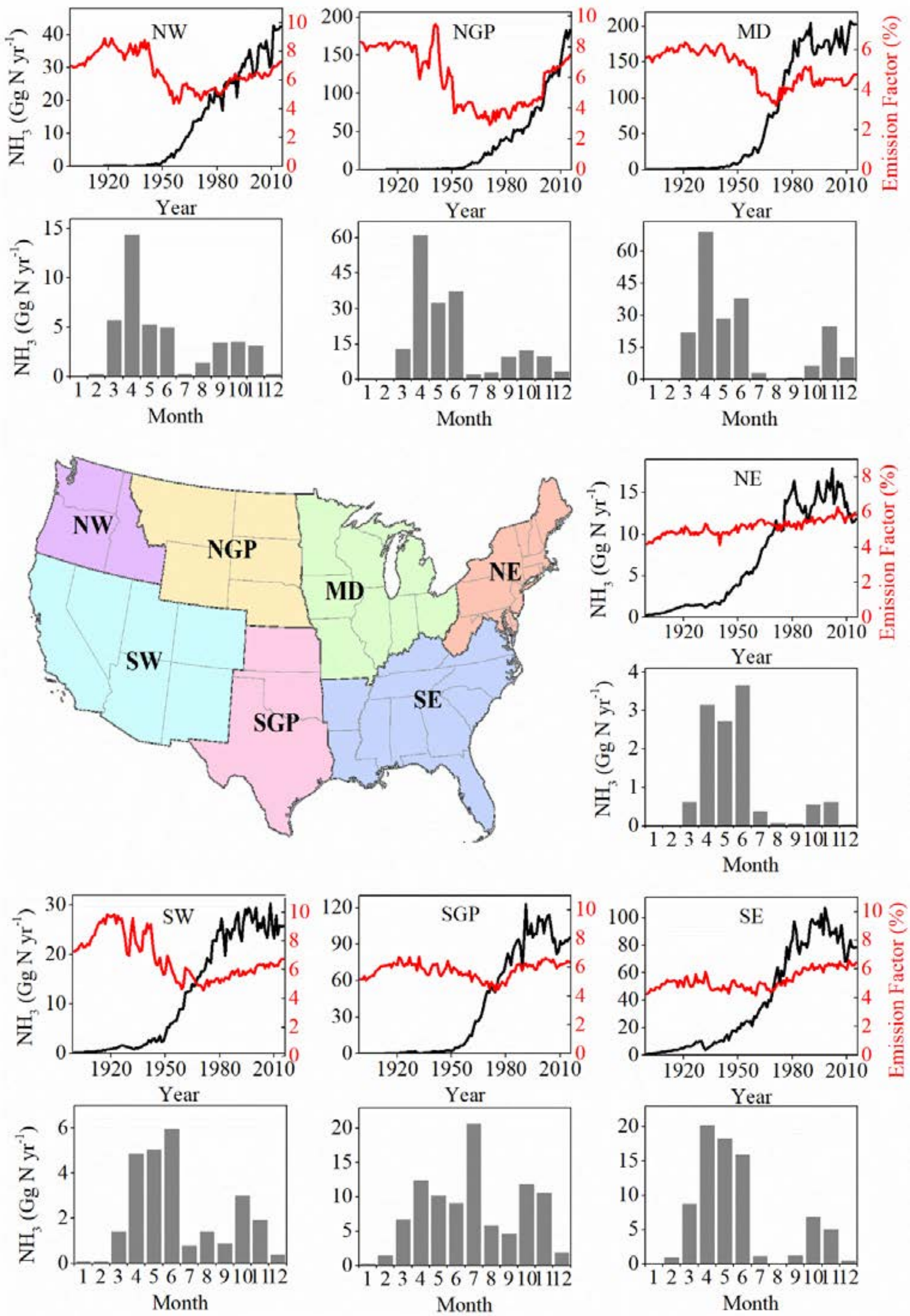
Atmospheric Chemistry and Physics
Open Access
Discussions



https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Figure 1. Contributions of major crop types and N fertilizer types to historical NH_3 emissions since 1900. (a) Crop specific NH_3 emissions, (b) Relative contributions of 12 major N fertilizer types to annual total NH_3 emission. Solid line in (a) refers to the NH_3 loss percentage to total N fertilizer input.

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020



https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics Discussions

Figure 2. Temporal and monthly pattern of NH_3 emissions in seven regions of the United States. Annual NH_3 emission is shown by black lines. Red lines represent the proportion of NH_3 emission to N fertilizer input. Gray bars indicate monthly NH_3 emissions of each region in 2015.

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics
Discussions

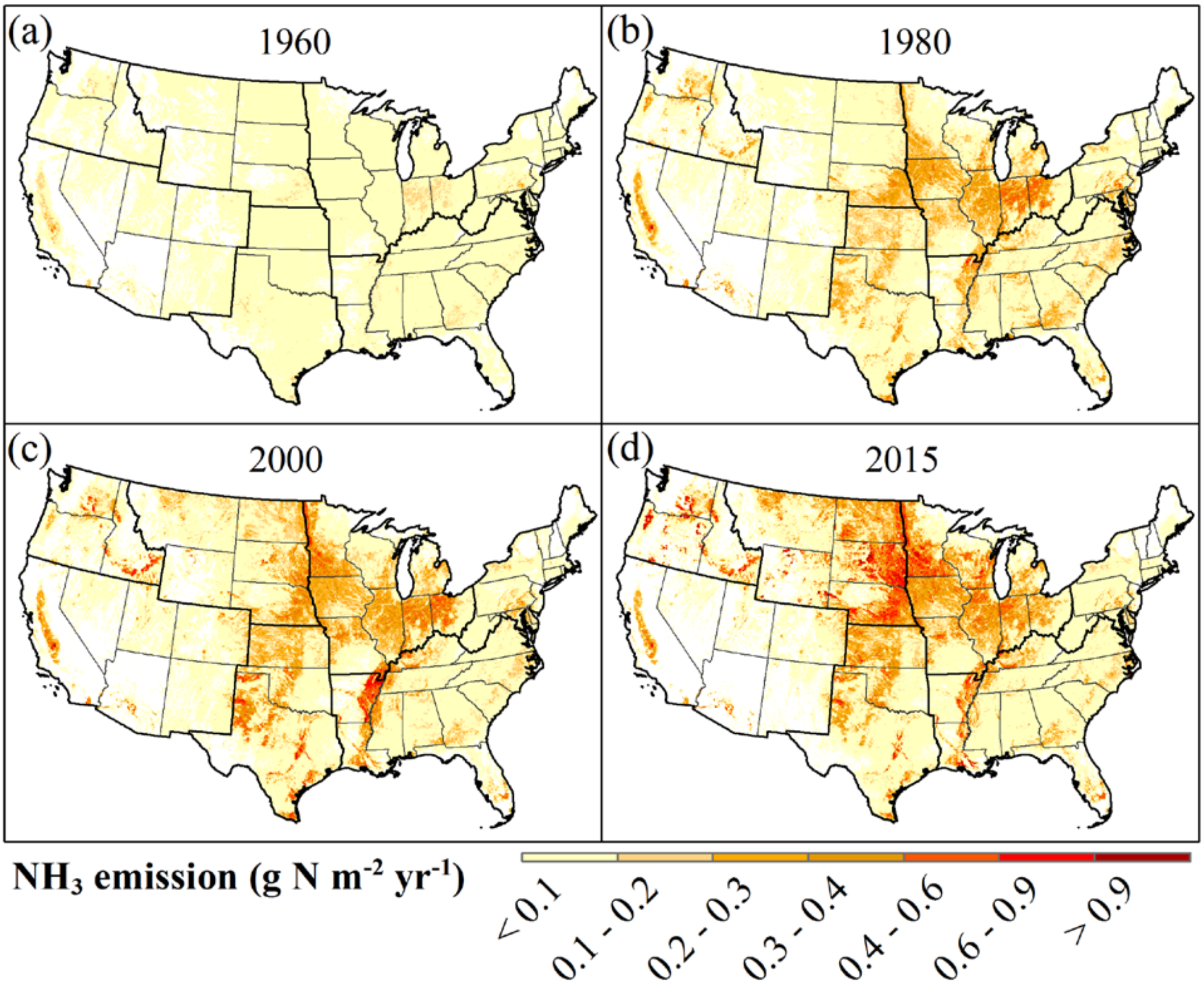
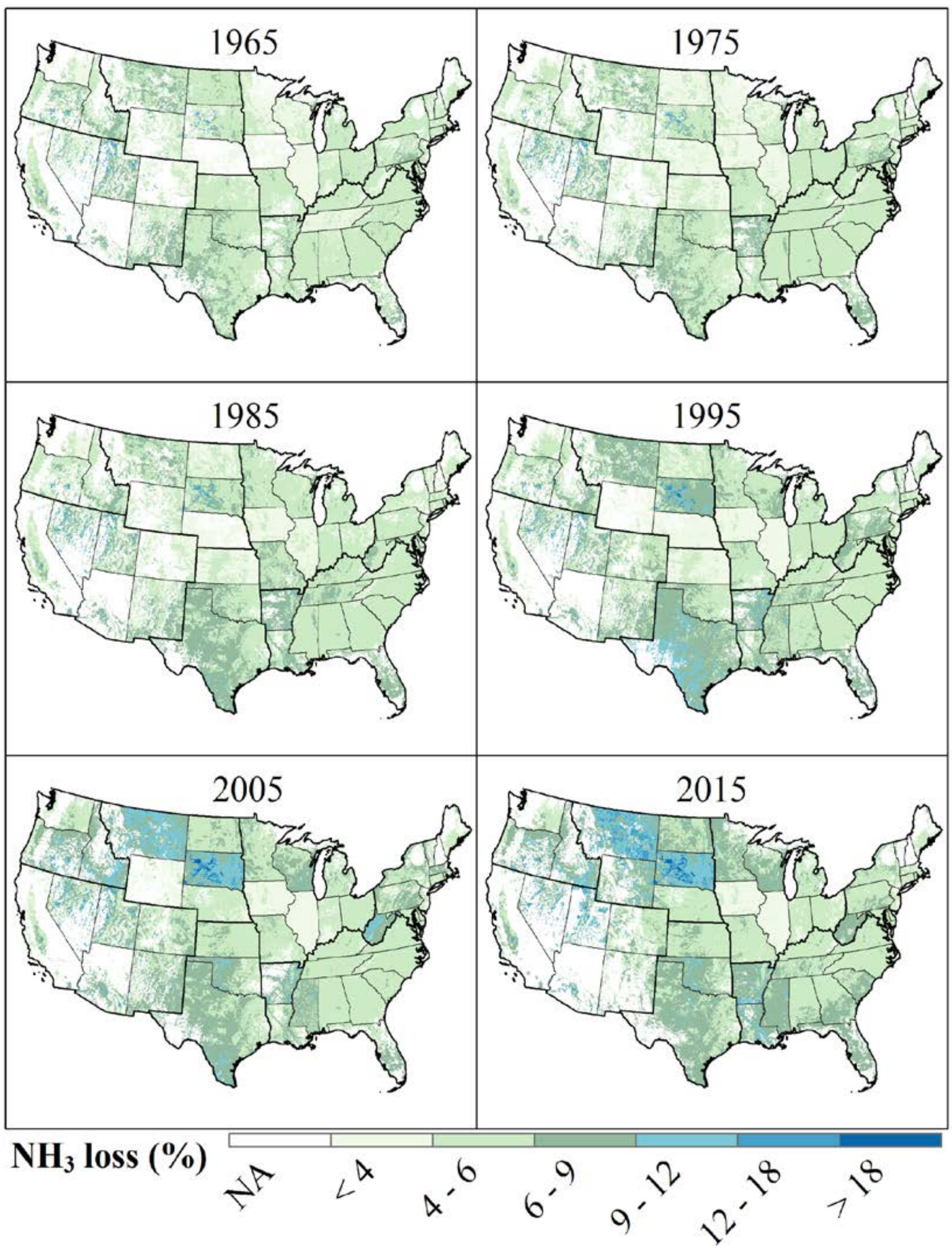


Figure 3. Spatial distribution of NH_3 emissions in the U.S. from 1960 to 2015. Values represent NH_3 emission from synthetic N fertilizer over all crops in each 5 km by 5 km grid cell.

520

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics
Discussions



https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Figure 4. Spatial and temporal patterns in NH_3 loss proportion relative to total N fertilizer input in the U.S. (the middle year of each decade is selected as an example).

525

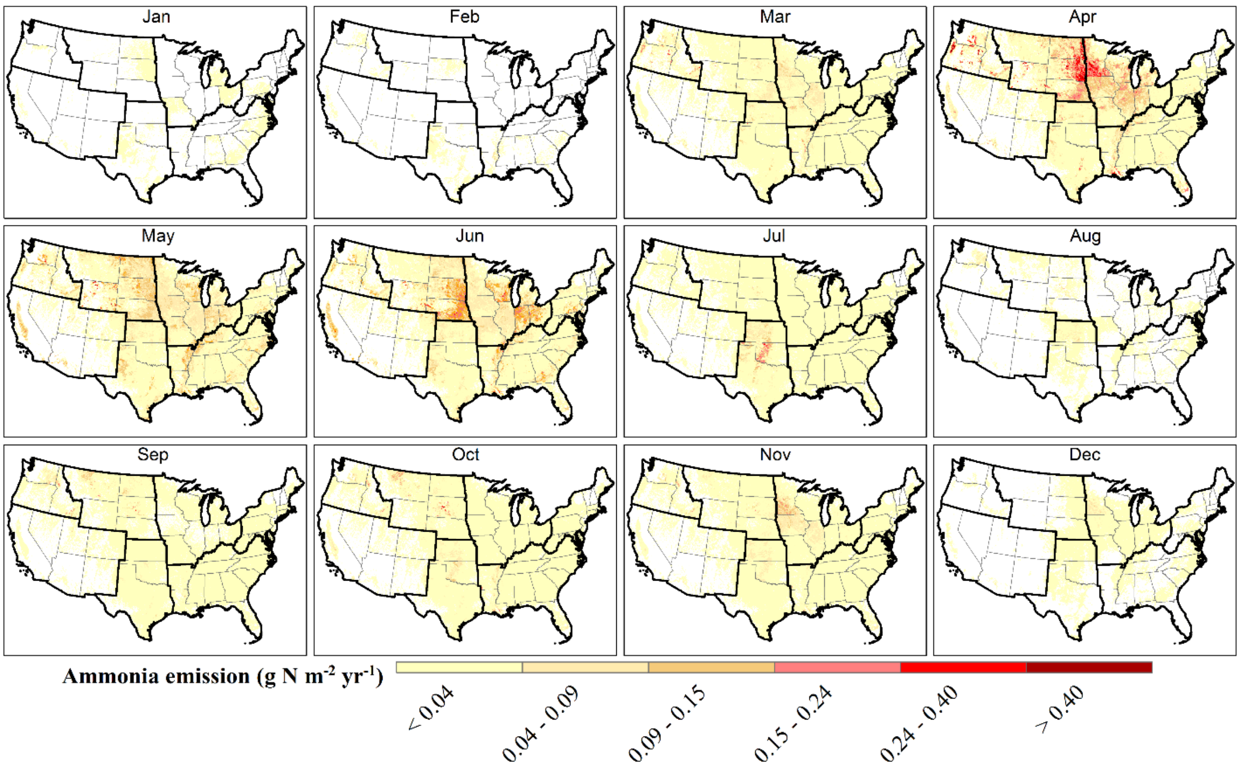
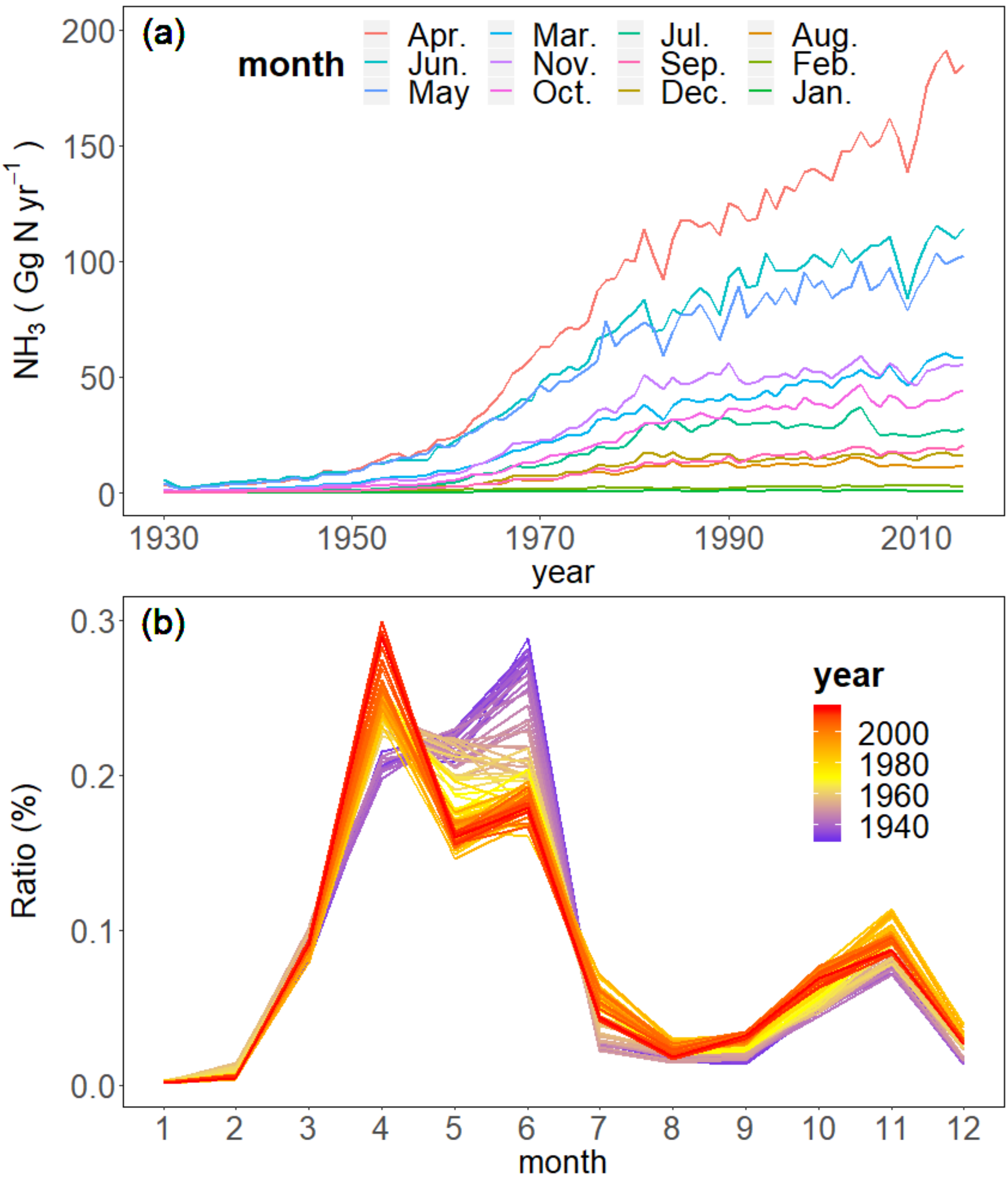


Figure 5. Spatial distribution of monthly estimated NH_3 emission across the U.S in 2015.

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

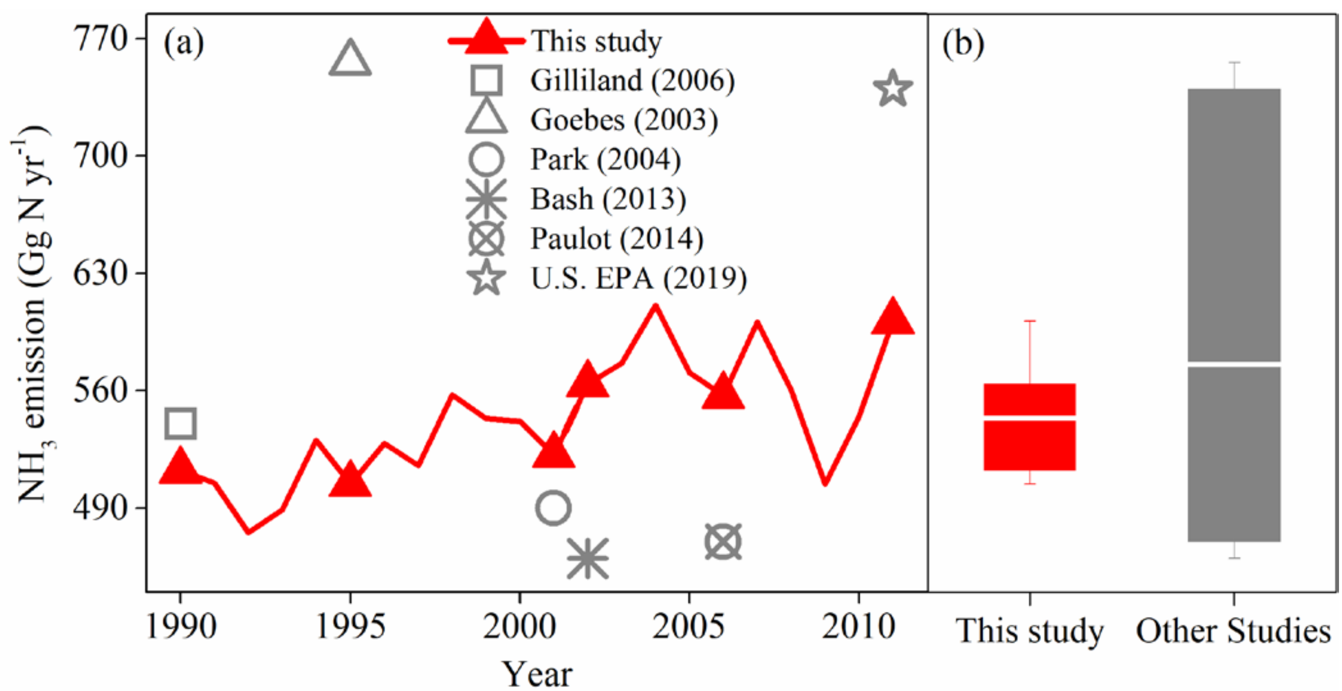
Atmospheric Chemistry and Physics
Open Access
EGU
Discussions



https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

530

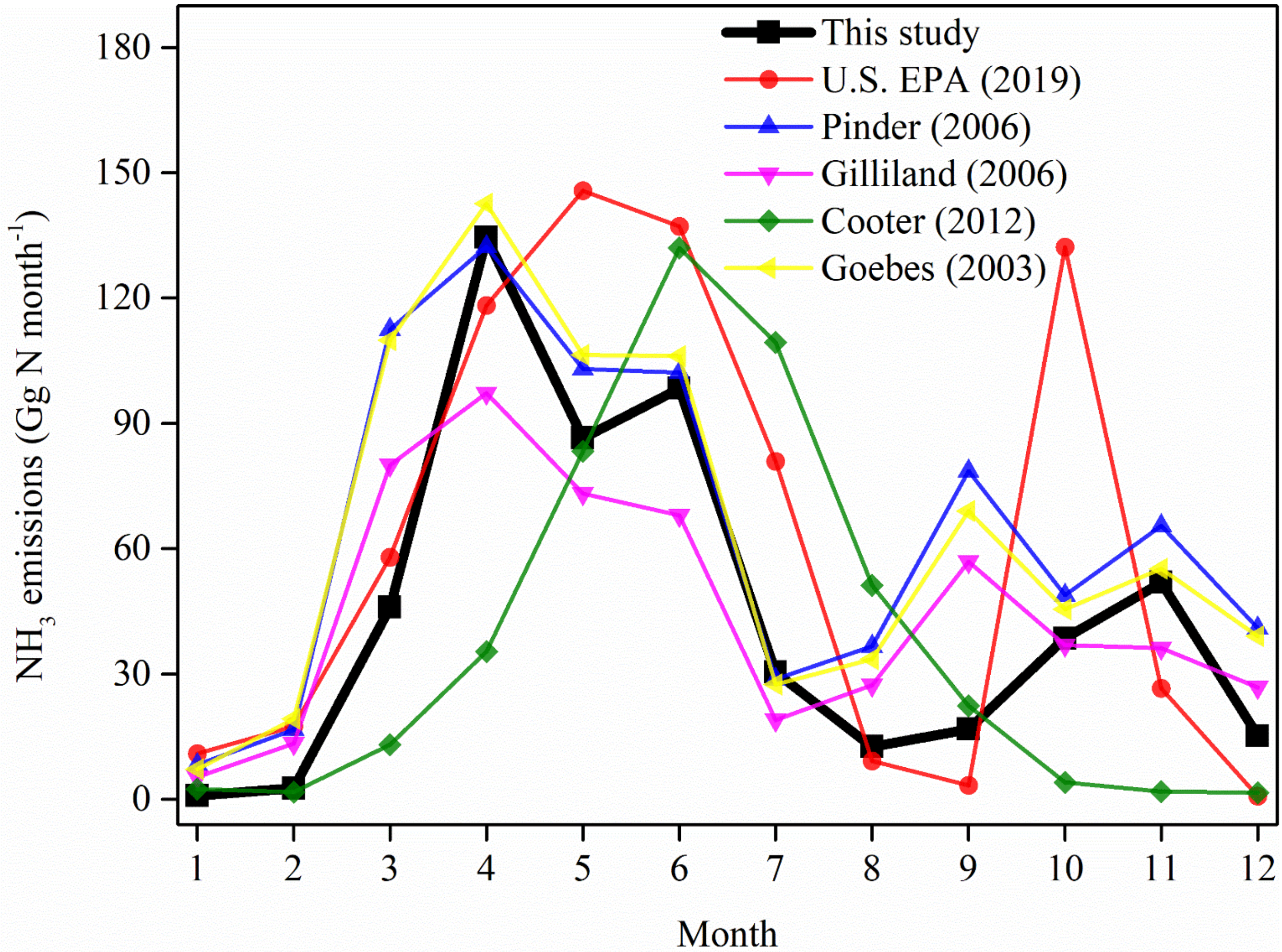
Figure 6. Temporal dynamics in monthly NH_3 emission rate (a) and share of each month to annual total (b) from 1930 to 2015. The month legend in (a) is vertically ordered by the NH_3 emission rate in 2015.



535 **Figure 7. Comparison of annual NH_3 emissions. (a) Paired comparison between our result and individual research, (b) Boxes include 25-75% of NH_3 emission of all chosen years estimated by our studies and other studies respectively, white lines are mean values, and whiskers comprise te whole range of data. NH_3 emission estimated by Paulot et al. (2014) represents average of 2005-2008, we compared their estimate against our result of 2006.**

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

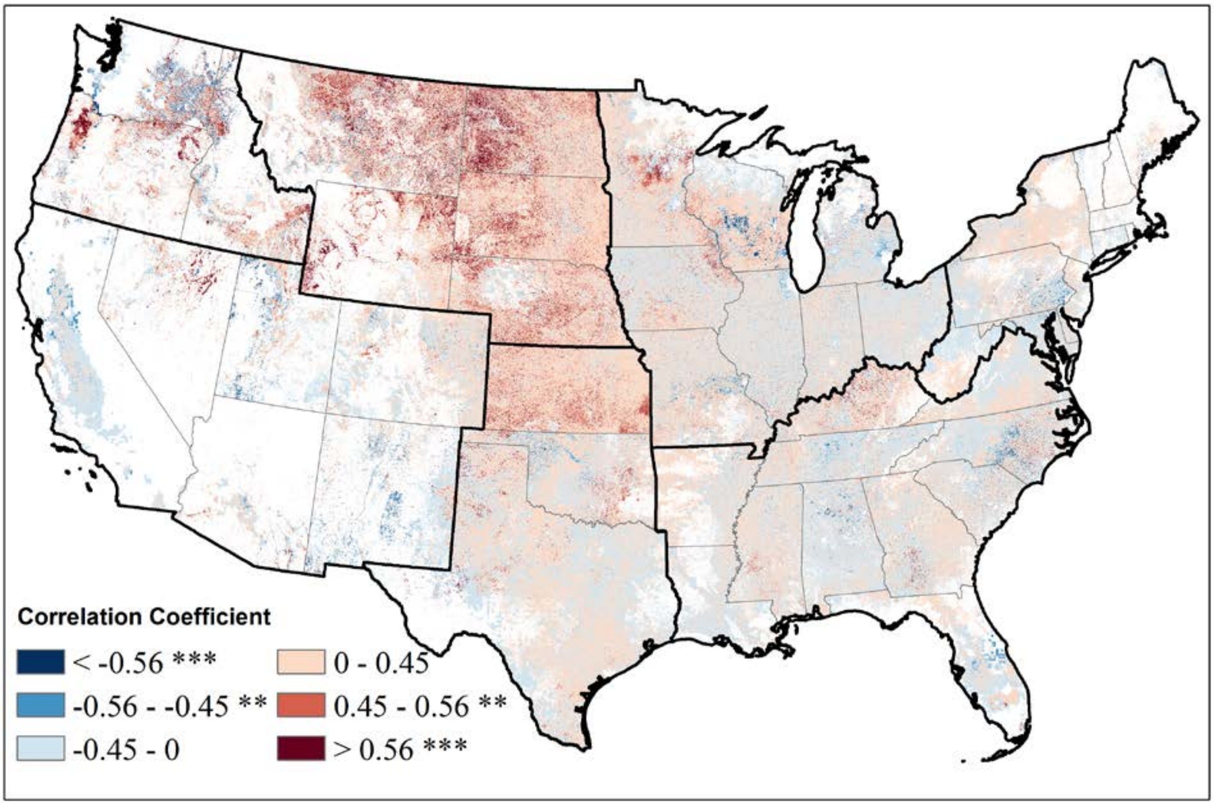
Atmospheric Chemistry and Physics Discussions



540 **Figure 8. Comparison of monthly NH_3 emission patterns between our estimate and other studies.**

https://doi.org/10.5194/acp-2020-97
Preprint. Discussion started: 19 February 2020

Atmospheric Chemistry and Physics
Open Access
Discussions
EGU



545

Figure 9. Correlation coefficient between NH_3 emission from N fertilizer uses and wet NH_4^+ deposition between 1985 and 2015. The correlation coefficient was calculated between the two time series at each 1km × 1km grid cell. ** refers to P-value < 0.01, * refers to P-value < 0.001.**

550