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Supplement of

Northwestward cropland expansion and growing urea-based fertilizer use enhanced NH_3 emission loss in the contiguous United States

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Supplement

This Supplement includes the followings:
1) REML model parameters.
2) Example of allocating annual N fertilizer use rate to monthly application
3) Difference of NH_3 loss proportion of each month between two periods: 1965-1980 and 2000-2015
4) Contributions of crop type to annual NH_3 emission
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8) Changing rate of planted area of non-legume crops between two periods of 1960-1980 and 1995-2015 in each state.
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10) Correlation coefficient between spring NH_3 emission and deposited NH_4^+ concentration

1 REML model parameters

By considering multiple factors summarized from 1667 NH_3 emission measurements in 148 studies, Bouwman et al. (2002) developed a residual maximum likelihood (REML) model. In the model, six factors were finally incorporated, which are crop type, fertilizer type, application method, soil pH, soil CEC, and temperature. To quantify the effects of various factors on NH_3 emission, functional grouping were used (Table S1). The factor class values for different factors determined by the REML model were based on the stepwise regression technique (Table S1).

Table 1. Factors and their corresponding values in the REML model (Bouwman et al., 2002).

Factor		Value
Crop type	Upland crops	-0.045
	Cropland pasture	-0.158
	Rice	0
Fertilizer type	Anhydrous ammonia	-1.151
	Aqua ammonia	-1.151
	Ammonium nitrate	-0.35
	Ammonium sulfate	0.429
	Nitrogen solution	-0.748
	Sodium nitrate	-1.585
	Urea	0.666
	Ammonium phosphates	0.014
	Calcium nitrate	-1.585
	Diammonium phosphate	0.065
	Monoammonium phosphate	0.065
	Others	0.014
Application method	Broadcast	-1.305
	Incorporate	-1.895
	solution	-1.282
	Broadcast and then flooded	-1.844
	Incorporate and then flooded	-1.844
Soil pH	≤ 5.5	-1.072
	5.5 - 7.3	-0.933
	7.3 - 8.5	-0.608
	> 8.5	0
Soil CEC	≤ 16	0.088
	16 - 24	0.012
	24 - 32	0.163
	> 32	0
Temperature	≤ 20 ^oC	-0.402
	> 20 ^oC	0

2 Example of allocating annual N fertilizer use rate to monthly application

We split the annual N fertilizer use rate into four application timings (i.e., fall application after previous year harvesting, before planting, at planting, and after planting) based on the USDA-AMRS survey. The date of application timing is identified by the fractional acreage completion of a given crop phenological development according to the USDA-NASS (2018) crop progress report, which is represented by a span of period with planting, green-up, or harvesting areas increasing from 5% to 95%. Here, we take N fertilizer use of corn in Iowa as an example.

Split annual N fertilizer use into four application timings*:* According to the survey, corn farmers in Iowa applied 39.8% (6.04 g N m^{-2}) of annual N fertilizer in the fall of 2014. Whereas 46.2% (7.01 g N m^{-2}), 3.4% (0.52 g N m^{-2}), and 10.5% (1.6 g N m^{-2}) of N fertilizer were applied in spring before planting, at planting, and after planting of 2015, respectively (Table S2).

Split at-plant N fertilizer application into the days of planting period: The USDA-NASS (2018) survey shows that 5%, 15%, 85%, and 95% of corn fields in Iowa were planted on April 19, April 25, May 18, and May 26. Whereas the harvested area of 5%, 15%, 85%, and 95% were reached on September 21, October 5, November 9, and November 21. While the period between April 25 and May 18 is the most active planting period, the other two periods (i.e., April 19-April 25 and May 18-May 26) account for 10% of area each with planting completion. Therefore, we assumed that 80% of N fertilizer use at planting (i.e., 0.42 g N m^{-2}) was applied during the period between April 25 and May 17, and that the rest 20% (0.05 g N m^{-2}) was applied to the other two planting periods. We assumed that N fertilizer split into each period is then evenly allocated to every day within the corresponding period by dividing N fertilizer use rate by the number of days (Table S2).

Similar strategy for before-, after-planting, and fall fertilizer application: We assumed that spring fertilizer application before planting and after planting have the same duration as planting but are one month earlier and later than planting, respectively. Likewise, fall application in 2014 has split fall N fertilizer amount into the same number of days as harvesting period (indicated by harvesting date with 5%, 15%, 85%, and 95% of area completion) but one month later. Thus, we spread the annual N fertilizer use rate of corn in Iowa over the active application days in a given year (Fig. S1). By summing up the daily application to the corresponding month, we generated the N fertilize use rate of each month in that year (Fig S1).

Table S2. Temporal allocation of annual N fertilizer use rate (g N m^{-2}) to daily application based on application timing and crop phenological development completion.

Annual	Four timings	Completion periods	Daily	Application periods
		0.7	0.12	**SPB** (Mar.19-Mar.24)
	7.01	5.61	0.23	**SPA** (Mar.25-Apr.17)
		0.7	0.08	**SPE** (Apr.18-Apr.26)
15.17		0.05	0.01	**PLB** (Apr.19-Apr.24)
	0.52	0.42	0.02	**PLA** (Apr.25-May.17)
		0.05	0.01	**PLE** (May.18-May.26)
	1.6	0.16	0.03	**APB** (May.19-May.24)

		1.28	0.05	**APA** (May.25-Jun.17)
		0.16	0.02	**APE** (Jun.18-Jun.26)
		0.6	0.04	**FLB** (Oct.21-Nov.4)
	6.04	4.84	0.14	**FLA** (Nov.5-Dec.8)
		0.6	0.05	**FLE** (Dec.9-Dec.21)

Note: SP refers to before planting in Spring, PL refers to at planting, AP refers to after planting, and FL refers to after harvesting in fall of previous year. The letters, B, A, and E, in the end of four timings refer to begin, active, and end respectively.

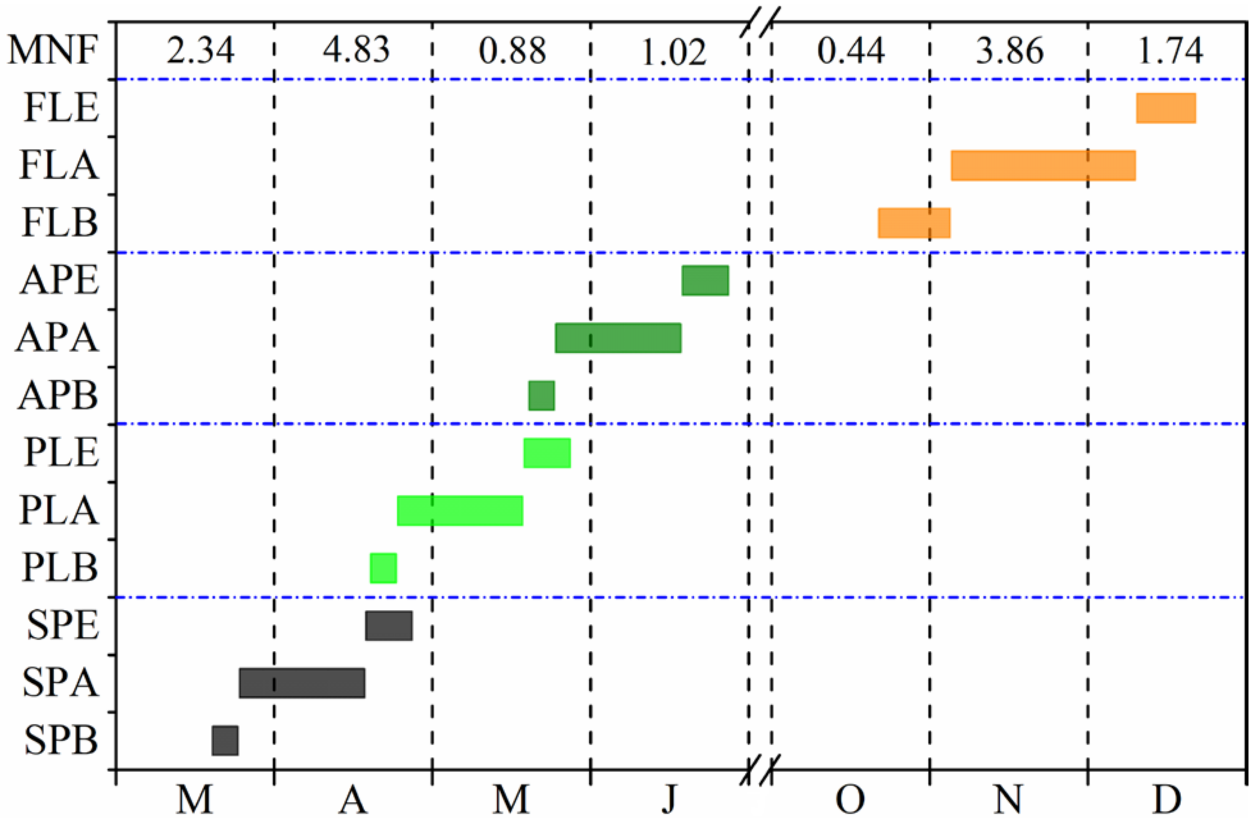

Figure S1. Temporal distribution of N fertilizer application at daily scale. The x-axis is month. MNF refers to monthly application rate (g N m^{-2}), which is aggregated from daily application in that month. SP refers to before planting in spring, PL refers to at planting, AP refers to after planting, and FL refers to after harvesting in fall of previous year. The letters, B, A, and E, in the end of four timings refer to begin, active, and end respectively.

3 Difference of NH_3 loss proportion of each month between two periods: 1965-1980 and 2000-2015

We calculated the difference of ratio, which represents the proportion of monthly emission to annual NH_3 emission, between the periods of 1965-1980 and 2000-2015 to identify regions with large ratio changes (Fig. S2). The shares of months in winter have moderately changed over the decades. Whereas April, May, June, and October show large variation across regions. Specifically, March, April, October, and November gained their shares in vast regions of the Midwest, the Northern Great Plains. While May and June received their greatest increase in the Northwest and the Southeast respectively. In contrast, the share of May dramatically decreased in the Southeast and North Dakota. September also had a large decrease of share in the Northwest between two periods.

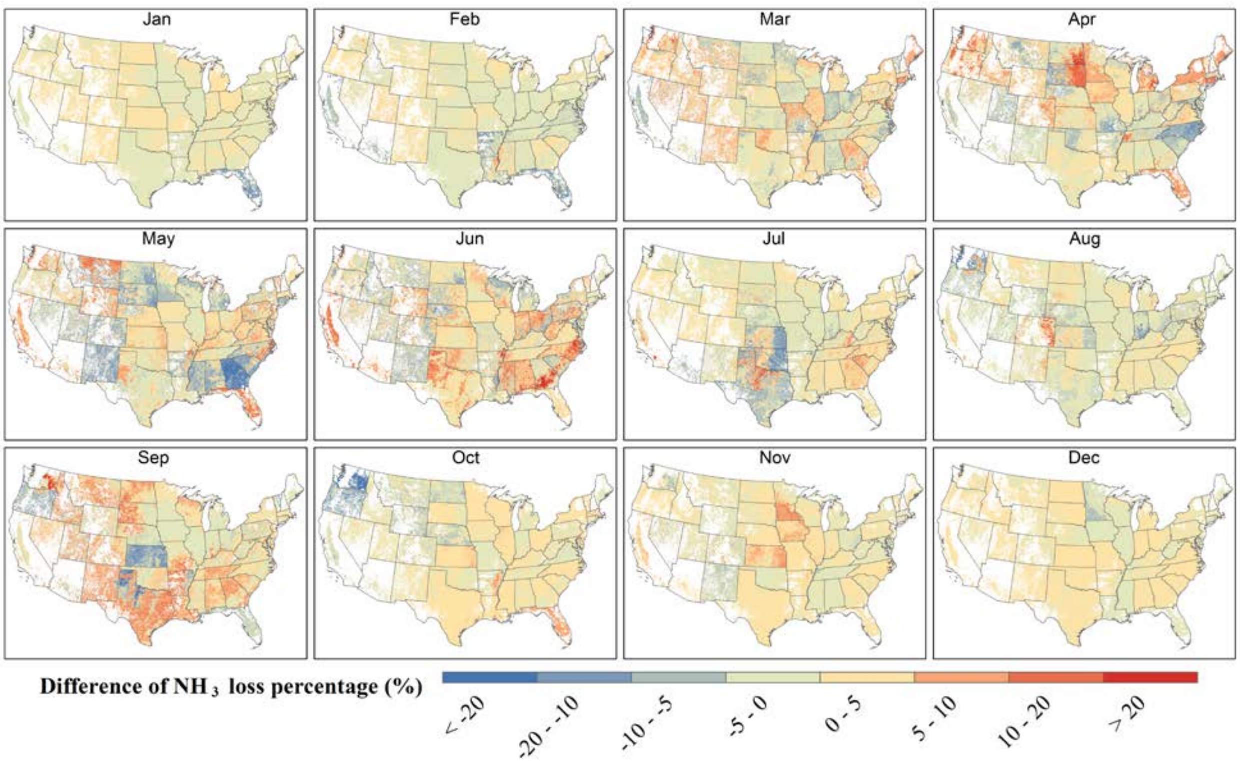

Figure S2. Difference of NH_3 loss proportion of each month between two periods: 1965-1980 and 2000-2015. The NH_3 loss proportion is calculated as the ratio of NH_3 emission to total N fertilizer input.

4 Contributions of crop type to annual NH_3 emission

We examined the contribution of crop types to annual NH_3 emission from 1920 to 2015 in the U.S (Table S3). Other crop types in total, cotton, and corn were major contributors, which accounted for nearly 90% of yearly NH_3 emission before 1960. NH_3 emission from corn field quickly gains its share to 44% in 1960 and maintained close to half of the total emission to present. In contrast, the contribution of cotton gradually dropped from 15% in 1960 to 3% in 2015 among all crop types. Meanwhile, NH_3 emission from all other crops decreased dramatically from 41.9% in 1920 to 23.7% in 1940 and kept less change at around 20% of the yearly total. Although the NH_3 emission amount is relatively small and accounts for less than 10% of total emission, spring wheat is the only crop type that continuously increased its contribution throughout the period.

Table S3. Contributions of crop type to annual NH_3 emission.

Crop types	1920	1940	1960	1980	2000	2015
Corn	2 (21)	5.9 (29.8)	43 (44)	187 (45)	222 (41)	304 (47)
Soybean	0 (0)	0 (0)	0.6 (0.6)	6.7 (1.6)	7.5 (1.4)	11 (1.7)
Winter wheat	0.9 (8.2)	1.7 (8.8)	11 (11)	60 (14)	74 (14)	73 (11)
Spring wheat	0.04 (0.4)	0.05 (0.3)	0.7 (0.7)	8.2 (2)	27 (4.9)	41 (6.3)
Cotton	2.8 (28)	6.9 (35)	14.3 (15)	18 (4.3)	35 (6.5)	20 (3)
Sorghum	0 (0)	0 (0)	5.9 (6)	23 (5.5)	15 (2.8)	16 (2.4)
Rice	0.04 (0.4)	0.1 (0.5)	0.9 (0.9)	6 (1.4)	9 (1.6)	9.5 (1.5)
Barley	0.02 (0.2)	0.3 (1.6)	4 (4.1)	8.3 (2.0)	14 (2.6)	5.2 (0.8)
Durum wheat	0.05 (0.5)	0.05 (0.3)	0.3 (0.3)	2.6 (0.6)	4.7 (0.9)	4.1 (0.6)
Cropland pasture	0 (0)	0 (0)	4.5 (4.7)	20 (4.9)	30 (5.6)	32 (5)
Others	4 (41.9)	4.7 (23.7)	12.6 (13)	78 (19)	104 (19.2)	127 (20)

Others include small grains, fruits, vegetables, and other crops other than listed crop types. Values before bracket are NH_3 emission amount with unit Gg N yr^{-1}. Values in the bracket are weighted percentage to annual total emissions with unit %.

5 Contributions of fertilizer type to annual NH_3 emission.

We compared the NH_3 emission from different N fertilizer types and assessed their contribution to annual emission during 1920-2015 in the U.S. (Table S4). Before 1940, all other N fertilizer types were the overwhelming contributor of annual NH_3 emission, which were over 65%. However, as the popularity of Urea and Nitrogen Solution since 1980, the share of all other N fertilizer types largely dropped to 13% in 2015. Whereas Urea has become the greatest NH_3 emission contributor (48%) in 2015, followed by Nitrogen Solution (20%).

Table S4. Contributions of fertilizer type to annual NH_3 emission.

Crop types	1920	1940	1960	1980	2000	2015
AnA	0 (0)	0.09 (0.5)	7.7 (7.9)	57(14)	46.7 (8.6)	39.1 (6.1)
AqA	0 (0)	0 (0)	0.7 (0.7)	1.3 (0.3)	0.7 (0.1)	0.8 (0.1)
AN	0.2 (2.4)	0.4 (2.2)	14 (14)	31 (7.5)	21.6 (4.0)	10.5 (1.6)
AS	1.3 (14)	2 (10)	7.2 (7.4)	12 (3.0)	16.2 (3.0)	29 (4.5)
NS	0 (0)	0 (0)	6.1 (6.3)	65 (16)	108 (20)	130 (20)
SN	0.5 (4.7)	1.3 (6.4)	0.7 (0.7)	0.1 (0.03)	0.05 (0.01)	0.02 (0.01)
UR	0.4 (4.2)	2.2 (11)	5.1 (5.2)	91 (22)	214 (39)	307 (48)
APs	0.1 (1.1)	0.9 (4.8)	4.6 (4.7)	4.5 (1.1)	1.5 (0.3)	1 (0.16)
CN	0.01 (0.05)	0.1 (0.04)	0.04 (0.04)	0.07 (0.02)	0.2 (0.04)	0.2 (0.02)

DAP	0 (0)	0 (0)	0.2 (0.2)	34 (8.1)	32 (5.9)	23.1 (3.6)
MAP	0 (0)	0 (0)	0.4 (0.4)	3.6 (0.9)	8.6 (1.6)	16.3 (2.5)
Others	7.3 (74)	13 (65)	53 (52)	117 (28)	94 (17)	85 (13)

Others refer to all other N fertilizer types, including single and mixed N fertilizers. Values before bracket are NH_3 emission amount with unit Gg N yr^{-1}. Values in the bracket are weighted percentage to annual total emissions with unit %.

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.

Table S5. 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

7 Comparison of the spatial pattern of NH_3 emission between National Emissions Inventory (NEI) and this study

We compared our NH_3 emission map with that estimated by EPA-NEI (2018) (Fig. S3). The spatial pattern and magnitude of our results show good agreement with NEI estimation. Such as the intensive emission in the corn-belt and the rice-belt, some regions in the Northwest, California, and the coastal area along the eastern coast of the U.S. However, there are also some discrepancies in two maps. For example, we estimated more intensive NH_3 emission in northern Texas.

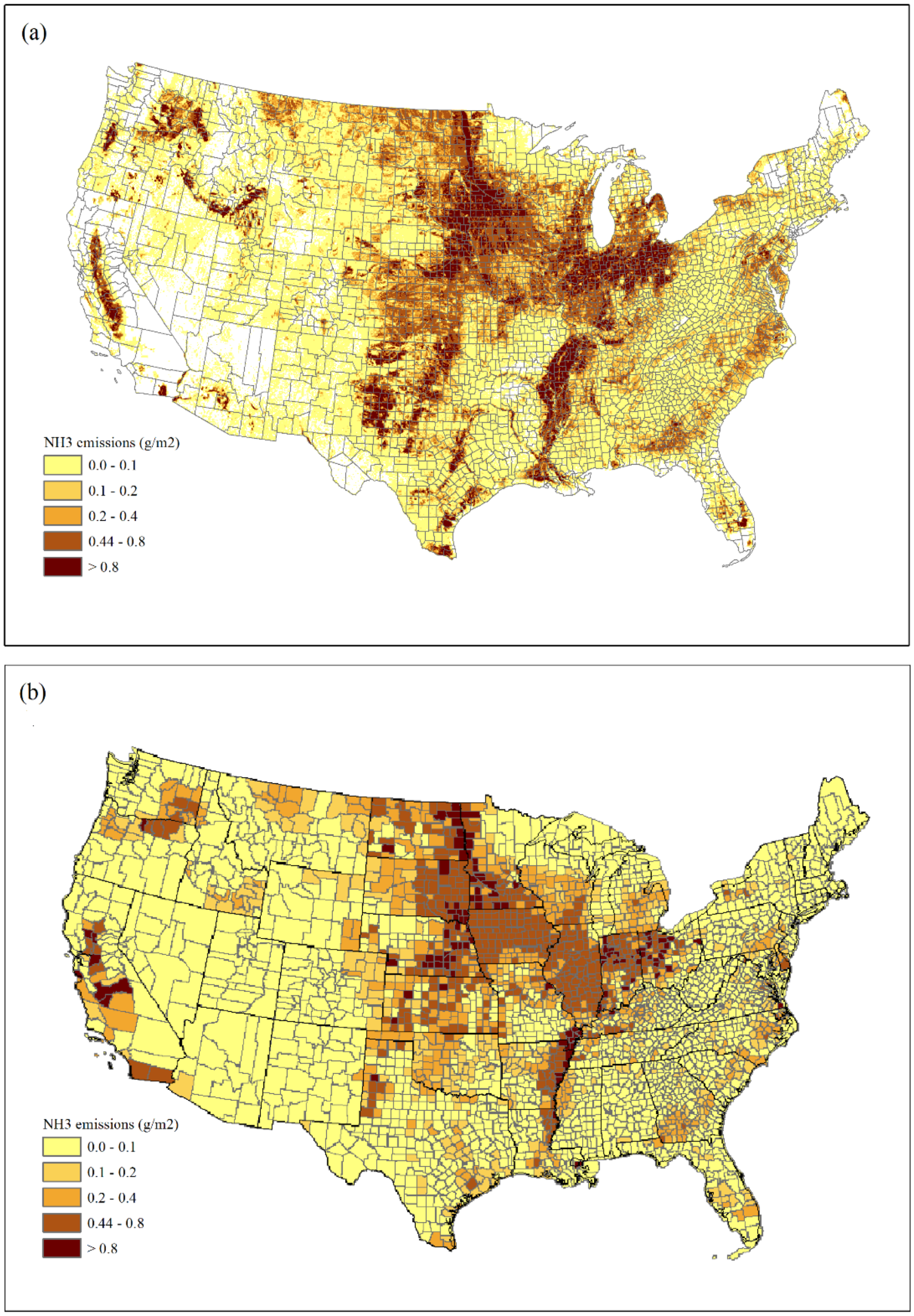

Figure S3. Comparison of spatial pattern of NH_3 emissions between our study (a) and EPA-National Emissions Inventory (b) in 2011.

8 Changing rates of planted area of non-legume crops between two periods of 1960-1980 and 1995-2015 in each state

To illustrate the cropland expansion and abandon information, we compared the acreage area change of four crop types between 1960-1980 and 1995-2015 among states in the contiguous

U.S (Fig. S4). We picked out four crop types that have the largest planting area in each state and calculated the change percentage and change the value of areas between two periods. The acreage of corn and spring wheat in the U.S. received the greatest increase with 12% and 22% and over 2.5 Million acres respectively. States in the Northern Great Plains generally increased the acreage of corn and spring wheat greater than other states. For example, North Dakota has increased the planting area of corn by 141% and spring wheat by 22% between two 20 years periods. Whereas Montana planting 55% more spring wheat in recent 20 years.

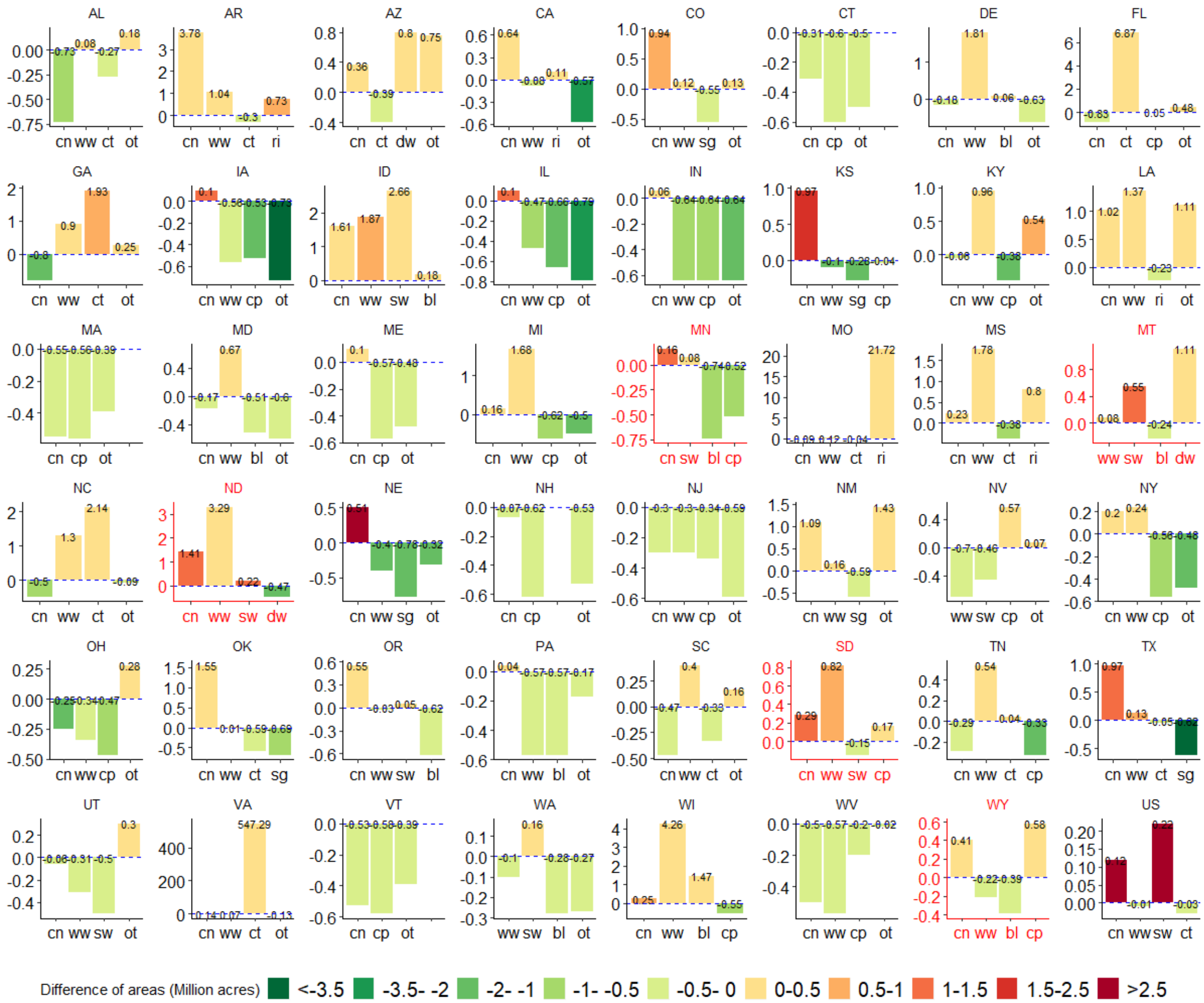

Figure S4. Changing rate of planted area of non-legume crops between two periods of 1960-1980 and 1995-2015 in each state. Four out of 10 crop types were chosen in each state based on the ranking planted area of crop types. 10 crop types are cn (corn), ww (winter wheat), sw (spring wheat), ct (cotton), sg (sorghum), ri (rice), bl (barley), dw (durum wheat), cp (cropland pasture), and ot (other crop types). The y axis represents the change percentage $(Y_2-Y_1)/Y_1$ between two periods. Minnesota and states of the Northern Great Plains are highlighted in red color.

9 Changing rate of N fertilizer consumption of each N fertilizer type between two periods of 1960-1980 and 1995-2015 in each state

We plotted the changing percentage and changing the value of N fertilizer use of each fertilizer type in each state to show the historical N fertilizer use change (Fig. S5). Four most used N fertilizer types were chosen in each state. It clearly shows that the urea-based fertilizer (Urea and N solution) gained the popularity between 1960-1980 and 1995-2015. Although other states largely increased the use of urea-based fertilizer, states in the Northern Great Plains increased the use by over 4000% in recent 20 years compared to 1960-1980. Specifically, Montana applied 11600% more urea during 1995-2015 compared to 1960-1980. Whereas Wyoming increased the use of urea by 9300% in recent 20 years.

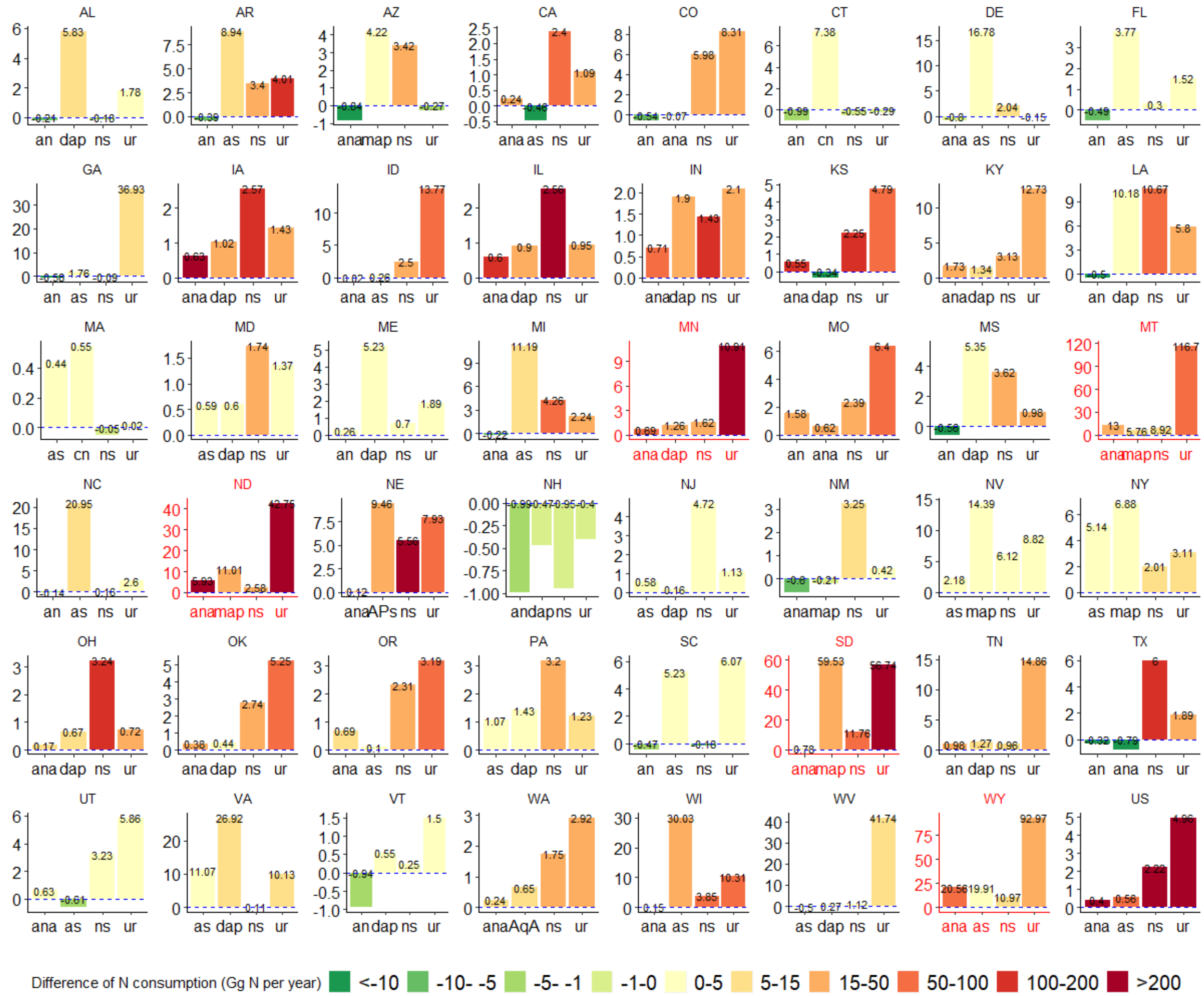

Figure S5. Changing rate of N fertilizer consumption of each N fertilizer type between two periods of 1960-1980 and 1995-2015 in each state. Four out of 11 N fertilizer types were chosen in each state based on the ranking N consumption of each N fertilizer type. 11 N fertilizer types are ana (Anhydrous Ammonia), aqa (Aqua Ammonia), an (Ammonium Nitrate), as (Ammonium Sulfate), ns (Nitrogen Solution), sn (Sodium Nitrate), ur (Urea), cn (Calcium Nitrate), dap (Diammonium Phosphate), map (monoammonium Phosphate), aps (Ammonium

Phosphates). The y axis represents the change percentage $(Y_2\text{-}Y_1)/Y_1$ between two periods. Minnesota and states of the Northern Great Plains are highlighted in red color.

10 Correlation coefficient between spring NH_3 emission and deposited NH_4^+ concentration

The majority of N fertilizer is applied around planting date in spring, resulting in a peak of NH_3 emission from March to June in the contiguous U.S. Therefore, we examined the relationship between fertilizer-induced NH_3 emission and deposited NH_4^+ concentration during this period using Pearson correlation coefficient at each 1 km pixel over 1985-2015 (Fig. S6). The spatial pattern is very similar to the correlation coefficient between the fertilizer-induced NH3 emission and deposited NH_4^+ concentration at an annual time scale. It implies the annual-scale relationship is mainly driven by the spring season.

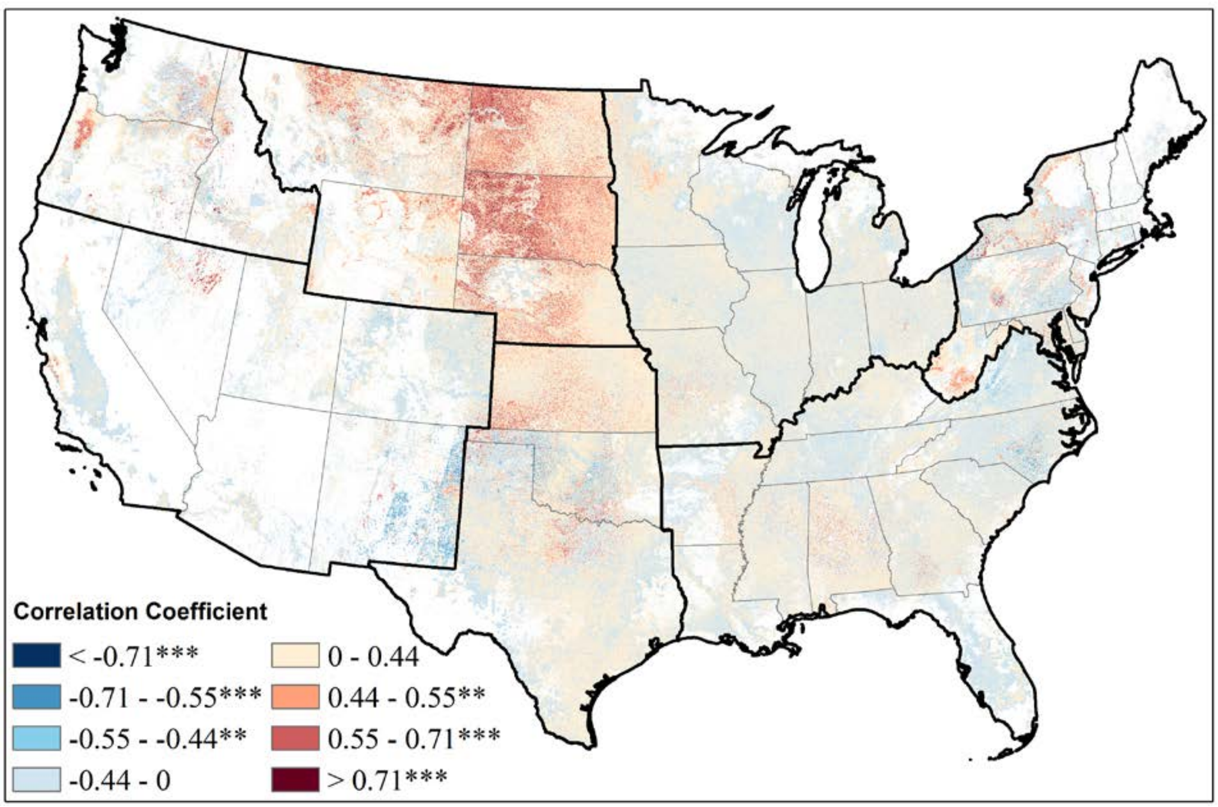

Figure S6. Correlation coefficient between spring (March-June) NH_3 emission from N fertilizer uses and NH_4^+ concentration in precipitation between 1985 and 2015. The correlation coefficient was calculated between the two time series at each 1km × 1km grid cell. ** refers to P-value < 0.01, *** refers to P-value < 0.001.

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