Response to Review 1:

We thank the reviewer for scrutinizing our manuscript and providing insightful comments and constructive suggestions, which greatly improve the quality of the manuscript. Please see our responses to the comments as follows.

In this study, Cao et al. derive US NH3 emissions associated with fertilizer application from 1900 to 2015. The strength of this study lies in the use of spatially-explicit time-series for cropland distribution and fertilizer application. The authors rely on a very simple emission scheme to estimate NH3 emissions. While this is acceptable considering the goal of this study, better quantification of the role of each factors and associated uncertainties for the authors' conclusions are needed before publication can be considered.

General comments

line 130 How would application of fertilizer at emergence (early spring) for winter wheat impact the authors' conclusions

Reply: We thank the reviewer for raising this insightful question. In this revised manuscript, we reconstructed the historical crop phenology and improved the N fertilizer application timing for winter wheat, fall barley, and cropland pasture to make it more reliable and reflect the real human practices. We believe this improvement solves the concern. The newly added information can be found in Methods **2.2.4 Crop phenology**, **2.2.5 Nitrogen fertilizer use dataset.**

We also added further discussions that are related to the newly added methodology. The discussion can be found in Discussion **4.3 Monthly peaks of NH_3 emissions shifting from 1930 to 2015**.

Line 122 to 154.

2.2.4 Crop phenology

We derived state-level crop phenology information from the USDA-NASS weekly crop progress report, which recorded the fractional acreage that has reached a given crop development stage (USDA-NASS, 2018). We linearly interpolated the weekly crop progress and identified the day at which crop development was 5%, 15%, 85%, and 95% complete. We extracted the planting and harvesting dates for all major crops except for cropland pasture. For winter wheat, we also obtained the date of dormancy breaking in the early spring (green-up) from 2014 to 2016. To gap-fill the planting date of a specific crop in a given state for missing years, we grouped states by latitude and adopted the distance-weighted interpolation (Eq. 3) using the mean date of the corresponding group.

$$Date_{i+k} = \frac{Mean_{i+k} \times Date_i}{Mean_i} \times \frac{k-i}{j-i} + \frac{Mean_{i+k} \times Date_j}{Mean_j} \times \frac{j-k}{j-i} \quad (3)$$

Where *Date* refers to the date of a given crop development stage that contains missing values, *Mean* refers to the mean date of the given stage of grouped states, the year *i* and *j* are the beginning and ending year of the gap, respectively, and the year *i*+*k* is the kth missing year.

The survey periods of crop progress provided by USDA-NASS vary across crops and states. For example, the data of durum wheat is available only in the years 2014 and 2015, while the data of barley started from 1996. The records of the other seven crops are available since the 1980s. To extend the crop-specific planting date records back to 1900, we adopted the approach used in the Environmental Policy Integrated Climate (EPIC) crop model, which considers daily heat unit accumulation (HU, Eq. 4) and heat unit index (HUI, Eq. 5) for crop phenological development estimation. It assumes that crops are ready to be planted or to break dormancy when the mean of daily maximum and minimum temperature equals to the base temperature (Tb) (i.e. when HU reaches 0), and to be harvested when the cumulative HU equals to potential heat units (PHU) (i.e. when HUI reaches 1). Based on the days at which 5%, 15%, 85%, and 95% crop development were completed between 1980-2015, we calculated the crop-specific Tb and PHU of each state with daily maximum and minimum temperature smoothed by a seven-day moving window from 1979 to 2015 for four percentages respectively. Instead of using the temperature at planting in fall as Tb, we used the temperature at green-up in early spring as Tb for winter wheat and fall barley to obtain a more accurate estimation of harvesting dates of these two crops. The averages of Tb and PHU in the earliest five available years of each crop type in each state were applied to Eq. 4 and Eq. 5 to calculate the dates of all four developments of all stages for missing years back to 1900.

$$HU_k = \frac{Tmax_k \times Tmin_k}{2} - Tb_c, \quad HU_k > 0 \tag{4}$$

where *HU* is heat unit, *Tmax* and *Tmin* are daily maximum and minimum temperature in ^oC, *Tb* is the crop-specific base temperature in ^oC, *k* refers to the day k, *j* refers to crop type j.

$$HUI_i = \frac{\sum_{k=1}^{i} HU_k}{PHU_j} \tag{5}$$

Where *HUI* is the heat unit index, which ranges from 0 at planting for spring-planted crops and at green-up for fall-planted crops to 1 at harvesting. *PHU* is the potential heat units required for harvesting, *i* and *k* are day i and day k, *j* refers to crop type j.

Line 177 to 180.

For winter wheat and fall barley, we allocated the use of N fertilizer after planting to the green-up stage in the following year. While for cropland pasture, we adopted the application timing strategy from Goebes et al (2003), in which 1/30 of the total N fertilizer amount is applied in January, February, October, November, and December, 1/12 in applied in May, June, July, and August, and 1/6 is applied in March, April, and September.

Page 12, line 364 to 365.

Whereas farmers in the Southern Great Plains prefer to apply most of N fertilizer after planting for cotton and a considerable amount of N fertilizer at green-up for winter wheat, resulting in peaks in summer and early spring.

line 305 relationship with wet deposition is not very compelling. As noted by the authors there are a lot of different factors that could be at play. I would suggest to focus on spring and fall months where the authors expect the fertilizer contribution to be maximum

Reply: We agree with the reviewer that focusing on spring and fall would strengthen the association between fertilizer-induced NH_3 emission and NH_4^+ deposition. However, the only NH_4^+ deposition maps that are available from the National Atmospheric Deposition Program are at an annual basis. To make a comparable analysis, we here used yearly NH_3 emission estimation rather than the seasonal estimation. According to Pearson's correlation table, we highlighted the pixels with a significance level of 0.01 and 0.001 respectively to examine the relationship between NH_3 emission and NH_4^+ deposition in the past 31 years. The result shows that the pixels with a significance level of 0.001 concentrated in the Northern Great Plains, Kansas, some parts of the Northwest and Minnesota, which supports our conclusion that the increase of NH_3 emission from N fertilizer may contribute to the NH_4^+ deposition trend in these regions. As the reviewer mentioned, we also discussed the roles of other factors such as forest fire and livestock played in these regions.

Trend attribution ——————

I recommend the authors better quantify the relative importance of the different factors that contribute to changes in the magnitude and seasonality of NH3 emissions. I would suggest the authors perform their analysis using a climatology for a) temperature, b) fertilizer type, c) spatial crop distribution, e) crop mix

Reply: We agree with the reviewer's suggestion. We designed additional simulation experiments to examine the contributions of five major factors, including temperature, cropland distribution, crop type, fertilizer rate, and fertilizer type, to long-term NH_3 emission. We found that N fertilizer use increase dominated the dynamic of NH_3 emission across the US. While springtime warming weakly enhanced NH_3 emission in most regions, it had an adverse effect in the Northern Great Plains and Northwest. Changes in cropland distribution and type played complicated roles impacting NH_3 emissions across regions and over time. In general, the spatial cropland area change slightly increased NH_3 emission in the intensively managed agricultural regions like the Midwest and the Great Plains but lowered the emissions in the Northeast and the Southwest. Whereas crop type rotation decreased NH_3 emission in most regions. However, it is noteworthy that the minor effects of cropland distribution and rotation are due to the N fertilizer input was kept constant at the level of 1960 and the cropland area changes represent the summation of cropland expansion and abandonment across the country. We added the revision in Method **2.3 Factorial contribution assessment**, Discussion **4.2 Spatiotemporal change in NH3 volatilization,** and Supplement **6 Factorial contribution analysis.**

Line 196 to 208.

2.3 Factorial contribution assessment

Environmental factors and human activities have considerable impacts on the dynamics of NH_3 emissions. We set up five simulation experiments to quantify the roles of five major factors including temperature, cropland distribution, cropland rotation, N fertilizer type, and N fertilizer application rate, in shaping NH_3 emission since the 1960s (Table 1). The first simulation experiment (S1) was designed to mirror the temperature effect by keeping all other four factors unchanged at the level of 1960. We set up the rest simulation experiments (S2-S5) by adding the annual change of cropland distribution, cropland rotation, N fertilizer use rate, and N fertilizer type successively to S1. In S2, we allowed the percentage of cropland in each grid cell to change following the prescribed input data but kept the crop type within grid cells unchanged. Whereas in S3, the cropland percentage and type changed simultaneously through years. We further added annual N fertilizer use rates into S4 with N fertilizer type ratio fixed in 1960. We treated 1960 as the baseline year and run all the simulations from 1960 to 2015. The value difference between the simulated year and 1960 in S1 was calculated to estimate the temperature effect. We calculated the differences between S2 and S1, S3 and S2, S4 and S3, and S5 and S4 to assess the impacts of cropland distribution, cropland rotation, N fertilizer rate, and N fertilizer type, respectively.

Line 333 to 337.

The conclusion drawn from our factorial contribution analysis shows that changes in cropland area and rotation have a minor influence on NH_3 emission in the nation (Fig. 7), which is primarily because N fertilizer input was kept constant at the level of 1960. Besides, the cropland area changes represent the summation of cropland expansion and abandonment across the country, resulting in a relatively small contribution to NH_3 emission increases.

Supplement:

6 Factorial contribution analysis

We set up five simulation experiments to examine the factorial contributions of temperature, cropland distribution, cropland rotation, N fertilizer type, and N fertilizer use rate to NH_3 emission change nationally and regionally. We calculated the difference every year between simulation experiments to assess the contribution of each factor and then averaged the difference within a decade (Table S5). The positive value in the Table S5 indicates a positive effect on NH_3 emission.

Supplement Table 5. Factorial contributions to NH_3 emission changes (Gg N $year^{-1}$) across the contiguous U.S.

Decade	Region	Temperature	Land use	Rotation	N fer rate	N fer type
1960s	US	0.98	-4.21	-5.33	87.35	-16.86
	NE	0.16	-0.49	0.11	2.50	0.23
	MD	0.41	-1.33	-0.85	39.55	-15.84
	NGP	-0.13	-0.38	-0.23	9.22	-2.61
	NW	-0.04	0.03	-0.03	3.60	0.97
	SGP	0.17	-0.38	-1.14	19.02	-3.79
	SE	0.32	-1.15	-3.04	10.09	2.78
	SW	0.07	-0.51	-0.14	3.38	1.39
1970S	US	0.31	3.05	-8.17	260.46	-40.75
	NE	0.11	-0.76	0.63	6.00	0.32
	MD	0.30	1.07	-1.15	112.17	-29.81
	NGP	-0.09	0.07	0.33	30.80	-7.89

	NW	-0.05	0.34	-0.04	11.40	0.94
	SGP	-0.04	1.04	-1.19	55.61	-12.47
	SE	-0.03	1.91	-7.19	33.68	7.88
	SW	0.10	-0.62	0.45	10.80	0.23
1980s	US	1.57	1.01	-8.51	354.80	7.67
	NE	0.14	-1.02	0.88	7.37	0.55
	MD	0.76	1.38	-0.55	153.27	-6.31
	NGP	-0.03	0.31	0.59	47.48	-7.53
	NW	-0.09	0.24	-0.02	14.69	3.18
	SGP	0.00	0.21	-1.31	73.85	-4.25
	SE	0.52	1.29	-8.84	43.12	20.74
	SW	0.26	-1.40	0.76	15.02	1.22
1990s	US	2.53	-3.08	-6.35	410.22	20.95
	NE	0.23	-1.54	0.68	8.58	0.86
	MD	1.19	0.73	-0.79	162.61	-17.30
	NGP	-0.04	0.42	1.04	67.83	-4.55
	NW	0.02	-0.13	-0.03	19.22	5.86
	SGP	-0.03	1.12	-2.58	86.86	4.03
	SE	0.76	-1.71	-5.04	47.41	29.95
	SW	0.40	-1.97	0.37	17.71	2.01
2000s	US	1.96	-5.55	-6.20	405.63	68.46
	NE	0.18	-1.87	0.73	9.02	1.52
	MD	0.61	0.24	-0.30	161.38	-14.10
	NGP	-0.16	0.33	0.92	81.85	28.16
	NW	-0.03	-0.38	0.13	21.10	11.31
	SGP	0.09	1.57	-2.99	78.05	9.34
	SE	0.68	-3.51	-4.00	38.35	28.42
	SW	0.58	-1.94	-0.69	15.88	3.75
2010s	US	3.77	-7.29	-5.64	434.21	94.37
	NE	0.21	-2.05	0.58	6.62	0.94
	MD	1.10	0.11	-0.46	177.10	-9.50
	NGP	-0.06	0.39	2.07	107.16	53.17
	NW	0.01	-0.50	0.56	23.37	11.63
	SGP	0.14	1.10	-0.71	69.74	8.39
	SE	1.70	-3.77	-6.58	34.38	25.65
	SW	0.66	-2.57	-1.12	15.83	3.91

There are two important factors that I would like the authors to analyze in more details a) planting dates The authors rely on a climatology for planting dates. However, Kucharik (2006) showed using the USDA crop report that corn planting took place ~2 *weeks earlier in 2005 relative to 1980. This dataset is available for other crops and it would be useful for authors to assess the impact of changing planting dates over this time period.*

There also exists simple parameterizations to estimate planting dates based on temperature/ precipitation that I would recommend the authors consider to estimate the variability in planting dates before 1979 (e.g., Bondeau (2007))

Reply: We appreciate the reviewer for raising this critical question and providing the information about the data source. Based on the reviewer's suggestion, we collected the crop-specific phenology changes in planting, green-up, and harvesting data in each state back to the 1980s from the USDA-NASS weekly crop progress report (https://www.nass.usda.gov/Quick_Stats/Lite/index.php). Then we used the crop model EPIC to estimate the crop-specific phenology in each state from 1900 to 2015. Then we used this dynamic phenology data to replace our original static phenology data. This data improvement has substantially improved our estimates of NH_3 emission and led to inter-annual variations of monthly NH_3 emission due to the dynamic crop phenology introduced. We added the improvement in Method **2.2.4 Crop phenology**, **2.2.5 Nitrogen fertilizer use dataset**, and Discussion **4.3 Monthly peaks of NH_3 emissions shifting from 1930 to 2015**. Please refer to our replies to the first comment raised above.

b) could the authors comment on the impact of long-term acidification that has been reported in several studies

Veenstra, J.J. and Lee Burras, C. (2015), Soil Profile Transformation after 50 Years of Agricultural Land Use. Soil Science Society of America Journal, 79: 1154-1162. doi:10.2136/sssaj2015.01.0027

Fuqiang Dai, Zhiqiang Lv, Gangcai Liu. (2018) Assessing Soil Quality for Sustainable Cropland Management Based on Factor Analysis and Fuzzy Sets: A Case Study in the Lhasa River Valley, Tibetan Plateau. Sustainabil-ity 10:10, pages 3477

Reply: We appreciate the reviewer's suggestion and references. We added the discussion in the section **4.2 Spatiotemporal change in the NH_3 emissions** to address the impact of long-term soil acidification on NH_3 emission.

Line 354 to 357

Although soil acidification through long-term agricultural land use may offset the effects of the increasing use of urea-based fertilizer, more effective policies and agricultural management are still needed in those high NH3 loss proportion regions (Veenstra and Lee, 2015; Dai et al., 2018), which can prevent air quality deterioration and enhance crop NUE.

Comparison with other inventories ——————————

the authors need to compare their inventory against other efforts to develop historical emissions from EPA, EDGAR, and CMIP6. I believe that only gridded NH3 emissions from agriculture may be readily available from EPA and CMIP6 but I encourage the authors to contact the inventories' developers to obtain their estimates for historical US fertilizer emissions.

http://www.globalchange.umd.edu/ceds/ -> code is freely available https://edgar.jrc.ec.europa.eu/

Reply: We appreciate the suggestion to show more comparisons with other NH_3 emission inventories and the inventory sources provided. Since our study focuses specifically on the NH_3 emission from synthetic nitrogen fertilizer, we cautiously chose the inventories which are comparable to valid the spatiotemporal and monthly pattern of NH_3 emission in our results. The CMIP6 GCM provided estimates of NH_3 emission from the agricultural sector in the US based on the emission factor calculated by EDGAR (Hoesly et al., 2018). Both CMIP6 and EDGAR have a solid methodology and database in estimating NH_3 emission globally and regionally. However, their estimates of NH_3 emissions from agricultural soil contains NH_3 emitted from nitrogen fertilizer, rice cultivation, nitrogen-fixing crops, crop residues, and so on, which includes broader emission sources than our work. As a result, CMIP6 and EDGAR reported 1431 Gg N year^{-1} and 1750 Gg N year^{-1} NH_3 emission from agricultural soil in 2014, whereas our study estimated 630 Gg N year^{-1} from N fertilizer use in the same year. EPA-NEI started the NH_3 inventory from 1990 and published the data discontinuously. In the inventory, other nitrogen inputs like nitrogen deposition were incorporated. Meanwhile, NH_3 absorbed and released by the canopy is also considered in their estimation. With input data and methodology evolving, monthly NH_3 emissions from "Fertilizer" were available since 2008. We selected the inventory of the year 2011 and 2014 (Version 2) to compare with our estimates in Fig. 8 for annual emission, and in Fig. 9 for monthly emission.

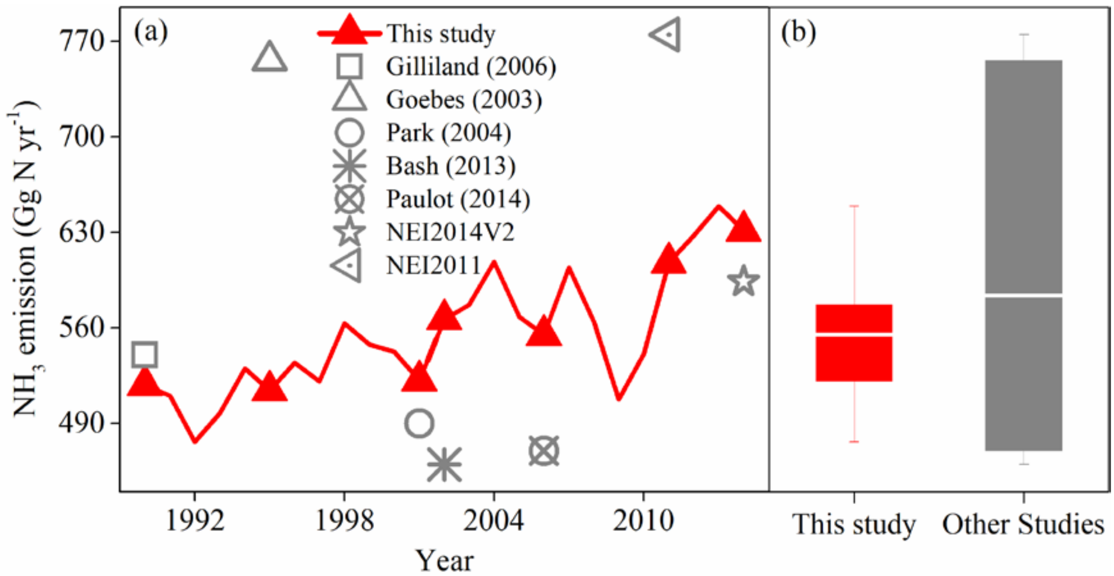


Figure 8. Comparison of annual NH_3 emissions. (a) Paired comparison between our result and individual research, (b) Boxes include 25-75% of NH_3 emission of all chosen years estimated by our study and other studies respectively, white lines are mean values, and whiskers comprise the whole range of data. NH_3 emission estimated by Paulot et al. (2014) represents the average of 2005-2008, we compared their estimate against our result of 2006.

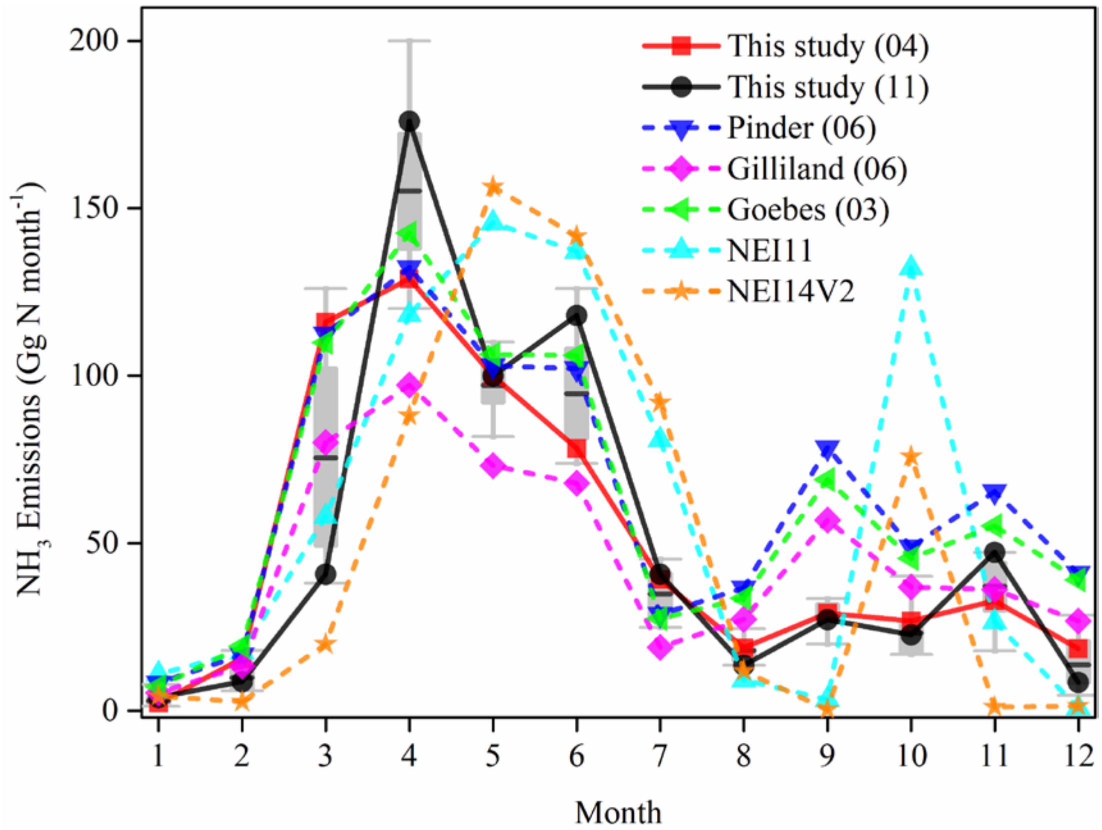
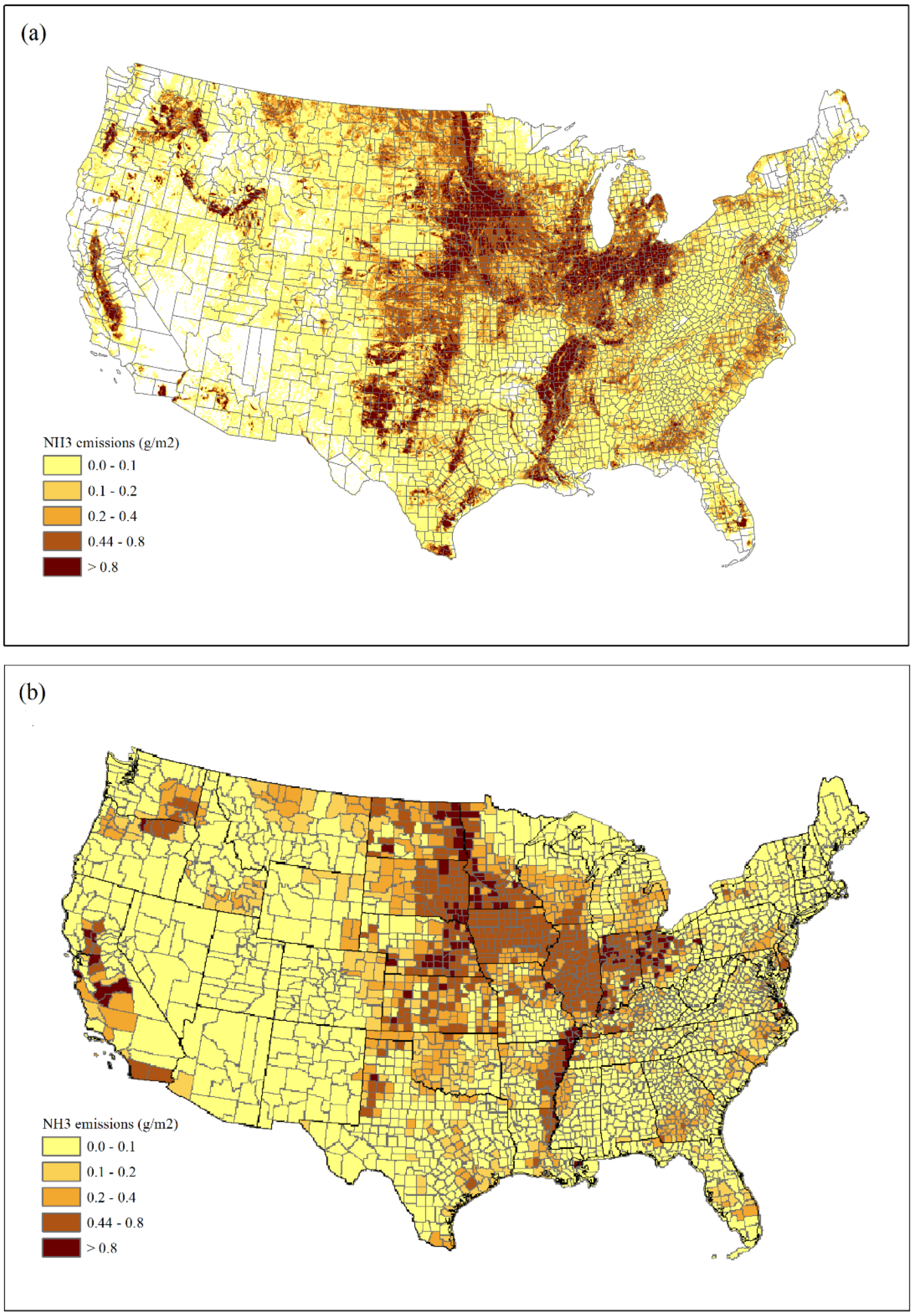


Figure 9. Comparison of monthly NH_3 emission patterns between our estimate and other studies. Two typical monthly patters of NH_3 emission in this study were used. The estimate of 2004 represents the pattern when planting date is early, whereas the simulation of 2011 stands for the pattern when planting date is delayed. Two simulations using different approaches by EPA-NEI were chosen in the comparison. Grey boxes include 25-75% of monthly NH_3 emissions during 2005-2015, black lines are mean values, and whiskers comprise the whole range of data.

We reached out to the EPA-NEI to request spatial maps of NH_3 emission. We were provided a gridded map of NH_3 emission in 2014. By comparison, we chose the image of the spatial pattern of NH_3 emission in 2011 from NEI FTP site (ftp://newftp.epa.gov/air/nei/2014/doc/2014v2_supportingdata/nonpoint/) instead of the gridded map in 2014 because the N fertilizer input used in 2011 is more comparable to our results. However, because the 2011 map is in a low resolution and hard to re-use, we listed the side-by-side comparison as Fig. S3 in the supplementary.



Supplement Figure 3. Comparison of spatial pattern of NH_3 emissions between our study (a) and EPA-National Emissions Inventory (b) in 2011.

Technical comments:

line 30: please rephrase to more clearly separate the impacts associated with N deposition and with PM2.5

Reply: We rephrased the description in section **4.4 Effects of increasing NH_3**

emissions on wet NH_4^+ deposition

Line 374 to 390.

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). Our result shows that the increase of NH_3 emissions from synthetic N fertilizer in the Northern Great Plains, the Northwest, and Kansas was significantly correlated to the increase of NH_4^+ wet deposition during 1985-2015 (Fig. 9). NH_4^+ deposition is highly affected by local NH_3 emissions because NH_3 volatilized into the atmosphere has a very short lifetime and deposits close to the source quickly. Therefore, In addition to growing forest fire and livestock numbers (Abatzoglou and Williams, 2016), our study reveals that NH_3 emissions from increasing N fertilizer use played an important role influencing the inter-annual variability of wet NH_4^+ deposition in the northwestern U.S. over recent decades. . 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 an 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 emissions may contribute to the $PM_{2.5}$ increase 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.

line 70 I would recommend discussing alternative (more recent) approaches used to derive NH3 emissions not only in the US but also in China and Europe. There have been a lot of progress in NH3 inventories since the work of Bouwman and the authors need to better explain why this approach was selected.

Reply: We agree with the reviewer's suggestion for including discussions in the model selection. Our study focus specifically on NH_3 emission from the single source: synthetic N fertilizer. Compared to inversed model approaches and process-based models, which mix other sources of NH_3 emission and require a deep understanding of various NH_3 emission drivers, empirical model-based emission factor has been proven an effective and valid tool for estimating NH_3 emission. Our work builds upon a newly developed N fertilizer management dataset including the crop-specific information of N fertilizer use rate, fertilizer type, application timing, and application method. Using high-spatial-resolution soil properties, daily temperature, dynamic crop distribution, and dynamic crop phenology as model drivers, the REML developed by Bouwman et al. (2002) can provide higher levels of detailed NH_3 emissions over space and time. We added the discussion in Discussion **4.5 Uncertainty**

Line 407 to 416

4.5 Uncertainty

Zhou et al (2015) developed a nonlinear Bayesian tree regression model as a function of N fertilizer rate to estimate NH3 emission in China and found the estimates match well with observations and satellite-based products. Thus, we may underestimate NH3 emissions under a high N fertilizer use rate. Another example is the use of nitrification and urease inhibitors. Nitrification inhibitors have been found to increase NH3 loss while urease inhibitors can limit NH3 volatilization (Lam et al., 2017). Therefore, the uncertainty of usage of nitrification and urease inhibitor is likely to misrepresent NH3 emissions. In addition, considering the bidirectional exchange process may improve the accuracy of seasonal NH3 emission estimation (Bash et al., 2013). However, our work builds upon the newly-developed N fertilizer management and crop phenology dataset that combines crop-specific N fertilizer use rate, fertilizer type, application timing, application method, and phenology for each state ranging from 1900 to 2015. The REML model we are using makes sufficiently use of these information and provides higher levels of details over space and time.

line 42 grammar: for quantifying long-term spatially explicit of NH3 emissions

line 63 objects -> goals

Reply: We thank the reviewer for these words correction and corrected them.

Line 136 The authors need to clarify that this dataset represents a climatology of present-day planting dates.

Reply: We reconstructed the historical crop phenology data, please find the response above.

line 196 I am not sure what reportedly means in this context

Reply: We have deleted the word.

Additional comment: I forgot to mention this recent study that the authors also need to consider:

https://onlinelibrary.wiley.com/doi/pdf/10.1111/gcb.14499

Reply: We have included this work.

Line 42 to 43.

Process-based modeling is a popular “bottom-up” approach for quantifying spatially explicit NH3 emissions over a long period (Cooter et al., 2012; Riddick et al., 2016; Xu et al., 2018).

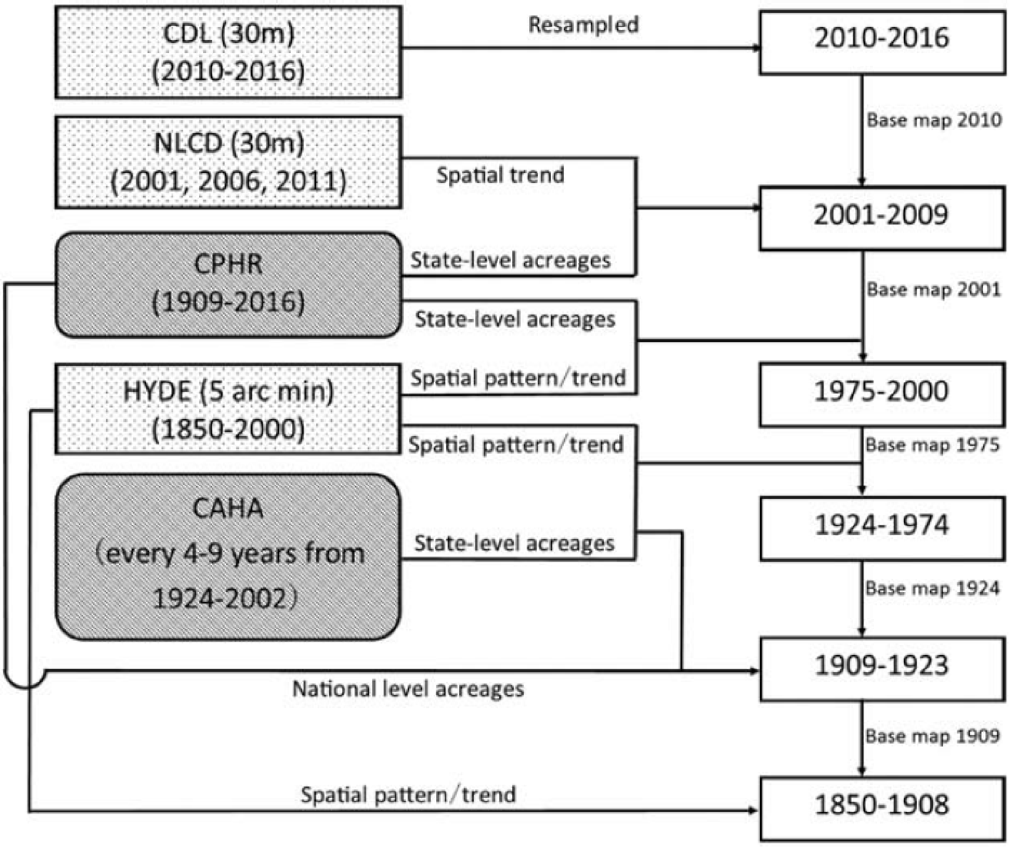
Response to Review 2:

We thank the reviewer for scrutinizing our manuscript and providing insightful comments and constructive suggestions, which improve the quality of the manuscript. Please see our responses to the comments as follows.

The manuscript by Cao et al. estimates NH3 emissions from fertilizer in the US over the past century. By tracking different types of fertilizer and crops, they identify variability in the spatial distribution of fertilizer emissions and emissions factors. Their results are consistent with previously noted studies of shifting spatial distribution in NH4 deposition, for example, but provide additional valuable levels of detail. My main suggestion would be to provide some quantitative assessments of uncertainty, which I think may constitute minor revisions, as they have at least qualitatively identified the key sources of uncertainty. This and a few other minor comments are included below.

Comments: 57-58: It's not clear to me what land and fertilizer use is being referred to here as distinct from the studies cited in the preceding lines.
107-119: I realize this lies somewhat outside the present paper and is likely within the work of Yu 2018, but could the authors briefly comment on how such spatial resolution was known for these distributions prior to the satellite era? Here they mention how satellites were used to determine spatial reconstructions but do not comment on any other method, which presumably would be necessary for the first half of the century, nor how such different methods have been harmonized into a single consistent dataset.

Reply: To reconstruct the spatially explicit cropland distribution maps that go back to 1900, we harmonized multiple state- and national-level inventory data and remote sensing products in different periods. USDA-CDL and NLCD provide the detailed spatial distribution of crop information and are directly resampled for the reconstruction of cropland maps during the recent decade. Another satellite-based database HYDE cropland maps, which were developed by assimilating both inventory and satellite data, was used to reconstruct the spatial maps before 2000 by depicting the potential distribution of agricultural land. Meanwhile, adjusted state- and national-level crop-specific land acreage from USDA survey data was used to limit the acreage of each crop for each state on maps. We think incorporating a detailed description of the methodology of cropland distribution map reconstruction is irrelevant to this study and therefore gave a brief summary and referred to the article that elaborates the cropland maps reconstruction process.



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

Fig 1 (a): I think it would be clearer to refer to this as loss "from" N fertilizer, not loss "to" fertilizer, since the process being described here is NH3 from fertilizer to the atmosphere, correct?

Reply: We agree with the reviewer and we have corrected it.

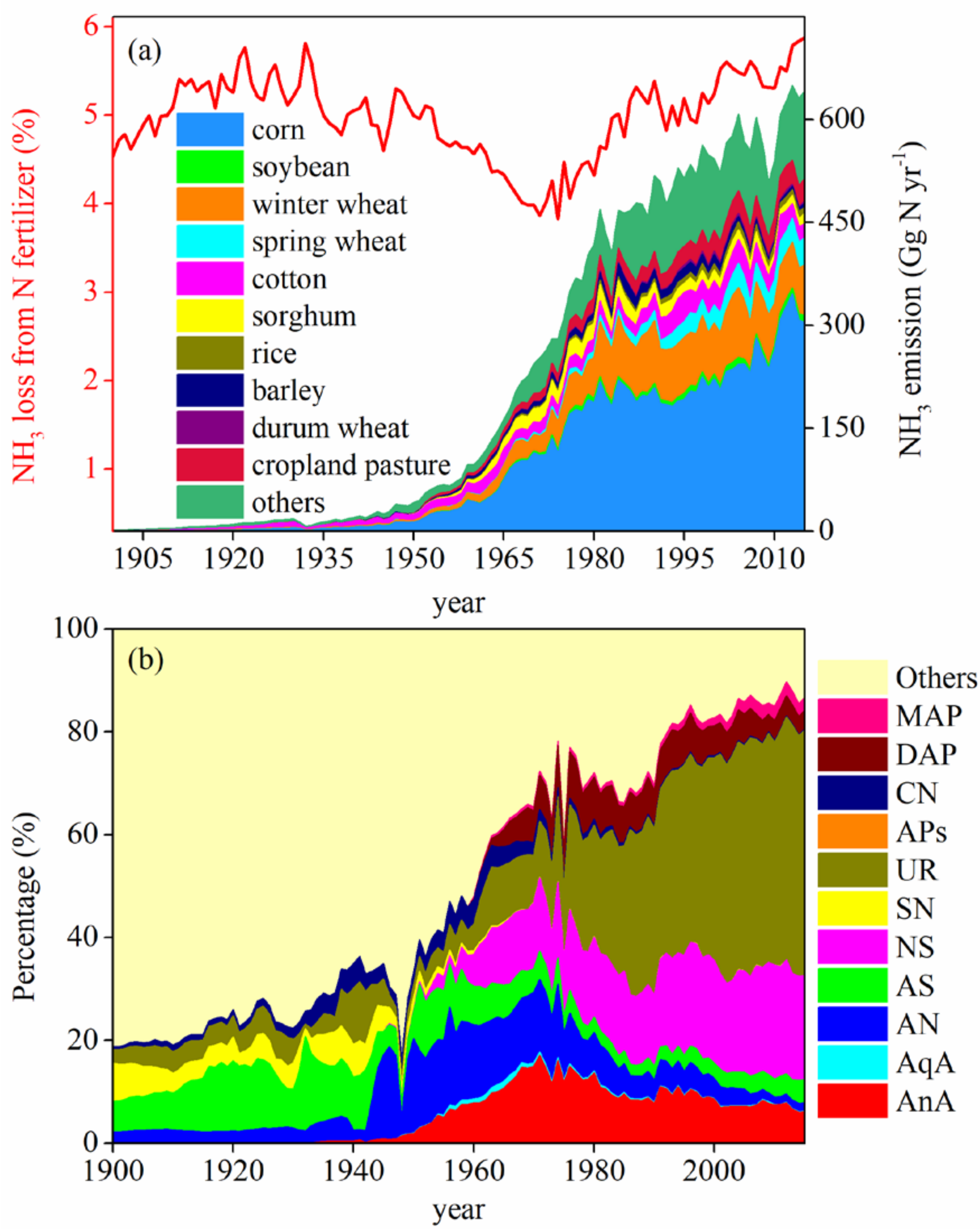


Figure 1. Contributions of major crop types and N fertilizer types to historical NH_3 emissions since 1900. (a) Crop specific NH_3 emissions, (b) Relative contributions of 12 major N fertilizer types to annual total NH_3 emission. Solid line in (a) refers to the NH_3 loss percentage to total N fertilizer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

173: Here emission growth just refers to fertilizer emission, right? Not emission from livestock, which is the larger component of total emissions.

Reply: We thank the reviewer for pointing out the vague expression here. Our study focused specifically on NH_3 emission from synthetic fertilizer. We added the clarification to address that NH_3 emission in this study refers to N fertilizer-induced NH_3 emission.

Line 62 to 65.

Based on spatially explicit time-series of cropland distribution maps and N fertilizer management database, we adopted empirical modeling of EF to calculate monthly NH_3 emissions from synthetic N fertilizer uses (Hereafter, NH_3 emission refers to the synthetic N fertilizer-induced NH_3 emission unless specified otherwise) in the contiguous U.S. at a resolution of 1 km × 1 km from 1900 to 2015.

Fig 2: What drives the drop in RF from the 40s to 50s in NW, NGP and SW?

Reply: We agree with the reviewer's comment. The widespread popularity of Anhydrous ammonia and Ammonium nitrate occupied the share of Urea in these regions, which largely reduced the ratio of NH_3 emission lost from fertilizer. This phenomenon can be found in five out of seven regions. We revised the sentence in **4.2 Spatiotemporal change in the NH_3 emissions** to include the region into discussion.

Line 317 to 318.

The "V" shape of historical national and regional NH_3 emission factors mainly resulted from the changing preference in using different N fertilizer types (Cao et al., 2018).

197: What do the authors mean by "reportedly" here?

Reply: We have deleted the word.

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

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Abstract. The increasing demands of food and biofuel have promoted ~~century-long~~ cropland expansion and nitrogen (N) fertilizer enrichment in the United States over the past century. 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 and time-series gridded data sets including ~~climate~~temperature, 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~~641 Gg N yr^{-1} in 2015, for which corn and spring wheat ~~planting is~~are the dominant ~~contributor~~contributors. Meanwhile, urea-based fertilizers gradually grew to the largest NH_3 emitter and accounted for 78% of the total increase during 1960-2015. The factorial contribution analysis indicates that the rising N fertilizer use rate dominated the NH_3 emission increase since 1960, whereas the impacts of temperature, cropland distribution and rotation, and N fertilizer type varied among regions and over periods. Geospatial analysis reveals that the hotspots of NH_3 ~~emission~~emissions 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~~May to April since the ~~1960s~~1930s. 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~~20th century (Cao et al., 2018; Erisman et al., 2008). The predictable rise in food demand may lead to ~~greater~~more N fertilizer consumption 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~~across 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.,~~Nationwide, 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~~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~~emissions at the regional and national scale (Gilliland et al., 2006; Liu et al., 2019)). However, this "top-down" approach has difficulty in separating the 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 over a long period (Cooter et al., 2012; Riddick et al., 2016; Xu et al., 2018). These models require detailed information ~~of~~on local environmental conditions and farming practices that is generally not available. ~~An alternate effective~~Besides, background emissions (i.e., prior to human disturbances) are always included in such modeling estimations. Another widely-used "bottom-up" approach to estimate the 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 estimations have been improved to provide 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~~across the ~~U.S.~~country during a short period, few studies have assessed the spatiotemporal patterns and the factorial contributions of NH_3 emissions ~~in the U.S.~~ on a century scale. The lack of long-term assessment and understanding of contributing factors may limit our ~~understanding and predictive~~ capability in predicting 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~~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 (Hereafter, NH_3 emission refers to the synthetic N fertilizer-induced NH_3 emission unless specified otherwise) 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~~driven by changes in historical temperature, land use, and N fertilizer management practices~~ change~~. Our ~~objects~~goals are to answer the following questions: (1) how did the NH_3 emission change over space and time? (2) what roles did ~~each~~temperature, land use, crop ~~type~~rotation, and ~~each~~ N fertilizer ~~type~~use play in ~~historical~~determining the changes in NH_3 emission? ~~(2) how did the fertilizer-induced NH_3 emission in~~(3) what is the ~~U.S. change over space and time? (3) how were the~~relationship between atmospheric NH_4^+ deposition dynamics ~~associated with inter-~~and NH_3 emission at an annual ~~variations in NH_3 emission~~basis?

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~~In this study, we used a widely-used residual maximum likelihood model (REML, Bouwman et al., 2002) derived emission factor (EF) to assess synthetic N fertilizer-induced NH_3 emissions. We calculated the REML-emission factors 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 the U.S. 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~~a harmonized database of crop ~~planting and harvesting~~phenology dates. The daily fertilizer input rate was ~~further~~then aggregated to ~~each month~~monthly time step. 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~~EF, we obtained spatially explicit estimates of 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~~MD), the Southeast (SE), and the Northeast (NE) according to the U.S. Fourth National Climate Assessment (2019)~~.~~ (Fig. 2).

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 a 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 EF and then calculate the NH_3 emission ~~factor.~~(Eq. 1, Eq. 2).

$$EF = exp(FV_{Tem} + FV_{pH} + FV_{CEC} + FV_{FT} + FV_{AM} + FV_{CT}) \quad (1)$$

$$NH_3 = N\ Fer * EF \quad (2)$$

Where ~~*EF* refers to Emission Factor~~in Eq. 1, *FV* refers to Factor Value of each key driver. The values of input data are grouped into broad classes. *Tem* refers to air Temperature and are grouped into two classes ~~by~~above and below 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~~N fertilizer 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. Where in Eq. 2, NH_3 refers to NH_3 emission and *N fer* refers to N fertilizer use rate. 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~~We downloaded the 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 resampled to 1km × 1km and aggregated to monthly average temperature.

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~~Cropland 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~~We adopted a newly developed cropland distribution and type maps of the contiguous U.S. at a resolution of 1 km × 1 km from 1900 to 2015 to drive the REML model (Yu et al., 2018; Yu and Lu, 2018). The cropland maps were reconstructed to characterize the area, type, and distribution of cultivated land annually by harmonizing various sources of inventory data and remote sensing images. By using this database, we identified and tracked the percent of cropped land area, and what crop was planted in each grid cell each year while excluding summer idle/fallow areas. Ten major crop types identified in the cropland maps and used in this study include 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. They helped us put the crop-specific N fertilizer use rate, application timings, and application methods into a spatial context.

2.2.4 Crop phenology

We derived state-level crop phenology information from the USDA-NASS weekly crop progress report, which recorded the fractional acreage that has reached a given crop development stage (USDA-NASS, 2018). We linearly interpolated the weekly crop progress and identified the day at which crop development was 5%, 15%, 85%, and 95% completed. We extracted the planting and harvesting dates for all major crops except for cropland pasture. For winter wheat, we also obtained the date of dormancy breaking in the early spring (green-up) from 2014 to 2016. To gap-fill the planting date of a specific crop in a given state for missing years, we grouped states by latitude and adopted the distance-weighted interpolation (Eq. 3) using the mean date of the corresponding group.

$$Date_{i+k} = \frac{Mean_{i+k} \times Date_i}{Mean_i} \times \frac{k-i}{j-i} + \frac{Mean_{i+k} \times Date_j}{Mean_j} \times \frac{j-k}{j-i} \quad (3)$$

Where *Date* refers to the date of a given crop development stage that contains missing values, *Mean* refers to the mean date of the given stage of grouped states, the year *i* and *j* are the beginning and ending year of the gap, respectively, and *k* is the kth missing year.

The survey periods of crop progress provided by USDA-NASS vary across crops and states. For example, the data of durum wheat is available only in the years 2014 and 2015, while the data of barley started from 1996. The records of the other seven crops are available since the 1980s. To extend the crop-specific planting date records back to 1900, we adopted the approach used in the Environmental Policy Integrated Climate (EPIC) crop model (Williams et al., 1989), which considers daily heat unit accumulation (HU, Eq. 4) and heat unit index (HUI, Eq. 5) for crop phenological development estimation. It assumes that crops are ready to be planted or to break dormancy when the mean of daily maximum and minimum temperature equals to the base temperature (Tb) (i.e. when HU reaches 0), and to be harvested when the cumulative HU equals to potential heat units (PHU) (i.e. when HUI reaches 1). Based on the days at which 5%, 15%, 85%, and 95% crop development were completed between 1980-2015, we calculated the crop-specific Tb and PHU of each state with daily maximum and minimum temperature smoothed by a seven-day moving window from 1979 to 2015 for four percentages respectively. Instead of using the temperature at planting in fall as Tb, we used the temperature at green-up in early spring as Tb for winter wheat and fall barley to obtain a more accurate estimation of harvesting dates of these two crops. The averages of Tb and PHU in the earliest five available years of each crop type in each state were applied to Eq. 4 and Eq. 5 to calculate the dates of all four developments of all stages for missing years back to 1900.

$$HU_k = \frac{Tmax_k \times Tmin_k}{2} - Tb_c, \quad HU_k > 0 \tag{4}$$

where *HU* is heat unit and indicates the planting date for spring-planted crops and green-up date for fall-planted crops when it reaches 0, *Tmax* and *Tmin* are daily maximum and minimum temperature in ºC, *Tb* is the crop-specific base temperature in ºC, *k* refers to the day k, *j* refers to crop type j.

$$HUI_i = \frac{\sum_{k=1}^{i} HU_k}{PHU_j} \tag{5}$$

Where *HUI* is the heat unit index, which ranges from 0 to 1 and indicates the harvesting date when it reaches 1. *PHU* is the potential heat units required for harvesting, *i* and *k* are day i and day k, *j* refers to crop type j.

2.2.5 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~~and others during the period 1900-2015. ~~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.~~

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~~information (USDA-NASS, ~~2010~~2018). 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~~ before planting ~~application~~ and after planting applications occur one month before and after planting date, respectively. ~~We obtained~~Among the ~~surveyed planting and harvesting~~ four dates ~~for~~of 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~~ crop phenological development stage (i.e., completion for 5%, 15%, 85%, and 95% ~~of cropland acreage~~area) we generated in ~~each state are either planted or harvested, respectively. The~~ section 2.2.4, the period between the dates of 15% and 85% completion is the most active range. Therefore, we ~~considered the most active period (15%-85%) accounts for~~assumed that 80% of N fertilizer use allocated in each application timing~~,~~ ~~whereas~~ is applied to the active period (15%-85%), while the periods of 5%-15% and 85%-95% ~~contribute to~~ each receive 10%, respectively. We evenly ~~allocated~~spread the N fertilizer use ~~to~~over every day ~~in each~~within the corresponding period ~~for~~of four application timings~~.~~ via dividing N fertilizer use rate by the number of days. After that, we aggregated the daily application to the monthly ~~application. See~~step. More details can be found in the example shown in Supplement ~~table~~Table S2 and Fig. S1. ~~We~~For winter wheat and fall barley, we allocated the use of N fertilizer after planting to the green-up stage in the following year. While for cropland pasture, we adopted the application timing strategy from Goebes et al. (2003), in which 1/30 of the total N fertilizer amount is applied in January, February, October, November, and December, 1/12 in applied in May, June, July, and August, and 1/6 is applied in March, April, and September. Because most crops in the others group such as oil seeds, legumes, small grains, fruits, and vegetables are spring-planted crops, we used the average ~~monthly allocation~~ ratio of monthly application to annual total over eight major crops by excluding winter wheat~~,~~, cropland pasture, and fall barley in each state to extract the monthly application rate of ~~cropland pasture and~~ all other crops.

USDA-ERS (2015) also reported how N fertilizer was applied and the ~~acreage~~ percentage of acreage that was treated with the same method of each crop in the surveyed state ~~receiving N fertilizer in this way.~~. We regrouped the methods of the 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 the soil and NS is only applied as a 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~~rates under multiple application methods of each N fertilizer type of each crop type in each state.

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~~Factorial contribution assessment

Environmental factors and human activities have considerable impacts on the dynamics of NH_3 emissions. We set up five simulation experiments to quantify the roles of five major factors including temperature, cropland distribution, cropland rotation, N fertilizer type, and N fertilizer application rate, in shaping NH_3 emission since the 1960s (Table 1). The first simulation experiment (S1) was designed to mirror the temperature effect by keeping all other four factors unchanged at the level of 1960. We set up the rest simulation experiments (S2-S5) by adding the annual change of cropland distribution, cropland rotation, N fertilizer use rate, and N fertilizer type successively to S1. In S2, we allowed the percentage of cropland in each grid cell to change following the prescribed input data but kept the crop type within grid cells unchanged. Whereas in S3, the cropland percentage and type changed simultaneously through the study period. We further added annual N fertilizer use rates into S4 with N fertilizer type ratio fixed in 1960. We treated 1960 as the baseline year and run all the simulations from 1960 to 2015. The value difference between the simulated year and 1960 in S1 was calculated to estimate the temperature effect. We calculated the differences between S2 and S1, S3 and S2, S4 and S3, and S5 and S4 to assess the impacts of cropland distribution, cropland rotation, N fertilizer rate, and N fertilizer type, respectively.

2.3 Correlation between NH_3 emission and wet NH_4^+ deposition

We obtained ~~2338 m~~2338m resolution annual wet NH_4^+ deposition data from 1985 to 2015 in the contiguous U.S. from the 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~~8% 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~~469 Gg

N yr^{-1} in 1981, followed by a slower rise to ~~640~~641 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 NH_3 emission growth in recent decades, contributing to 52% during 1980-2015, and ~~81~~83% 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~~14% of the fertilizer-NH_3 emission increase can be attributed to spring wheat production.

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~~11.5% 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~~after 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~~losing 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 March, April, May, and June (Fig. 5). In addition, the emission hotspots showed ~~a~~ large spatial ~~variation~~variations 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). Meanwhile, NH_3 emissions in March and April showed large inter-annual fluctuations compare to other months. The NH_3 emissions in April have consistently increased by ~~85~~64%, from 100 Gg N month^{-1} in 1980 to ~~185~~164 Gg N month^{-1} in 2015, while the emissions in June and May slowly increased by ~~47~~43% and ~~44~~42%, from ~~78~~70 Gg N month^{-1} and ~~71~~69 Gg N month^{-1} to ~~115~~100 Gg N month^{-1} and ~~102~~98 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~~1960s, May dominated the annual emissions, followed by ~~May~~June and April. In this study, we find that maximum emissions have gradually shifted to earlier months and peaked in April since the ~~1950s~~1960s. 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~~,~~ and the Northwest (Fig. S2). On the contrary, although ~~large~~minor increases were found in the corn-belt, large decreases (< -10%) in May occurred in the Dakotas, Minnesota, and 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.~~.

3.4 Factorial contributions

Our simulation experiments show that N fertilizer input is the dominant contributor to boost NH_3 emissions across the US since 1960, especially in the Northeast, the Midwest, the Great Plains, and the Southwest (Fig. 7, Table S5). The roles of other factors affecting NH_3 emissions differed among regions and over periods. We find that temperature posed a weakly positive effect on NH_3 emission in most regions except the Northern Great Plains and Northwest during the simulation period. Cropland area and rotation changes overall led to decreases in NH_3 emission but had complicated impacts among regions since 1960. In the intensively managed regions, such as the Midwest, the Great Plains, cropland use change slightly increased NH_3 emission, whereas decreased NH_3 emission in the Northeast and the Southwest regions (Fig. 7b, 7h). Crop rotation lowered NH_3 emissions in the US and most regions except the Northeast. Changes in N fertilizer type had largely increased NH_3 emission in regions such as the North Great Plains, the Northwest, and the Southeast, especially after the 1990s.

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~~8). 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 the 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~~is 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; 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~~9). All studies agreed that the majority of NH_3 is released in spring and June 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~~three of these studies, which is consistent with our estimates. Whereas EPA-NEI, considering canopy uptake and release of NH_3, found a delayed peak in May. Several studies found relatively higher NH_3 emissions in March (Gilliland, 2003; Goebes et al., 2003; Pinder et al., 2006). Our estimate in 2004 also showed the same pattern, in which the planting date was early. However, NH_3 emission in March was very low in 2011 from our study due to the delayed planting date and thus resulted in greater April NH_3 emission. Owing to the limited data of actual fertilizer use history, these studies used the recommendation from fertilizer experts to ~~assume that~~spread the N fertilizer after planting over February and March in the following year at the green-up of winter wheat with a fixed ratio. However, we allocated this proportion of N fertilizer ~~applied in fall (i.e., before planting for winter wheat) should be applied in~~ to early spring~~, before~~ based on the annual green-up date of winter wheat~~. Therefore, they estimated higher NH_3 emissions~~ in ~~March than ours. This different assumption~~each state derived from USDA-NASS. The discrepancies in crop phenology and N fertilizer application timing ~~of winter wheat may~~ also ~~introduce~~introduced more disagreements to the secondary peak in fall (Fig. ~~8). Applying N fertilizer before winter wheat greening-up may reduce~~

~~the risk~~9). Different from a single large peak in October estimated by EPA-NEI, other studies found two smaller peaks in September and November. Our results, however, indicated relatively smaller emissions compared to other studies, which is because the ratio of N ~~leaching and denitrification. However, there is a lack of detailed sub-national information about the fertilizer~~ application ~~rate and date for green-up of winter wheat. Therefore, we allocated~~ in fall we extracted from USDA-ERS is smaller. Although some states, such as Iowa, applied a considerable proportion of annual N fertilizer ~~by strictly following the crop planting and harvest schedule of winter wheat~~input in fall, the N fertilizer use in fall is low in the entire US. In summary, our estimate of monthly NH_3 emission is generally consistent with other studies but with large inter-annual variations based on crop phenology survey.

4.2 Spatiotemporal change in the NH_3 emissions

The "V" shape of historical national and regional NH_3 emission factors mainly resulted from the changing preference in using different N fertilizer types~~.~~ (Cao et al., 2018). 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~~emission factor from the 1970s to the present was caused by the popularity of Urea-based fertilizer (Fig. 1b, Fig. 7, 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 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, the NH_3 emission factor varied substantially across the U.S., ranging from 2.5% to 29% (Fig. 4). We ~~find~~found the highest loss proportion (> 12%) in the Northern Great Plains and the Northwest. ~~We may be able to seek~~Adopting better N fertilizer management practices, such as ~~adopting appropriate~~appropriate application timing and method, is recommended 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 the 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). The conclusion drawn from our factorial contribution analysis shows that changes in cropland area and rotation have a minor influence on NH_3 emission in the nation (Fig. 7), which is primarily because N fertilizer input was kept constant at the level of 1960. Besides, the cropland area changes represent the summation of cropland expansion and abandonment across the country, resulting in a relatively small contribution to NH3 emission increases. 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~~contributed to the steep increase of NH_3 emission during this period (Fig. 2, Fig. 7). Even worse, the alkaline soil in the Northern Great Plains and the Northwest ~~leads~~led 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 regions (Lu et al., 2019) (Fig. 4). ~~High NH_3 emission can significantly degrade air quality and largely decrease crop NUE. Therefore~~Although soil acidification through long-term agricultural land use may offset the effects of the increasing use of urea-based fertilizer, more effective policies and agricultural management are still needed in those high NH_3 loss proportion regions~~.~~ (Veenstra and Lee, 2015; Dai et al., 2018), which can prevent air quality deterioration and enhance crop NUE. 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~~1930 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~~the largest 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~~a considerable amount of N fertilizer ~~use into fall and after planting~~at green-up for winter wheat, resulting in peaks in summer and ~~fall~~early spring. 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. The hotpots of NH_3 emission shifted from the central US to the Northern Great Plains and Minnesota (Fig. 3). 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~~was also driven by an advanced crop planting date. Due to the development of genotypes and improvement of agricultural management and equipment, the corn-planting date became earlier by approximately 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)~~(Duvick, 1989; 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 wet NH_4^+ deposition in recent decades (Abatzoglou and Williams, 2016). Our analysis indicated~~Our result shows 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).~~was significantly correlated to the increase of NH_4^+ wet deposition during 1985-2015 (Fig. 9). NH_4^+ deposition is highly affected by local NH_3 emissions because NH_3 volatilized into the atmosphere has a very short lifetime and deposits close to the source quickly. Therefore, In addition to growing forest fire and livestock numbers (Abatzoglou and Williams, 2016), our study reveals that NH_3 emissions from increasing N fertilizer use played an important role influencing the inter-annual variability of wet NH_4^+ deposition in the northwestern U.S. over recent decades. . 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 an 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 emissions may contribute to the $PM_{2.5}$ 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 level 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). Zhou et al (2015) developed a nonlinear Bayesian tree regression model as a function of N fertilizer rate to estimate NH_3 emission in China and found the estimates match well with observations and satellite-based products. Thus, we may underestimate NH_3 emissions under a high N fertilizer use rate. Another example is the use of nitrification and urease 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~~and urease inhibitor is likely to misrepresent NH_3 emissions. In addition, considering the bidirectional exchange process may improve the accuracy of seasonal NH_3 emission estimation (Bash et al., 2013). However, our work builds upon the newly-developed N fertilizer management and crop phenology dataset that combines crop-specific N fertilizer use rate, fertilizer type, application timing, application method, and phenology for each state ranging from 1900 to 2015. The REML model we are using makes sufficiently use of these information and provides higher levels of details over space and time.

5 Conclusion

This study comprehensively examined the spatiotemporal patterns of NH_3 emission owing to ~~historical~~the changes in temperature, cropland ~~expansion~~area, rotation, 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~~641 Gg N yr^{-1} in 2015, among which corn and spring wheat are the major contributors. In addition, ~~increasing~~enhanced 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~~Springtime warming, cropland expansion, and N fertilizer management ~~practice changes~~practices change also altered the seasonal pattern of NH_3 emission in the U.S., shifting the peak emission month from

~~June~~May to April since the ~~1960s~~1930s. 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~~comprehensively assessing the 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).

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.

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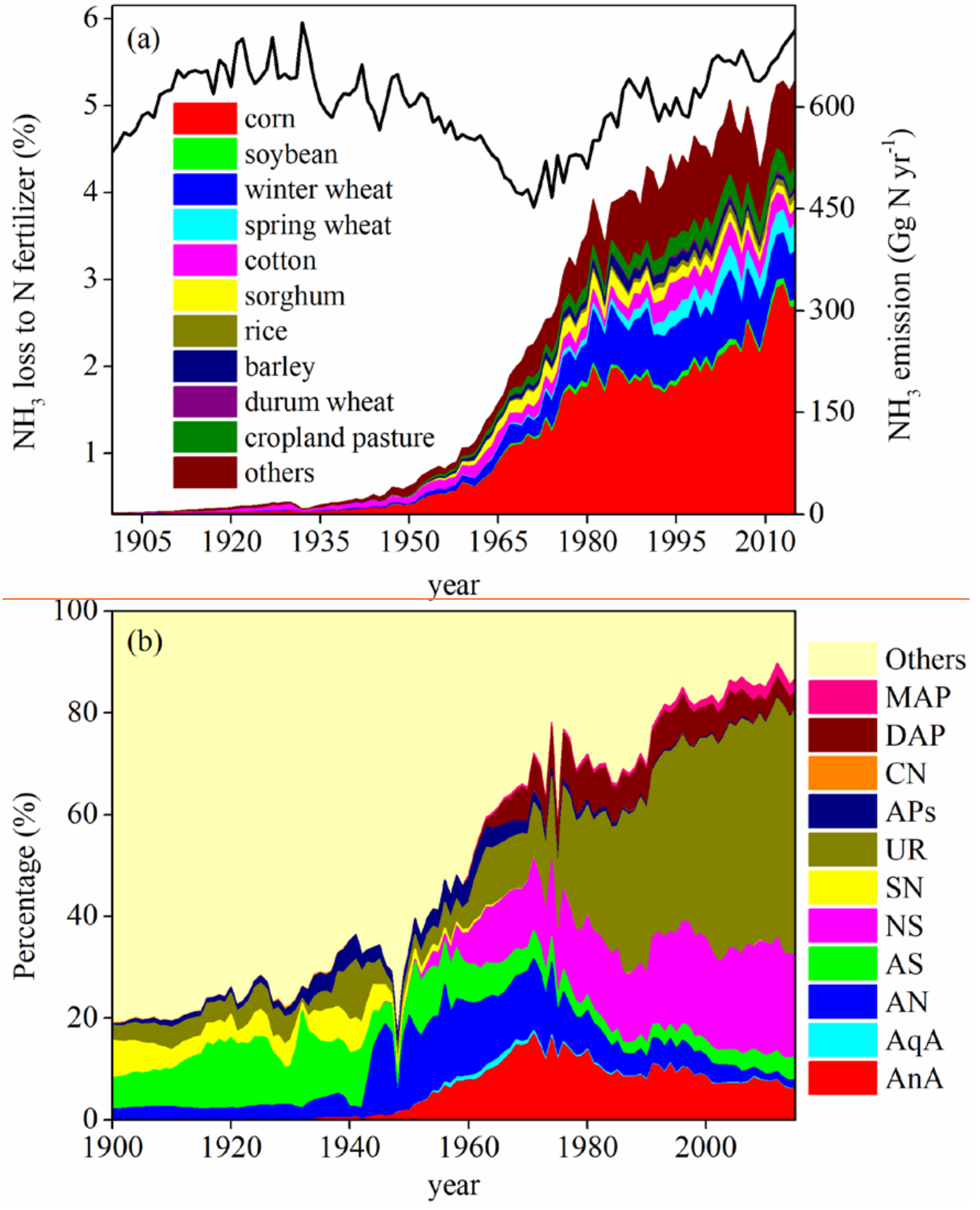
Table 1. Experiments designed in this study

Experiments	Abbr	Tem	Distribution	Rotation	Nfer rate	Nfer type
Tem only	S1	1960-2015	1960	1960	1960	1960
Tem + Dis	S2	1960-2015	1960-2015	1960	1960	1960
Tem + Dis + Rot	S3	1960-2015	1960-2015	1960-2015	1960	1960
Tem + Dis + Rot + Nfer rate	S4	1960-2015	1960-2015	1960-2015	1960-2015	1960
Tem + Dis + Rot + Nfer rate + Nfer type	S5	1960-2015	1960-2015	1960-2015	1960-2015	1960-2015

Note: Tem refers to temperature, Dis refers to cropland distribution, Rot refers to Rotation, Nfer rate refers to N fertilizer use rate, Nfer type refers to N fertilizer type. S5 allows all the factors to change through the study period, and provides the major results of this study


(a)
corn
soybean
winter wheat
spring wheat
cotton
sorghum
rice
barley
durum wheat
cropland pasture
others
NH_3 loss to N fertilizer (%)
NH_3 emission (Gg N yr^{-1})
year
(b)
Others
MAP
DAP
CN
APs
UR
SN
NS
AS
AN
AqA
AnA
Percentage (%)
year

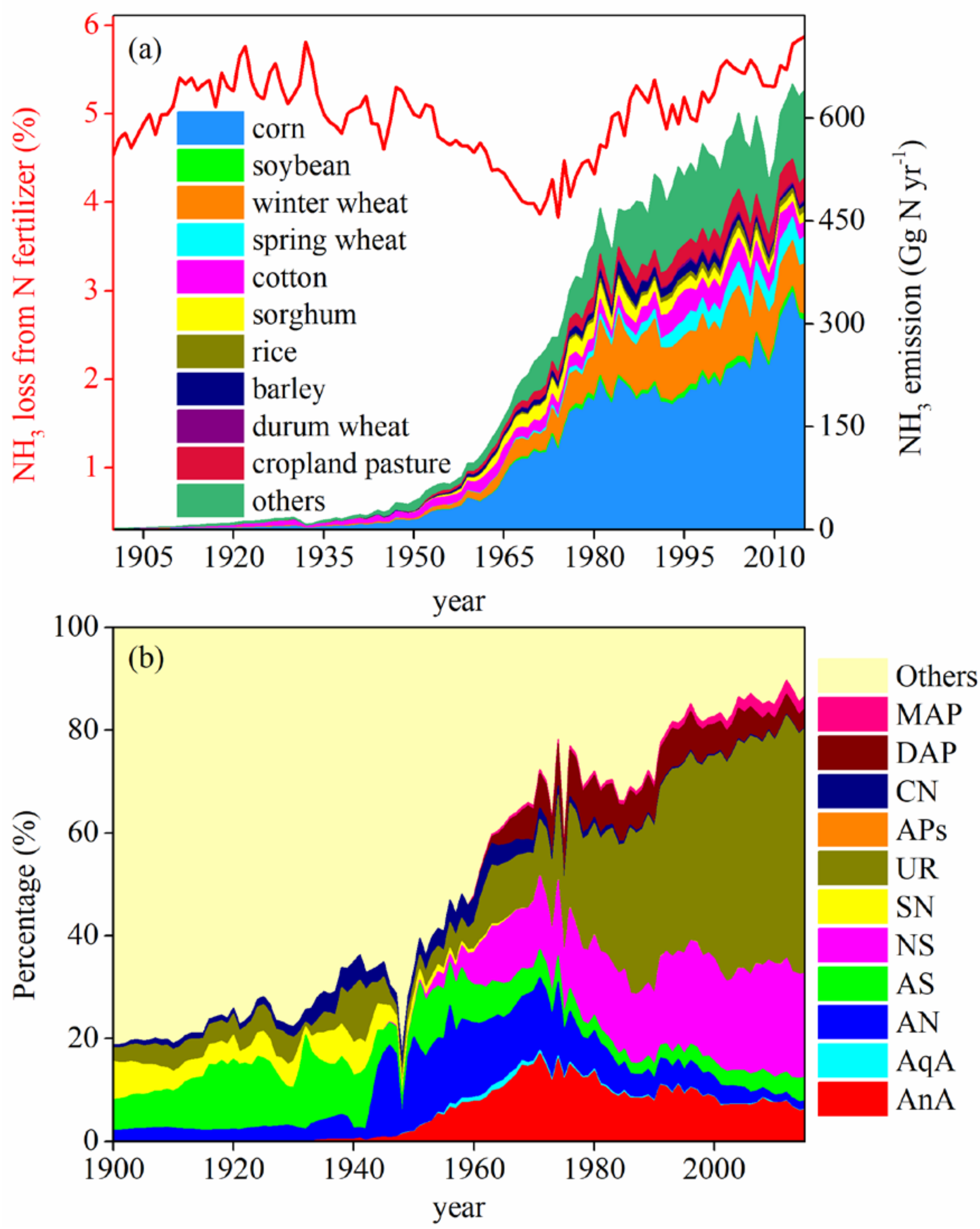
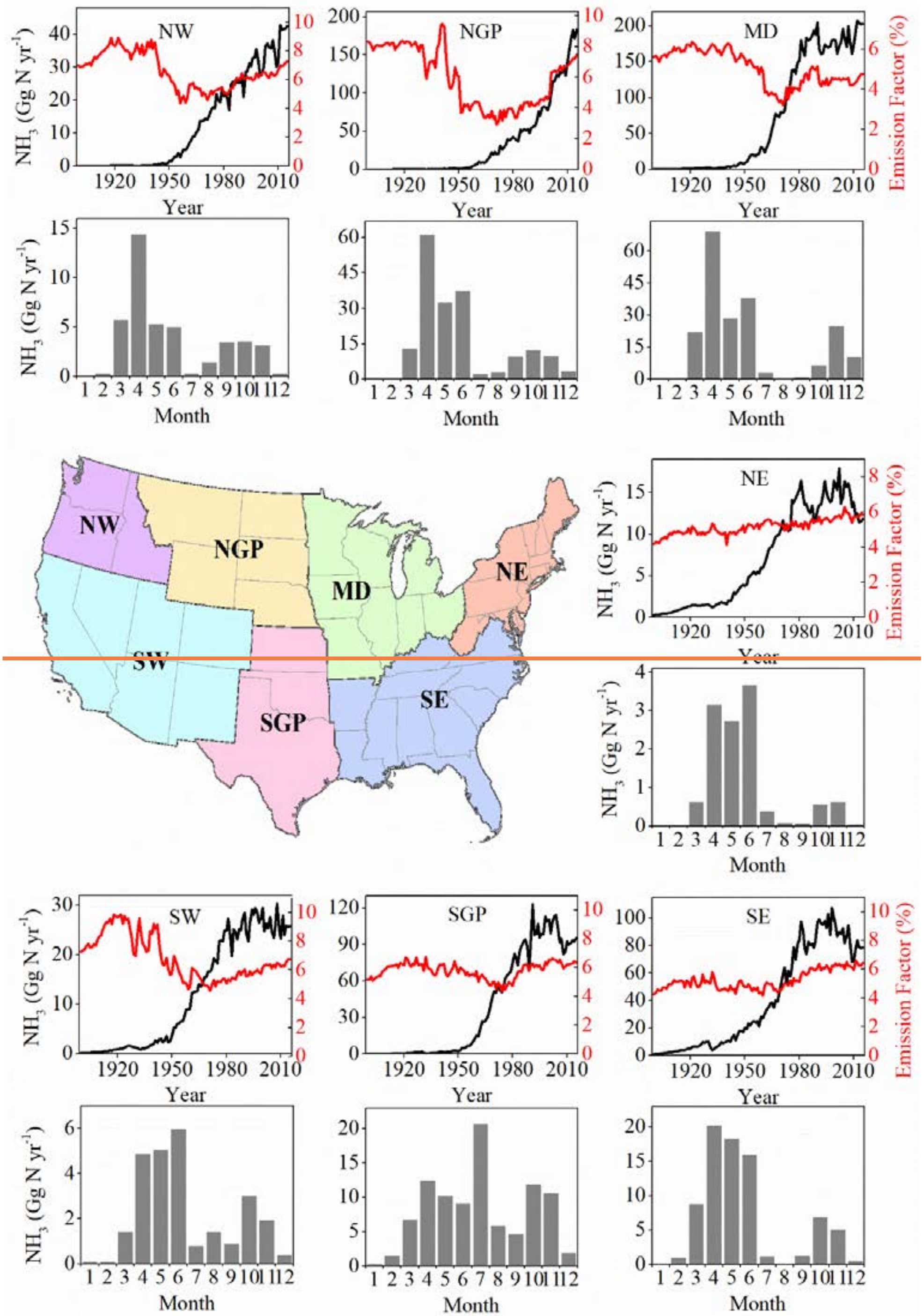


Figure 1. Contributions of major crop types and N fertilizer types to historical NH_3 emissions since 1900. (a) Crop specific NH_3 emissions, (b) Relative contributions of 12 major N fertilizer types to annual total NH_3 emission. Solid line in (a) refers to the NH_3 loss percentage to total N fertilizer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


NW
NGP
MD
NE
SW
SGP
SE
NH$_3$ (Gg N yr^{-1})
Emission Factor (%)
Year
Month

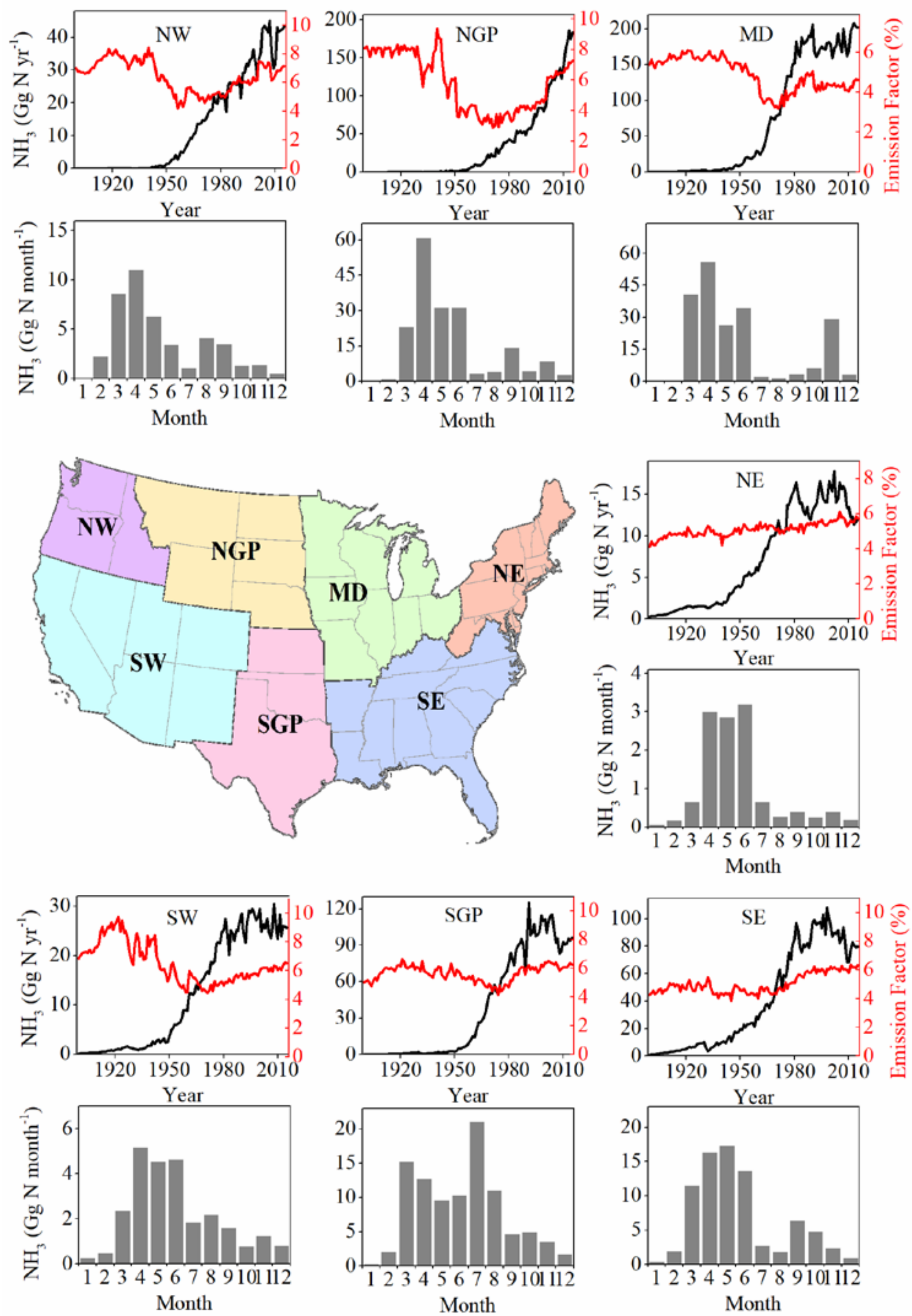
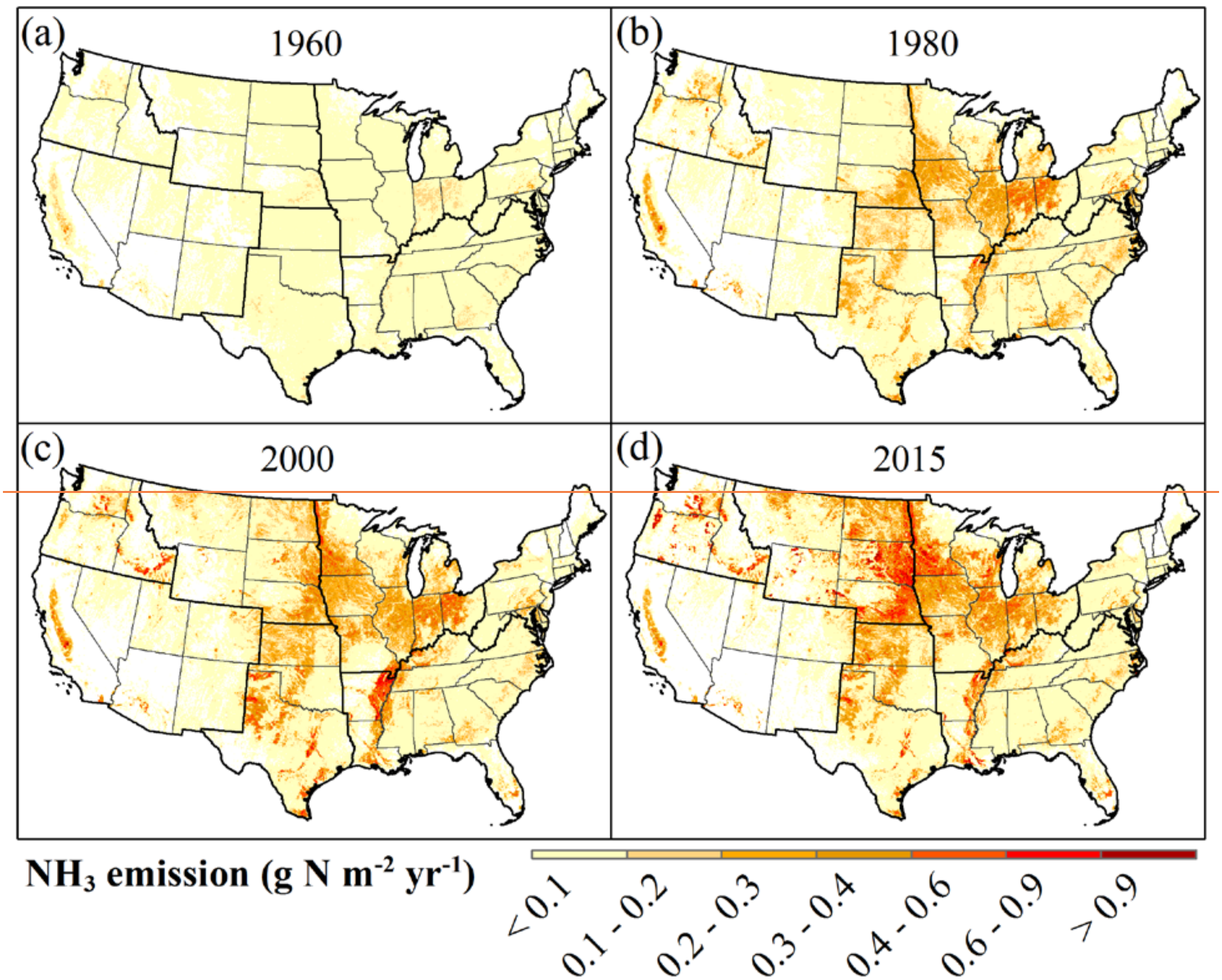


Figure 2. Temporal and monthly pattern of NH_3 emissions in seven regions of the United States. The seven regions include the Northwest (NW), the Northern Great Plains (NGP), the Midwest (MD), the Northeast (NE), the Southwest (SW), the Southern

Great Plains (SGP), and the Southeast (SE). **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.**



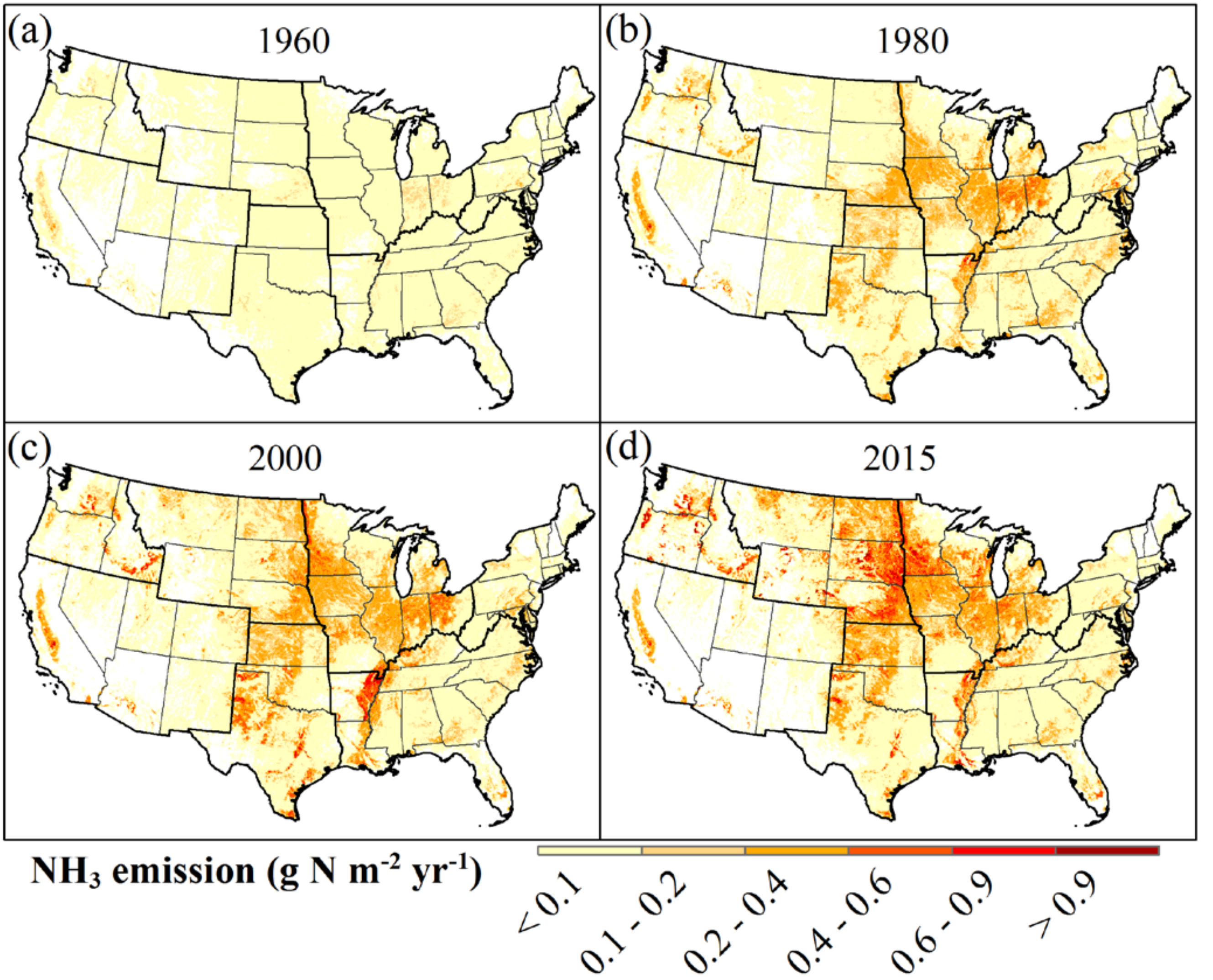
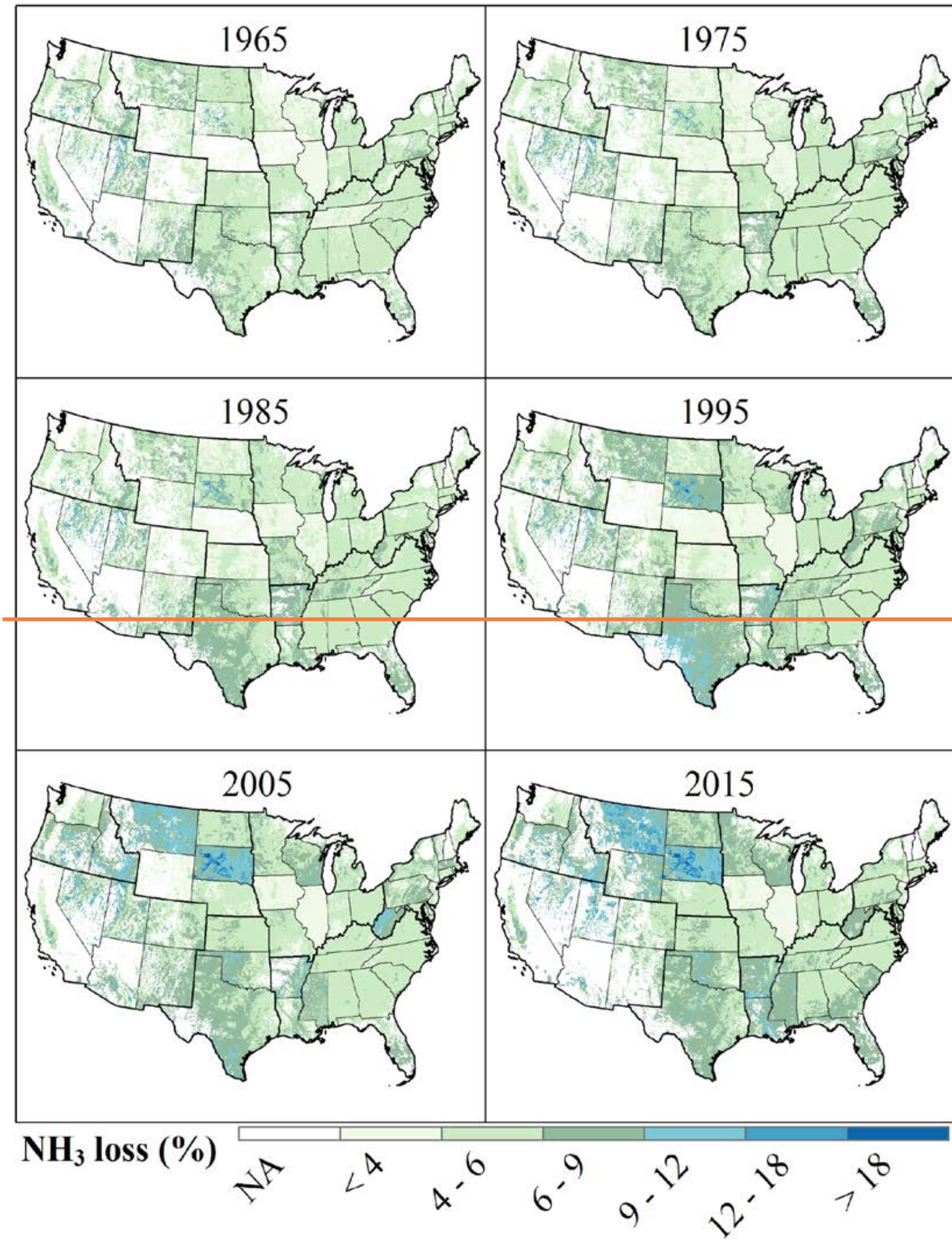


Figure 3. Spatial distribution of NH_3 emissions in the U.S. from 1960 to 2015. Values represent NH_3 emission from synthetic N fertilizer applied over all crops in each 5 km by 5 km grid cell.


1965
1975
1985
1995
2005
2015
NH₃ loss (%)
NA
< 4
4 - 6
6 - 9
9 - 12
12 - 18
> 18

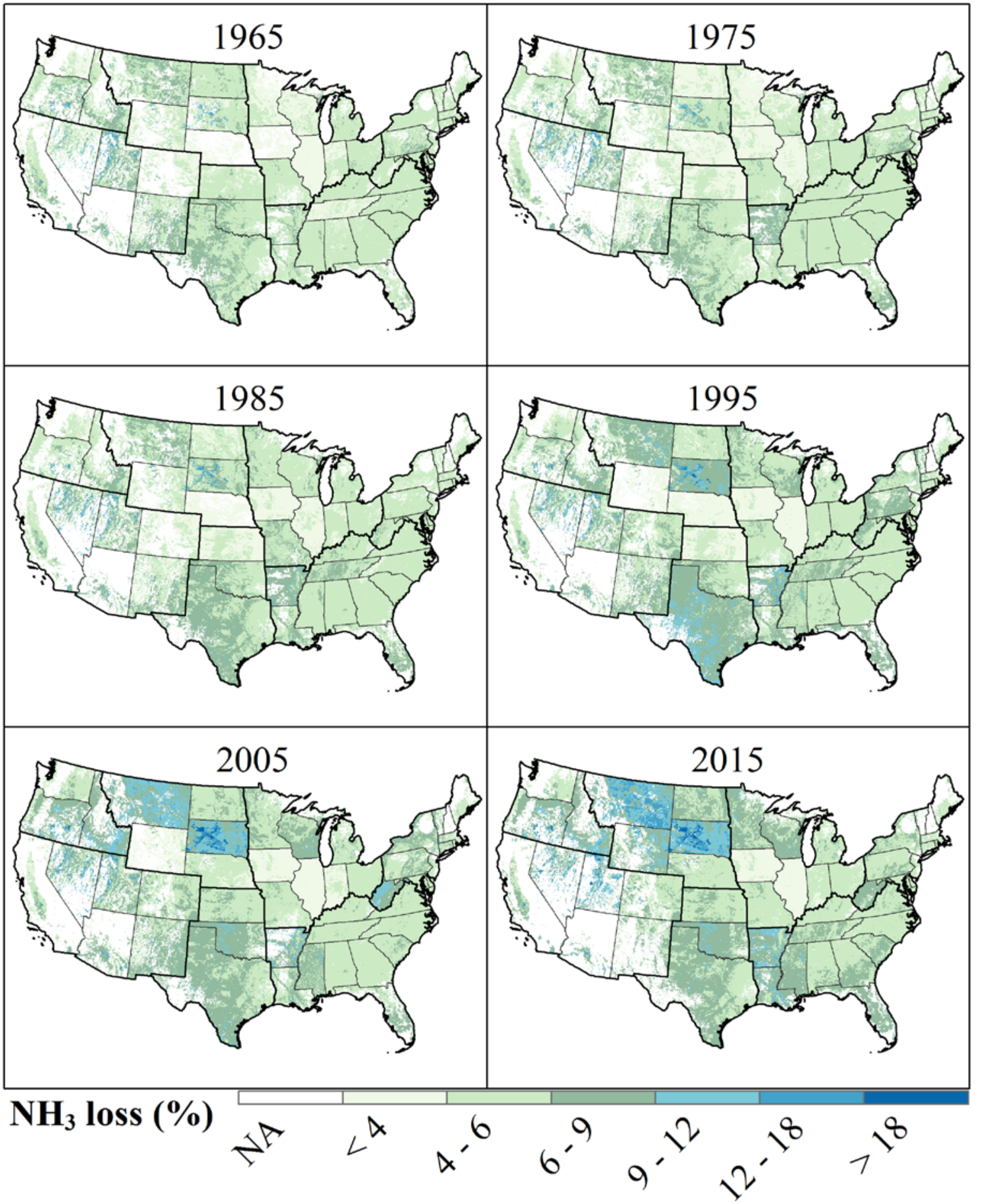
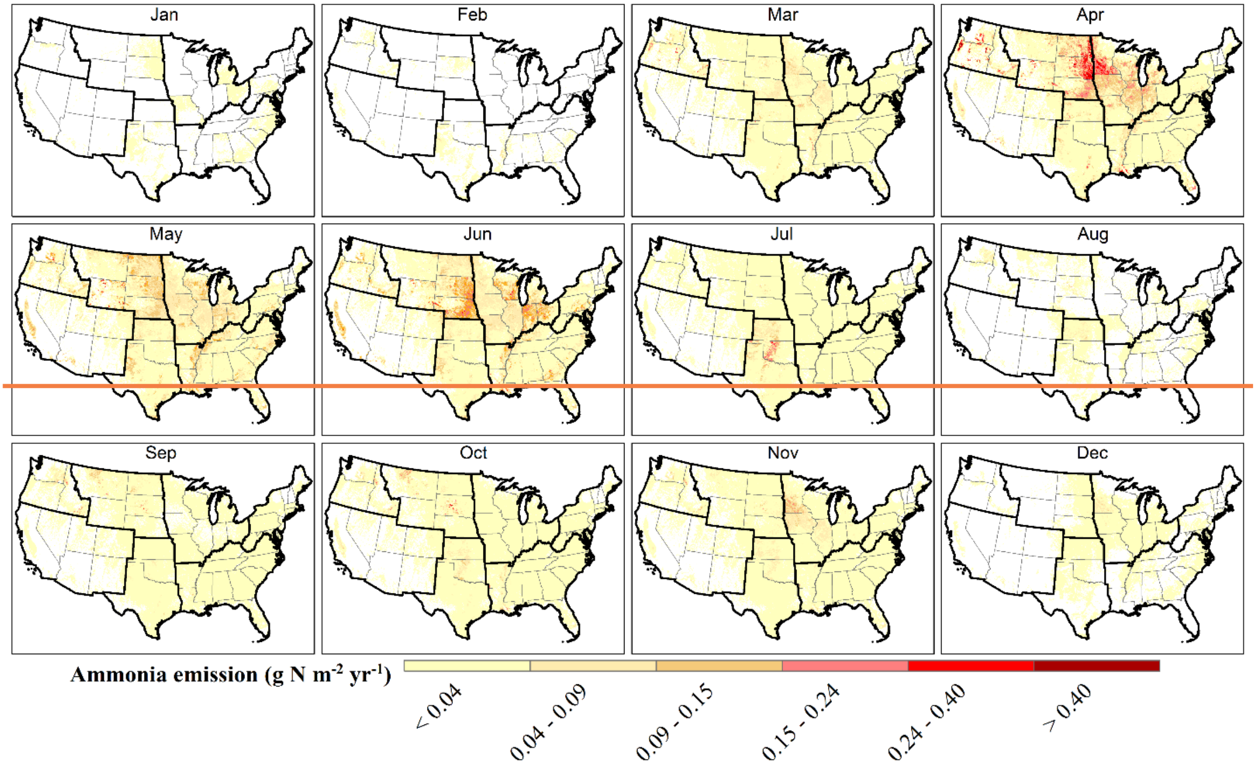


Figure 4. Spatial and temporal patterns in NH_3 loss proportion relative to total N fertilizer input in the U.S. (the middle year of each decade is selected as an example).


Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Ammonia emission (g N m^{-2} yr^{-1})
< 0.04
0.04 - 0.09
0.09 - 0.15
0.15 - 0.24
0.24 - 0.40
> 0.40

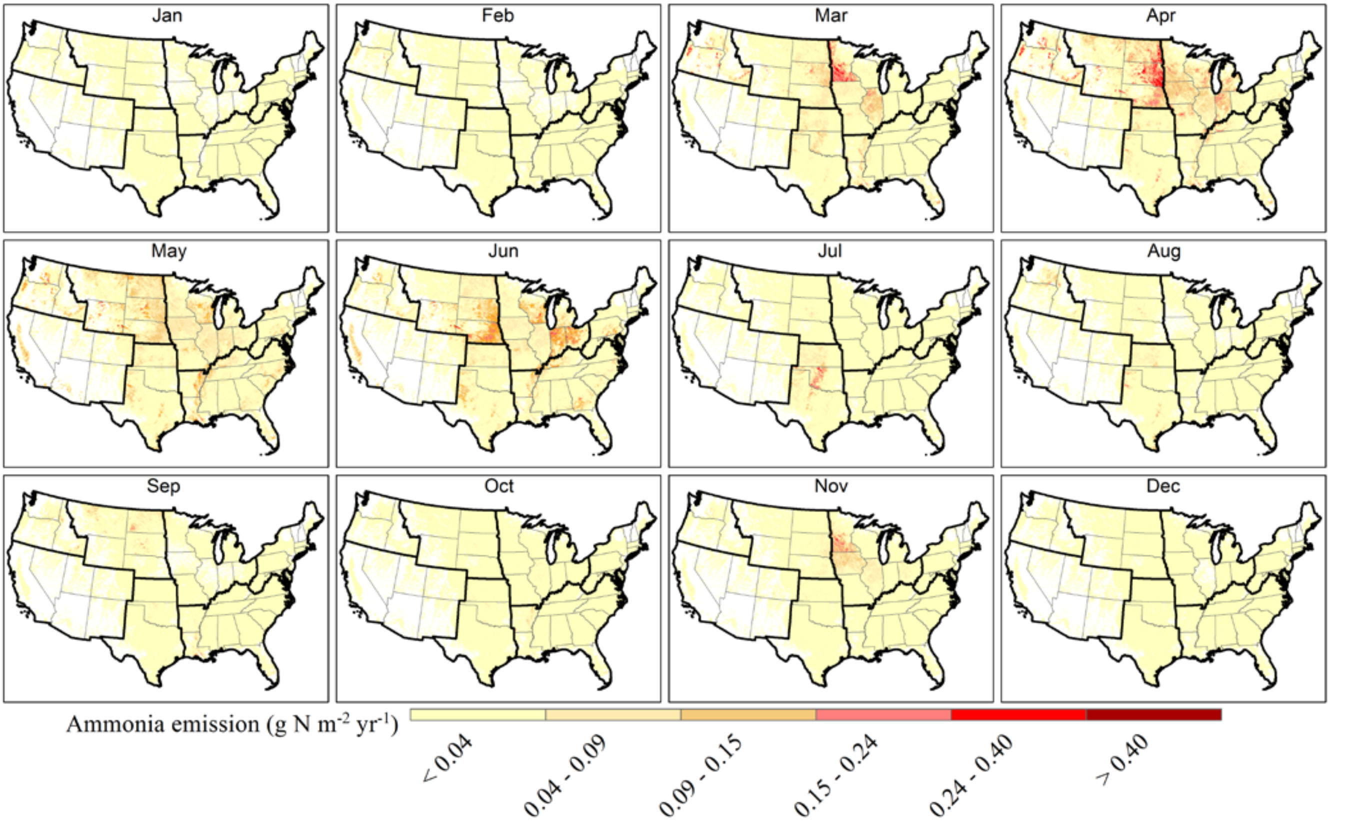
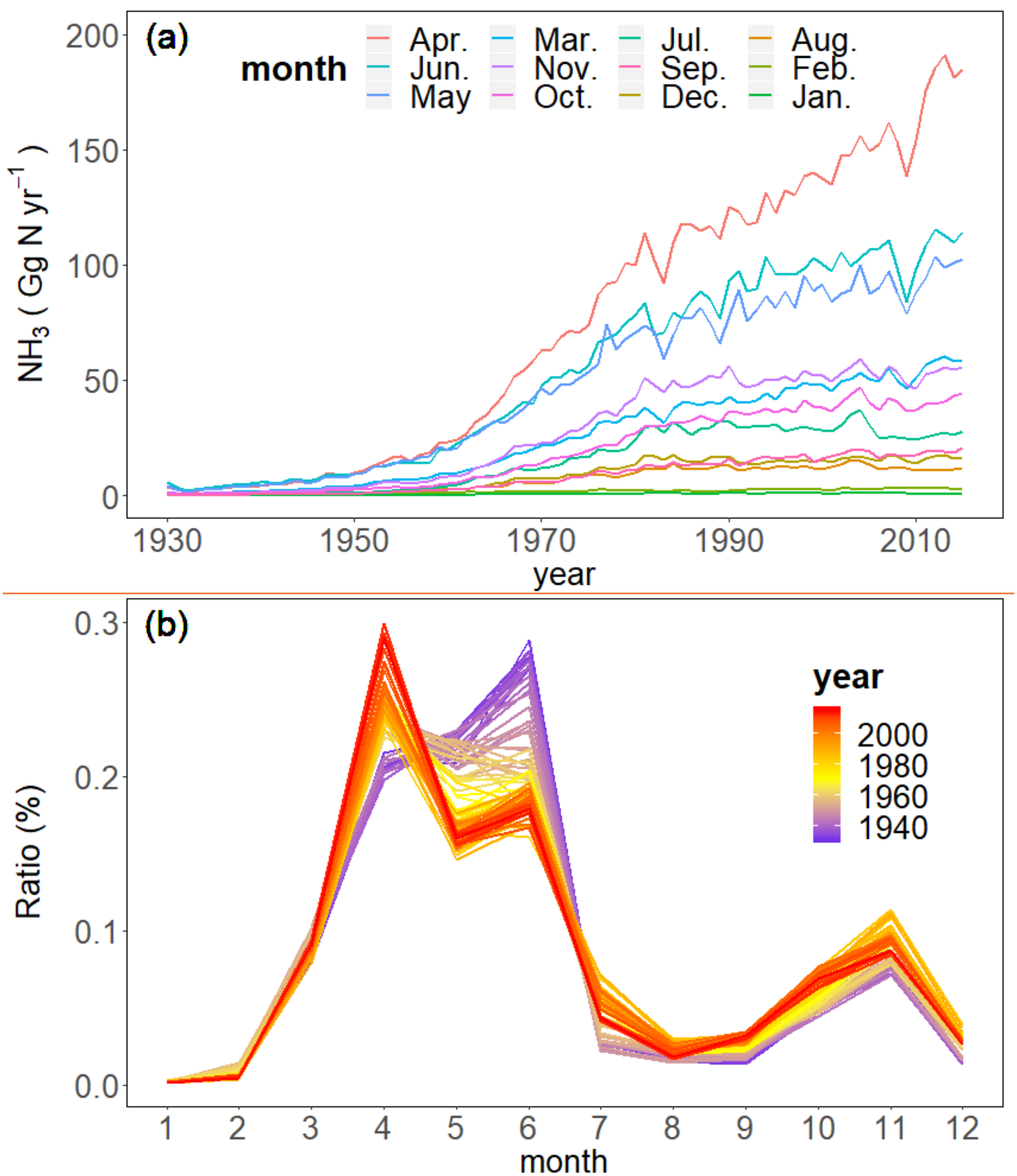


Figure 5. Spatial distribution of monthly estimated NH_3 emission across the U.S in 2015.


(a)
month
Apr.
Jun.
May
Mar.
Nov.
Oct.
Jul.
Sep.
Dec.
Aug.
Feb.
Jan.
NH3 (Gg N yr-1)
0
50
100
150
200
1930
1950
1970
1990
2010
year
(b)
year
2000
1980
1960
1940
Ratio (%)
0.0
0.1
0.2
0.3
1
2
3
4
5
6
7
8
9
10
11
12
month

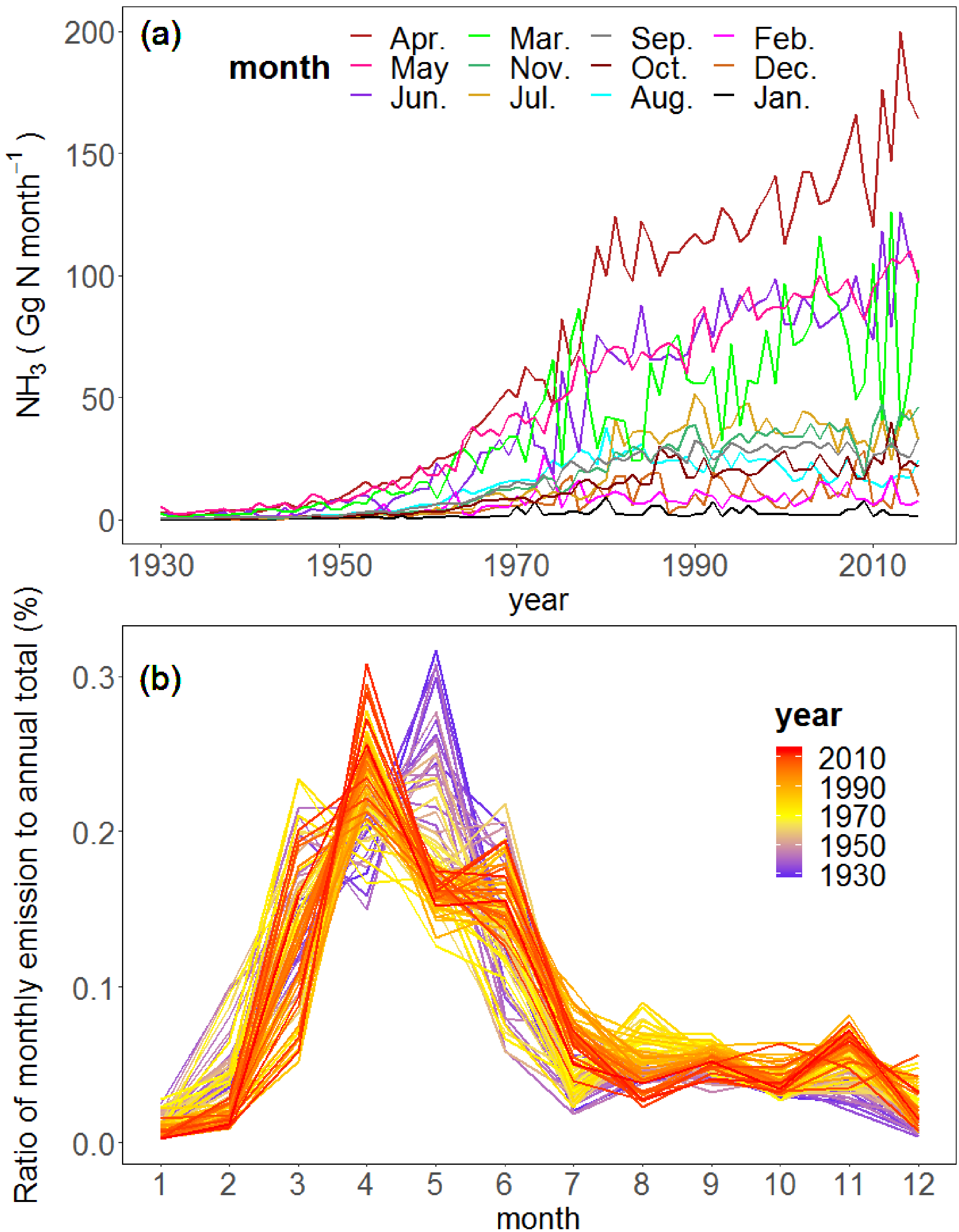
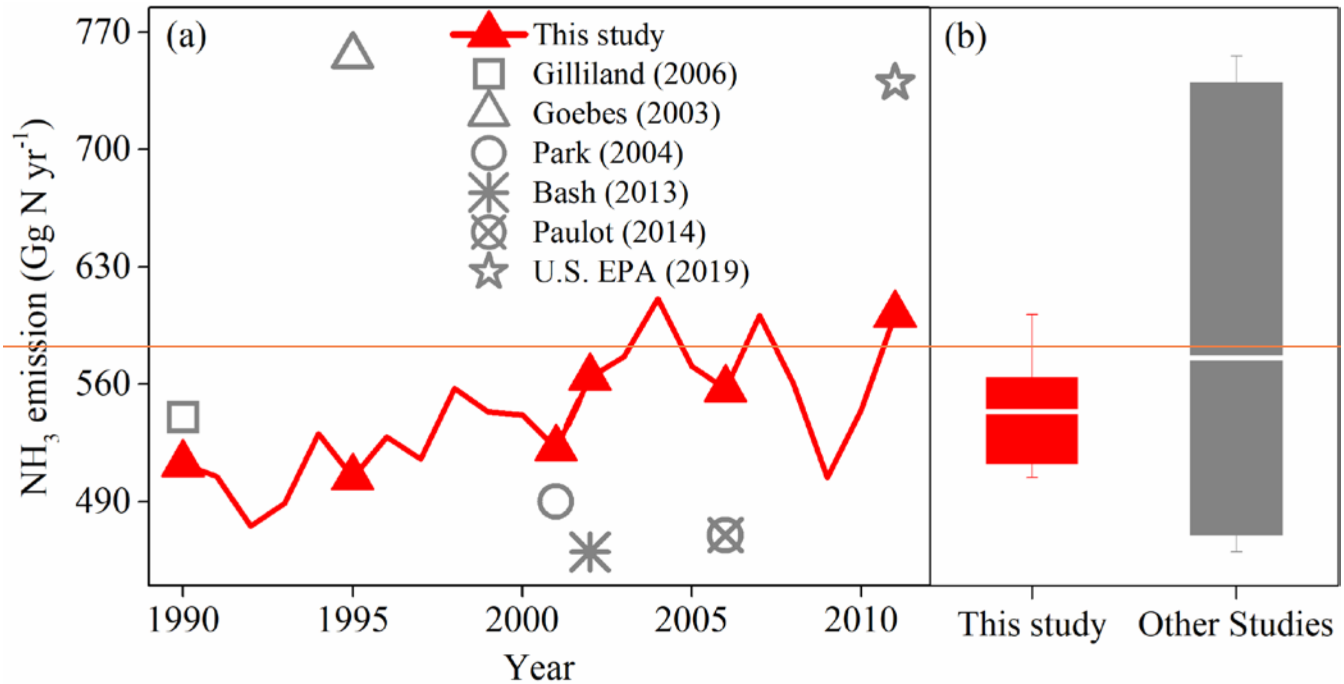
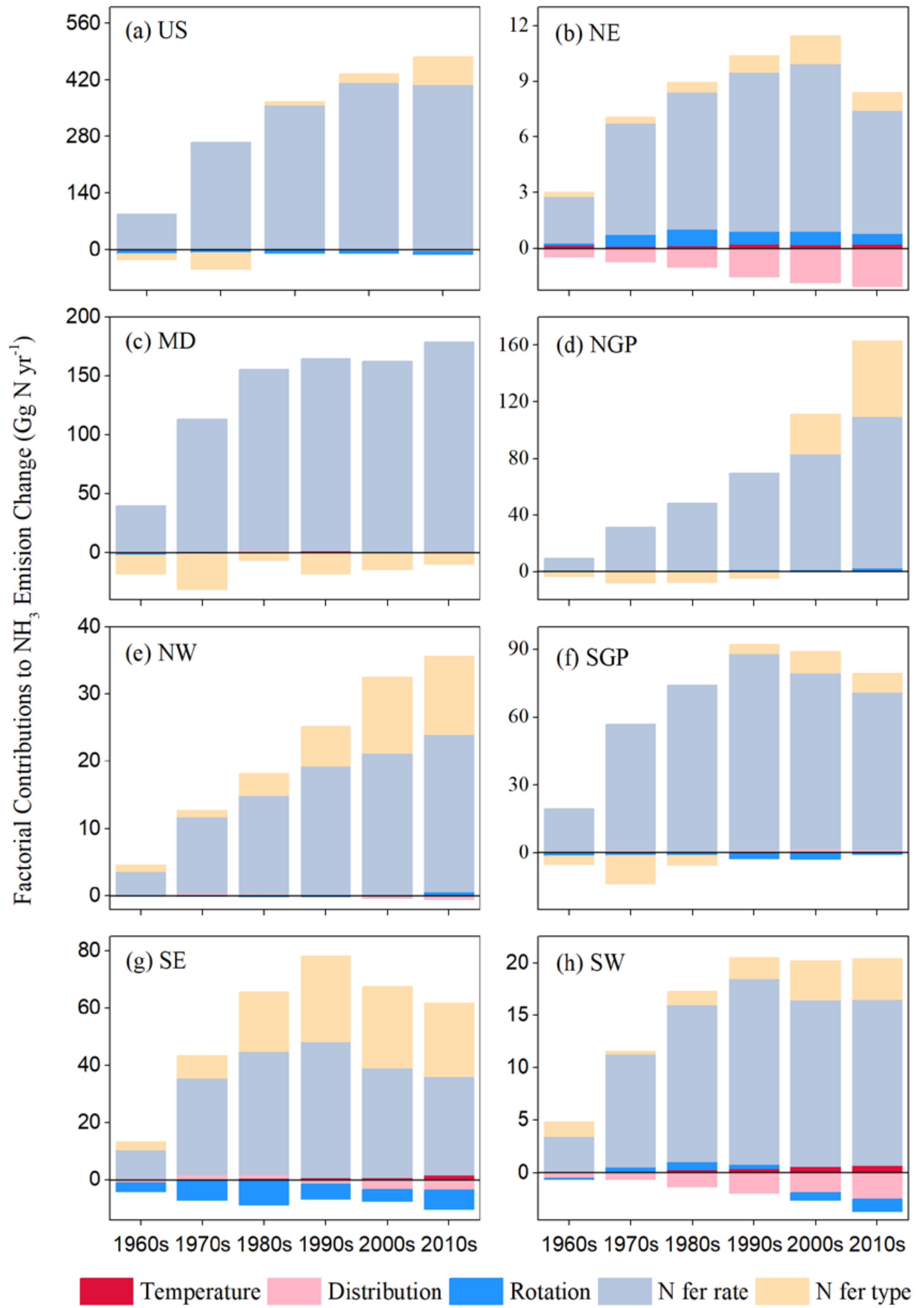

(a)
month
Apr.
May
Jun.
Mar.
Nov.
Jul.
Sep.
Oct.
Aug.
Feb.
Dec.
Jan.
NH3 (Gg N month-1)
200
150
100
50
0
1930
1950
1970
1990
2010
year
(b)
year
2010
1990
1970
1950
1930
Ratio of monthly emission to annual total (%)
0.3
0.2
0.1
0.0
1
2
3
4
5
6
7
8
9
10
11
12
month

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.





(a) US
(b) NE
(c) MD
(d) NGP
(e) NW
(f) SGP
(g) SE
(h) SW
Factorial Contributions to NH_3 Emision Change (Gg N yr^{-1})
1960s 1970s 1980s 1990s 2000s 2010s
Temperature
Distribution
Rotation
N fer rate
N fer type

Figure 7. **Decadal-average factorial contributions of temperature, cropland distribution, cropland rotation, N fertilizer use rate, and N fertilizer type to NH_3 emission change in the contiguous US and seven sub-regions. The seven sub-regions are the Northeast (NE), the Midwest (MD), the Northern Great Plains (NGP), the Northwest (NW), the Southern Great Plains (SGP), the Southeast (SE), and the Southwest (SW).**

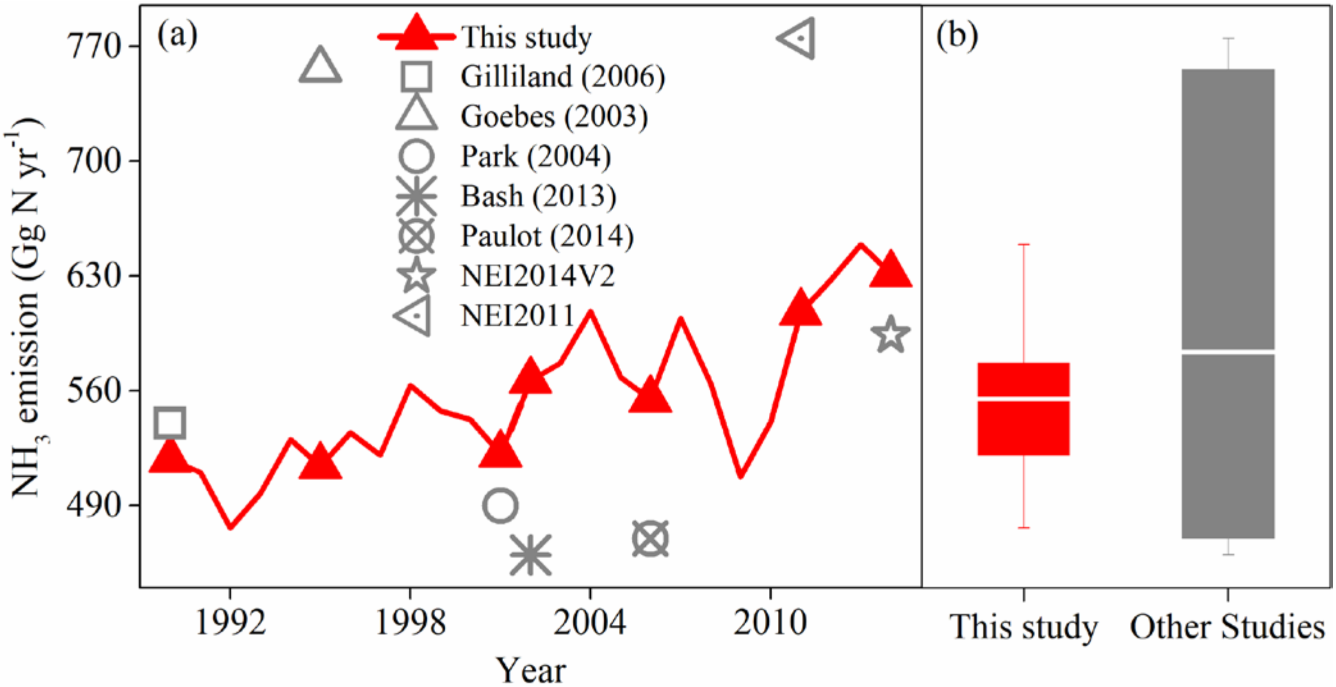


Figure 8. Comparison of annual NH_3 ~~emissions.~~emission estimates between this study and others. (a) Paired comparison between our result and individual research, (b) Boxes include 25-75% of NH_3 emission of all chosen years estimated by our ~~studies~~study and other studies, respectively~~, white~~. White lines are mean values, and whiskers ~~comprise te whole~~represent the min-max range of data. NH_3 emission estimated by Paulot et al. (2014) represents the average of 2005-2008, against which we compared ~~their~~our estimate ~~against our result~~ of 2006.

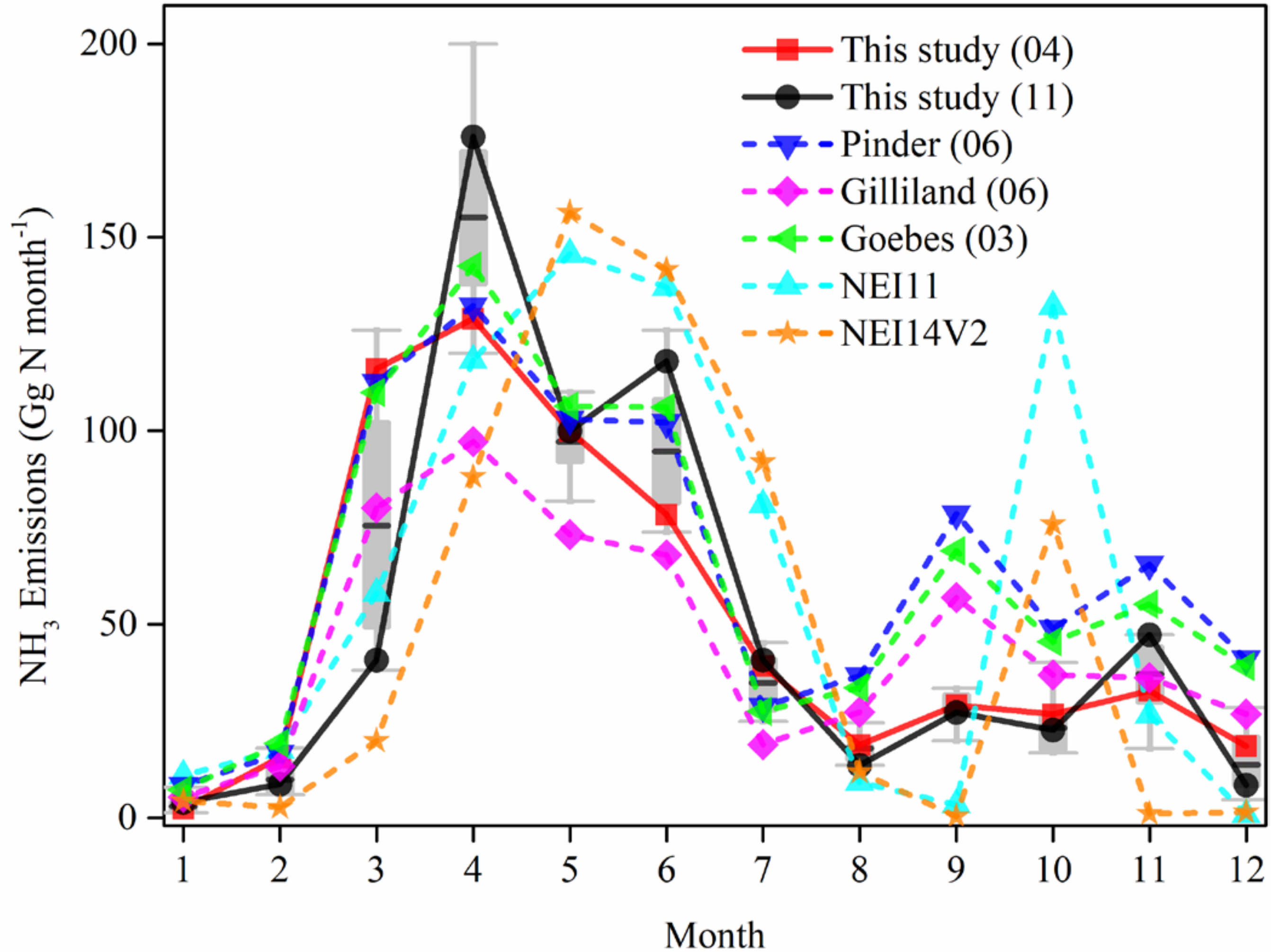
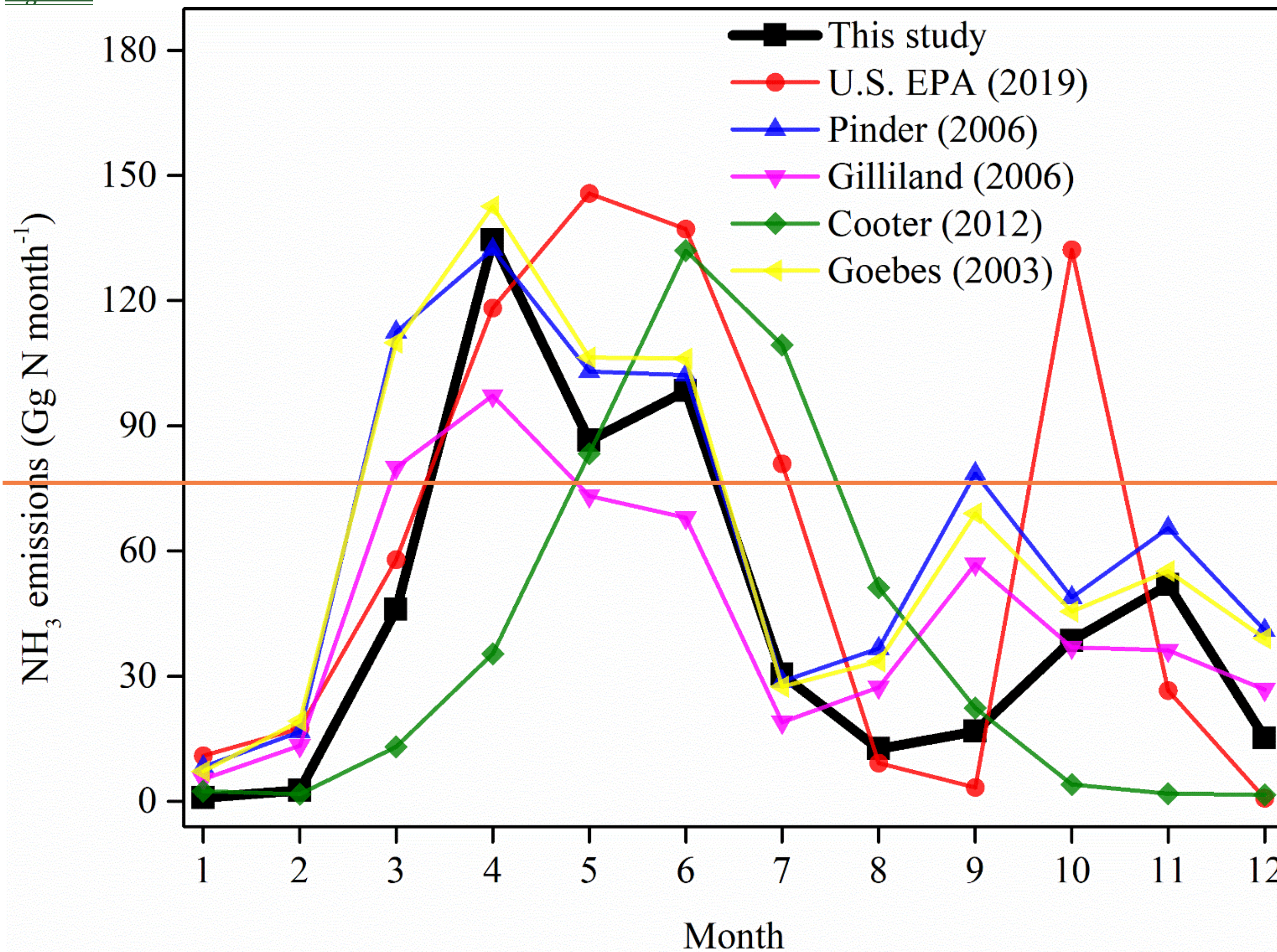
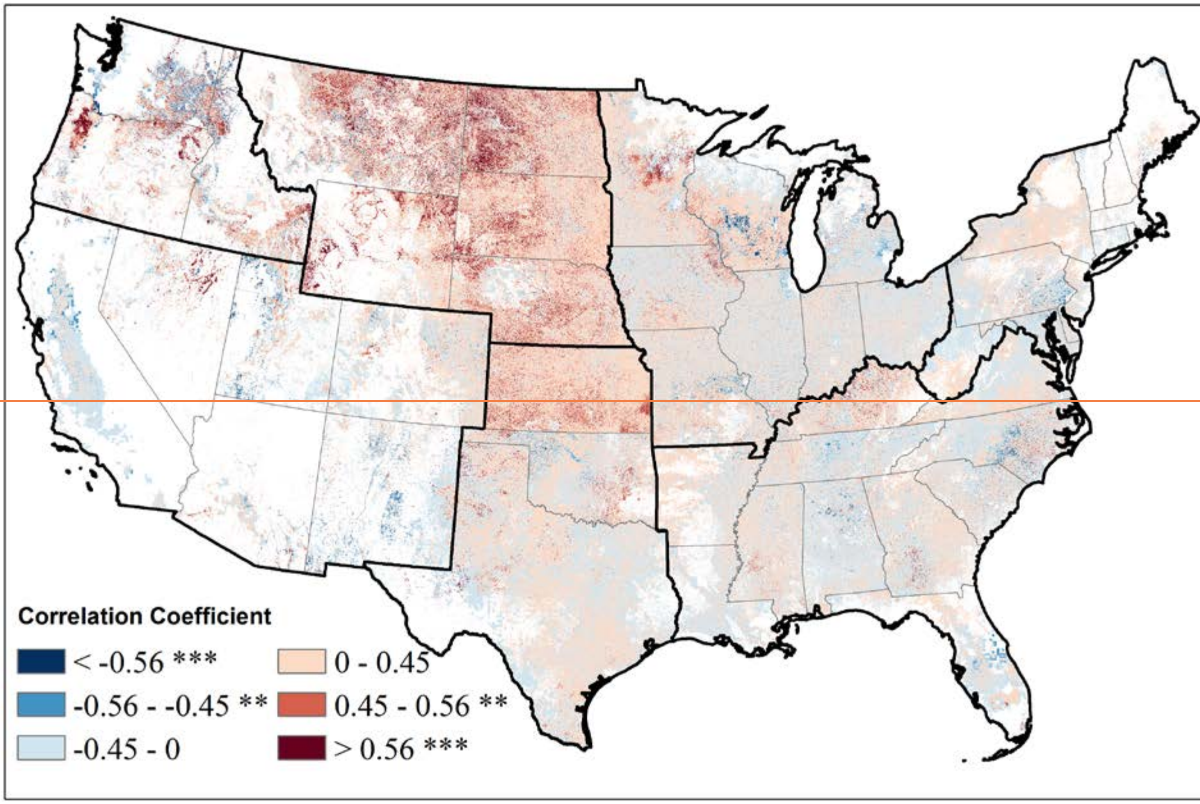

This study (04)
This study (11)
Pinder (06)
Gilliland (06)
Goebes (03)
NEI11
NEI14V2
NH3 Emissions (Gg N month-1)
Month
0
50
100
150
200
1
2
3
4
5
6
7
8
9
10
11
12

Figure 9.



~~Figure 8.~~ **Comparison of monthly NH_3 emission patterns between our estimate and other studies.** Two typical monthly patters of NH_3 emission in this study were used. The estimate of 2004 represents the pattern when planting date is early, whereas the simulation of 2011 stands for the pattern when planting date is delayed. Two simulations using different approaches by EPA-NEI were chosen in the comparison. Grey boxes include 25-75% of monthly NH_3 emissions during 2005-2015, black lines are mean values, and whiskers comprise the whole range of data.


Correlation Coefficient
< -0.56 ***
-0.56 - -0.45 **
-0.45 - 0
0 - 0.45
0.45 - 0.56 **
> 0.56 ***

~~Figure 9.~~

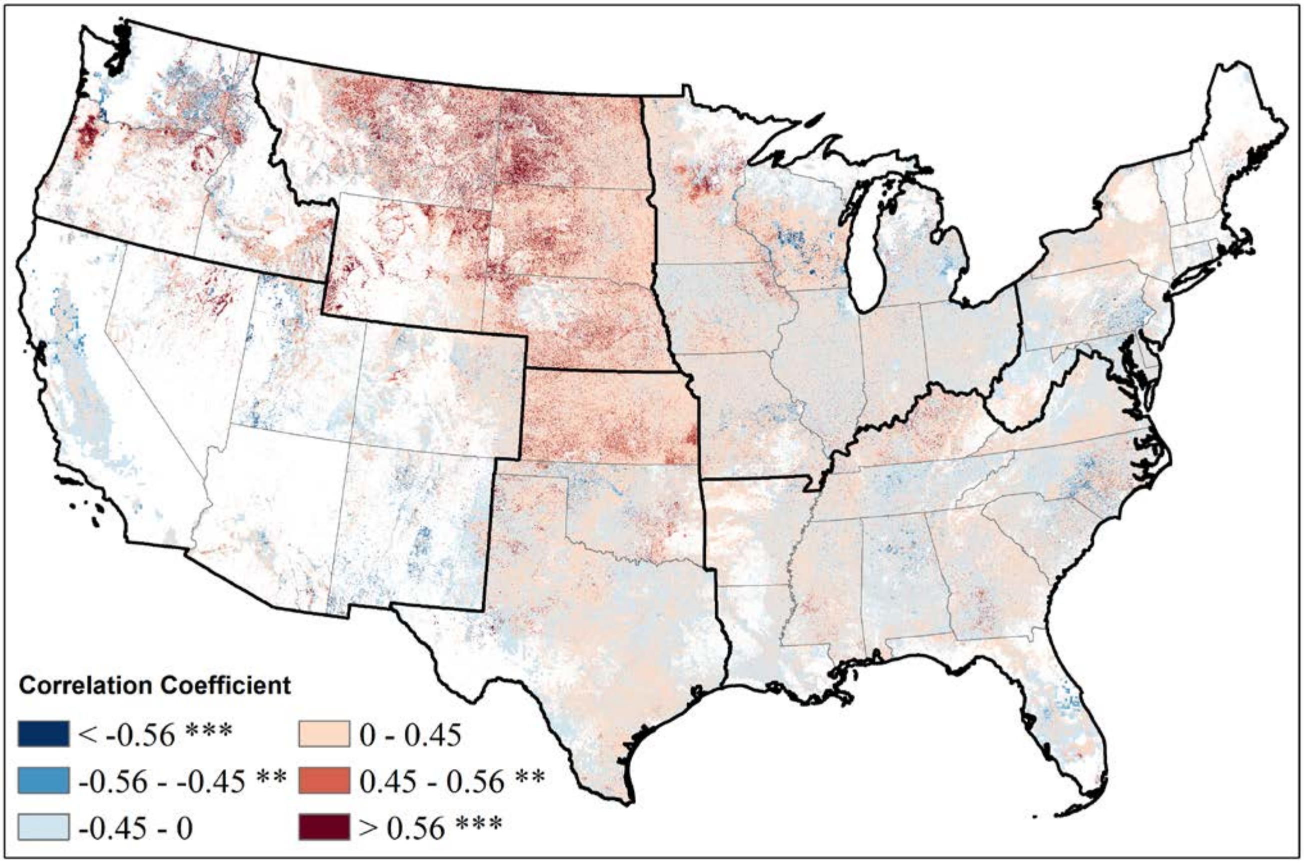


Figure 10. Correlation coefficient between NH_3 emission from N fertilizer uses and wet NH_4^+ deposition between 1985 and 2015. The correlation coefficient was calculated between the two time series at each 1km × 1km grid cell. ** refers to P-value < 0.01, * refers to P-value < 0.001.**