

# High resolution inventory of ammonia emissions from agricultural fertilizer in China from 1978 to 2008

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## ABSTRACT

The quantification of ammonia (NH<sub>3</sub>) emissions is essential to the more accurate quantification of atmospheric nitrogen deposition, improved air quality and the assessment of ammonia-related agricultural policy and climate mitigation strategies. The quantity, geographic distribution and historical trends of these emissions remain largely uncertain. In this paper, a new Chinese agricultural fertilizer NH<sub>3</sub> (CAF\_NH<sub>3</sub>) emissions inventory has been compiled that exhibits the following improvements: (1) a 1 × 1 km gridded map on the county level was developed for 2008; (2) a combined bottom-up and top-down method was used for the local correction of emission factors (EFs) and parameters; (3) the temporal patterns of historical time trends for 1978-2008 were estimated and the uncertainties were quantified for the inventories; and (4) a sensitivity test was performed in which a province-level disaggregated map was compared with CAF\_NH<sub>3</sub> emissions for 2008. The total CAF\_NH<sub>3</sub> emissions for 2008 were 8.4 TgNH<sub>3</sub> yr<sup>-1</sup> (a 6.6-9.8 Tg interquartile range). From 1978 to 2008, annual NH<sub>3</sub> emissions fluctuated with three peaks (1987, 1996 and 2005), and total emissions increased from 3.2 to 8.4 Tg at an annual rate of 3.0%. During the study

29 period, the contribution of livestock manure spreading increased from 37.0% to 45.5%  
30 because of changing fertilization practices and the rapid increase in egg, milk and  
31 meat consumption. The average contribution of synthetic fertilizer, which has a  
32 positive effect on crop yields, was approximately 38.3% (minimum: 33.4%;  
33 maximum: 42.7%). With rapid urbanization causing a decline in the rural population,  
34 the contribution of the rural excrement sector varied widely between 20.3% and 8.5%.  
35 The average contributions of cake fertilizer and straw returning were approximately  
36 3.8% and 4.5%, respectively, thus small and stable. Collectively, the CAF\_NH<sub>3</sub>  
37 emissions reflect the nation's agricultural policy to a certain extent. An effective  
38 approach to decreasing PM<sub>2.5</sub> concentrations in China would be to simultaneously  
39 decrease NO<sub>x</sub>, SO<sub>2</sub> and NH<sub>3</sub> emissions.

40

## 41 **1. Introduction**

42 NH<sub>3</sub> is a colorless alkaline gas with high reactive ability and solubility in the  
43 atmosphere, where its presence has undesirable consequences. The gas reacts with  
44 HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in the air to form ammonium salts (NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and  
45 (NH<sub>4</sub>)HSO<sub>4</sub>) (Pinder et al., 2007), which further contribute to visibility degradation  
46 and regional haze and have adverse health effects (Kim et al., 2006;Ye et al.,  
47 2011;Langridge et al., 2012). Such salts could account for 7.1-57% of the total  
48 quantity of atmospheric fine particulate matter (PM<sub>2.5</sub>: aerodynamic diameter of  
49 particle size ≤2.5 μm) (Yang et al., 2011;Huang et al., 2014;Zhang et al., 2014a). NH<sub>3</sub>  
50 comprises nearly half of all reactive nitrogen released into the atmosphere and plays a  
51 key role in soil acidification, eutrophication and the disruption of ecosystems by dry  
52 deposition (Vanbreemen et al., 1984;Hellsten et al., 2008;Bouwman et al., 1997). In  
53 addition, although NH<sub>3</sub> exerts a cooling effect on the planet as a result of radiation  
54 forcing by aerosol particles (Martin et al., 2004), it is an indirect source of the major  
55 greenhouse gas nitrous oxide from the Intergovernmental Panel on Climate Change  
56 (IPCC, 2006). Therefore, efforts to decrease NH<sub>3</sub> emissions could have the triple

57 benefit of slowing global climate change, decreasing regional air pollution and  
58 protecting human health (Zheng et al., 2012;Erisman et al., 2013).

59 Agriculture in China utilizes approximately 7% of the world's cultivated land area to  
60 support 22% of the global human population. To meet the demand for food of China's  
61 large and increasing population (30-50% more food will be required over the next two  
62 decades) (Zhang et al., 2013;Cui et al., 2014;Ma et al., 2013), the government has  
63 initiated a series of agricultural policies that aim to increase the will of farmers,  
64 including farmers who overuse agricultural fertilizers (including synthetic and organic  
65 fertilizers), to increase yields. Policy-driven measures to increase the use of fertilizer  
66 and low nitrogen-use efficiency have resulted in continually increasing NH<sub>3</sub> emissions  
67 (Vitousek et al., 2009;Gu et al., 2012;Zhang et al., 2014b). Therefore, to achieve the  
68 balance of food demand and environment effects, NH<sub>3</sub> emissions must be accurately  
69 estimated in a manner that reflects the spatial and temporal pattern of their sources.

70 Previous studies mainly estimated NH<sub>3</sub> emissions in China based on EFs and activity.  
71 In the 1990s, China's NH<sub>3</sub> emissions were estimated based on uniform or overseas  
72 EFs for the entire country (Sun and Wang, 1997;Wang et al., 1997;Olivier et al.,  
73 1998;Xing and Zhu, 2000;Streets et al., 2003;Yan et al., 2003), which decreased the  
74 accuracy of these estimates because of the differences in regional environmental  
75 conditions. Subsequent studies, in which national or provincial statistical data on the  
76 rural population, fertilizers and agricultural production were used to estimate NH<sub>3</sub>  
77 emissions, generally downscaled to realize higher spatial resolution (e.g., Yamaji et al.,  
78 2004; Huang et al., 2012, and EDGAR v.4.2, 2013). Thus, biases could occur. Paulot  
79 et al. (2014) improved the bottom-up emission inventory to incorporate  
80 sector-resolved information on global agricultural activities known as MASAGE\_NH<sub>3</sub>,  
81 which is still limited to specific sectors, such as precipitation and the monitoring  
82 networks provide high-density data (Paulot et al., 2014). Additionally, the previous  
83 emission inventories provide no or only coarse temporal distributions in the year,  
84 which could result in underestimation during summer and overestimation during

85 winter (Wang et al., 1997; Yan et al., 2003).

86 In addition, studies have attempted to focus on implementing the bidirectional  
87 exchange of  $\text{NH}_3$  in many air quality models, e.g., the Community Multi-scale Air  
88 Quality (CMAQ) model (Cooter et al., 2012; Bash et al., 2013; Pleim et al., 2013; Fu  
89 et al., 2015), and the GEOS-Chem global chemical transport model (Zhu et al., 2015).  
90  $\text{NH}_3$  deposition, emission, reemission, and atmospheric lifetime can be affected by  
91 rigorous treatment of the bidirectional flux of  $\text{NH}_3$ , and vegetation and soil can be  
92 either a sink or a source of atmospheric  $\text{NH}_3$  (Sutton et al., 2007). Fu et al. (2015)  
93 provides the first online estimate of  $\text{NH}_3$  emissions from agricultural fertilizer use  
94 China, based on coupling the CMAQ model with a bi-directional  $\text{NH}_3$  exchange  
95 module and the Environmental Policy Integrated Climate (EPIC) model, this method  
96 considers an increased number of influencing factors, such as meteorological fields,  
97 soil and fertilizer application, and provides improved  $\text{NH}_3$  emissions with higher  
98 spatial and temporal resolution, whereas, gaps still exist for this method owing to the  
99 uncertainties of more model parameterization and input data. Zhu et al. (2015)  
100 developed the adjoint of bidirectional exchange in GEOS-Chem model which  
101 suggests that although the implementing bidirectional exchange greatly extends the  
102 lifetime of  $\text{NH}_3$  in the atmosphere via deposition and reemission processes and  
103 conducts a better fundamental description of  $\text{NH}_3$  emissions from fertilizers, whereas,  
104 it does not uniformly ameliorate estimation of  $\text{NH}_3$  concentrations,  $\text{NH}_4^+$  wet  
105 deposition and nitrate aerosol concentrations due to the  $\text{NH}_3$  re-emissions from the  
106 ammonium soil pool that accumulates ammonium from previous months or the  
107 ammonium soil pool preserves ammonia/ammonium in the soil rather than emitting it  
108 directly after fertilizer application during the growing seasons (e.g., bidirectional  
109 exchange significant decreases  $\text{NH}_3$  gross emissions in southeastern China and  $\text{NH}_3$   
110 concentrations in China in April of 2008, but changes in  $\text{NH}_4^+$  wet deposition are not  
111 very large in April).

112 In this study, a  $1 \times 1$  km gridded new CAF  $\text{NH}_3$  emission inventory based on

113 county-level activity data was developed for 2008 and historical time series of NH<sub>3</sub>  
114 emissions based on province-level activity data from 1978 to 2007. An effort was  
115 made to improve accuracy and decrease uncertainty by considering more  
116 comprehensive emission sources. In addition, a combined bottom-up and top-down  
117 method was used for the local correction of EFs and parameters. We analyzed the  
118 emission totals, source apportionment, spatial and temporal patterns and uncertainty,  
119 and compared our results with previous studies. Then, we compared the 2008  
120 emission map with a province-level disaggregated map. We also provided a clear  
121 description of the change in NH<sub>3</sub> emissions in CAF historical emissions between 1978  
122 and 2008. Finally, the implications of the higher spatial and temporal resolution NH<sub>3</sub>  
123 emission inventory are discussed, with a focus on the control of N deposition, the  
124 improvement of air quality, NH<sub>3</sub> emission-related agricultural policy and climate  
125 mitigation strategies.

126

## 127 **2. Methodology and data sources**

### 128 **2.1 NH<sub>3</sub> Emission Sources**

129 Five NH<sub>3</sub> emission sources, including synthetic fertilizers (i.e., chemical and  
130 compound fertilizers) and organic fertilizers (i.e., rural excrement, livestock manure  
131 spreading, cake fertilizer and straw returning. In this study, straw returning represents  
132 crop residue compost which adds soil nutrients in the rural China, and NH<sub>3</sub> is released  
133 during composting through aerobic and anaerobic microbial processes. Sludge is not  
134 considered to be an agricultural fertilizer, and the quantity of green manure that is  
135 applied is limited) (Gao et al., 2011), are included in our emissions model. China's  
136 NH<sub>3</sub> emissions from agricultural fertilizer ( $E_{NH_3}$ , TgNH<sub>3</sub> yr<sup>-1</sup>) are calculated with the  
137 following equation:

$$138 \quad E_{NH_3} = \sum_i A_{nij} \cdot EF_{ij} \cdot f(RP_{nijm}, C_m) \quad (1)$$

139 where subscripts  $n$ ,  $i$ ,  $j$  and  $m$  is the year, the emission source, the region (county in  
140 2008 and province in 1978-2007) and the parameter, respectively;  $A$  is the activity

141 data;  $EF$  is the region-specific emission factor (EF);  $RP_{nijm}$  represents a  
142 region-specific emission controlling parameter  $m$  for activity data or EF;  $f(\cdot)$   
143 represents a function whose shape depends on the source type, which responds to  
144  $RP_{nijm}$  and  $C$ ; and  $C$  stands for a coefficient. More detailed descriptions of the  
145 equations used for each source (Section S1), the activity data, the RPs, and the EFs  
146 (Section S2) can be found in Supporting Information (SI) and are briefly summarized  
147 below.

148

## 149 **2.2 Data Sources**

150 In this paper, county-level data for the annual quantities of synthetic fertilizer (5  
151 types), livestock (8 types), crop (17 types), and rural population in 2008 were derived  
152 for 2 376 counties from 329 municipal statistical registers in Mainland China, Hong  
153 Kong, Macau and Taiwan (Hong Kong and Macau primarily have no agriculture, and  
154 thus all activity data of them equal zero). Annual above-province-level data for  
155 Mainland China from 1978 to 2008 were obtained from the China Agriculture  
156 Yearbook (NBSC, 2009a) and the China Compendium of Statistics (NBSC, 2009b).  
157 Taiwanese data for 1991 to 2008 were collected from the Yearly Report of Taiwan's  
158 Agriculture (COA, 1992-2009). We obtained the 2008 unavailable fertilizer, crop, and  
159 livestock data for 332 counties in Mainland China and Taiwanese annual  
160 above-province-level data for 1978-1990 based on temporal interpolation (Zhou et al.,  
161 2014). We disaggregated these activity data into 1×1 km maps based on China's land  
162 use pattern to determine their spatial distribution. In addition, regarding activity data  
163 collected in international statistics databases for 2008, the synthetic fertilizers data  
164 were obtained from the IFA (<http://www.fertilizer.org/>), the rural population data were  
165 obtained from the World Bank (<http://data.worldbank.org/>) and the crop and livestock  
166 data were obtained from the FAO (<http://faostat.fao.org/>). The meteorological data for  
167 Mainland China were provided by the China Meteorological Data Sharing Service  
168 System (<http://cdc.nmic.cn/home.do>), and the Taiwanese meteorological data were

169 provided by the Central Weather Bureau (<http://www.cwb.gov.tw>). Complementary  
170 gridded activity data include soil pH (1 × 1 km) (the Harmonized World Soil  
171 Database v1.2,  
172 <http://webarchive.iiasa.ac.at/Research/LUC/External-World-soildatabase/HTML/>) and  
173 the secondary classification of land-use data (1 × 1 km) (Liu et al., 2010b).

174

### 175 **2.3 EFs for NH<sub>3</sub>**

176 The EFs reported in the literature are associated with large uncertainty because of  
177 differences in ambient temperatures, planting practices, soil properties, and other  
178 crucial influential factors. In this paper, for synthetic fertilizer sources, a previously  
179 developed EF correction model was used. Because direct measurements of EFs are  
180 limited in number, the EFs were adjusted for soil pH, fertilization method, application  
181 rate, precipitation and local temperature conditions to establish their spatial and  
182 temporal variations (i.e., the county or provincial level; monthly emissions) according  
183 to the top-down NASRSES model (Webb et al., 2006) (for detailed information, see  
184 Xu et al. (Xu et al., 2015)). For livestock manure spreading sources, the original NH<sub>3</sub>  
185 EFs compiled to develop the bottom-up RAINS model were found in the EEA's  
186 inventory guidebook (EEA, 2009). However, the values for region-specific N  
187 excretion in livestock manure management and the feeding days for livestock  
188 species/categories are based on published measurements for China and the results for  
189 the Livestock Manure Sector in the National Pollution Source Survey Database  
190 (NPSS) (Huang et al., 2012; MEP, 2008; SCC, 2013). Although the age and growth  
191 stage of livestock are likely to cause a certain degree of variation in the quantity of  
192 fecal excretion, this effect is only reflected by specific parameters (i.e., some form of  
193 dietary manipulation) on the farm scale (Ross et al., 2002). The activity levels and the  
194 EFs of the national- or regional-scale emission inventories do not distinguish  
195 according to the factors included in this study because EFs are restricted by activity  
196 level, i.e., animal industry statistical data. In addition, although Chinese statistics can

197 be approximate, theoretically, they can be refined, as a number of inventories that  
198 have previously considered these factors have attempted (Huang et al., 2012).  
199 However, Chinese statistics currently contribute little to emissions inventories because  
200 of a lack of functionality and practical significance. It was assumed that the number of  
201 livestock is the same during each month of the year. The proportion of livestock EFs  
202 for different seasons, which were used to establish the annual livestock EFs, was  
203 derived from Huang et al. (2012), and Hutchings et al. (2001) reported that the EFs  
204 for the same season of different months are equivalent and the different seasons are  
205 different (Huang et al., 2012; Hutchings et al., 2001). These principles were applied in  
206 this study. Regarding the remaining sources, a literature review was aimed at  
207 collecting relevant EFs, whereby the arithmetic mean of different experiments was  
208 used. Additionally, we performed only regional correction for activity data when  
209 calculating the NH<sub>3</sub> emission of cake fertilizers and straw returning. The emissions  
210 from these sources were equally divided into 12 months because of their smaller  
211 application and EFs. All of the EFs and parameters used in this inventory are listed in  
212 Table S1 and Table S2.

213

#### 214 **2.4 Uncertainty Analysis**

215 A Monte Carlo simulation that consisted of 10 000 calculations of the NH<sub>3</sub> emission  
216 inventory was run to characterize the uncertainty caused by the variations in the  
217 activity data, the EFs and related parameters. The coefficient of variation (CV) of  
218 each activity data is assumed to be equal to the absolute value of the average  
219 difference between a given dataset for China used in to determining CAF\_NH<sub>3</sub> and a  
220 default global dataset (e.g., IFA, FAO, World Bank) for 2008. In addition, the CV of  
221 each activity data in 1978-2007 is assumed to be equal to the CVs of the 2008 data  
222 based on expert judgments. The CV values for sugarcane, highland barley, alfalfa,  
223 peanuts, other oil crops, other beans and other tubers were set at 0.2 because they are  
224 absent from the global datasets (Zhou et al., 2014). The CV values for the EFs and



225 related parameters were based on values found in the literature (Wang et al.,  
226 2012;Huang et al., 2012;Zhou et al., 2014;Xu et al., 2015). For activity data, uniform  
227 distributions were assumed. Normal distributions were adopted for the EFs and other  
228 parameters. The precise CV values are summarized in Table S3. Medians and the  $R_{50}$   
229 (difference between the 75th and 25th quartiles) were aimed at estimating the  
230 emissions and representing the uncertainties.

231

### 232 **3. Results**

#### 233 **3.1 NH<sub>3</sub> Emissions in China in 2008**

234 The total NH<sub>3</sub> emissions ( $E_{total}$ ) from CAF for 2008 were estimated as 8.4 TgNH<sub>3</sub> yr<sup>-1</sup>  
235 (median, 6.6-9.8 Tg as  $R_{50}$ ), and the contribution of synthetic fertilizer application,  
236 livestock manure spreading, rural excrement, cake fertilizers and straw returning were  
237 3.3, 3.8, 0.7, 0.3, and 0.3 Tg, respectively. Detailed information on the contribution of  
238 each source to  $E_{total}$  from CAF for 2008 is presented in Fig. 1. Regarding the synthetic  
239 fertilizer contribution, 1.9, 1.3, 0.02, 0.003, and 0.05 Tg could be attributed to  
240 ammonium bicarbonate (ABC), urea, ammonium nitrate (AN), ammonium sulfate  
241 (AS) and others, respectively. Among the various sources of livestock manure (Fig.  
242 S1), cattle were the largest emitter (30.2%), followed by pigs (28.9%), poultry (26.2%)  
243 and dairy cattle (7.9%). Rural excrement (8.5%), cake fertilizer (3.2%) and straw  
244 returning (3.9%) were of less importance but non-negligible.

245

#### 246 **3.2 Spatial and Temporal Distribution**

247 Fig. 2 shows the 1 km ×1 km and county-level geographic distributions of NH<sub>3</sub>  
248 emissions in 2378 counties for 2008. The mean per-unit cultivated area NH<sub>3</sub> emission  
249 was 5.9 tNH<sub>3</sub> km<sup>-2</sup> yr<sup>-1</sup>. Using county-level data to create this NH<sub>3</sub> emissions map  
250 reveals the strong spatial association of the emissions with the distribution of arable  
251 land. The average emission density (per-unit cultivated area NH<sub>3</sub> emission) over  
252 western, central and eastern China is 4.7, 6.4 and 6.5 tNH<sub>3</sub> km<sup>-2</sup> yr<sup>-1</sup>, respectively. The  
253 three regions are defined in Fig. S2. Eastern China (36.7% of China's cultivated area)

254 was the largest contributor of NH<sub>3</sub> emissions and responsible for approximately  
255 41.6% of the total. In central China, synthetic fertilizer was the largest contributor  
256 (44.4%). This contribution was substantially higher than that of western (34.0%) and  
257 eastern (36.3%) China. However, the contribution of livestock manure spreading  
258 (37.6%) in central China was substantially less than in western (50.3%) and eastern  
259 (50.2%) China. In addition, high emission densities were presented in the North China  
260 Plain, the Northeast Plain, the Huaihe River Basin, the Lianghu Plain, the Sichuan  
261 Basin, the Tarim Basin and the Weihe Plain. Most of China's grain and livestock  
262 production is concentrated in these areas. High NH<sub>3</sub> emission densities were also  
263 found in western China, such as Tibet, Sichuan and Qinghai, where livestock is raised  
264 on a large scale and less cropland exists. We compared our results with the global NH<sub>3</sub>  
265 column distribution using satellite monitoring from the Infrared Atmospheric  
266 Sounding Interferometer (IASI) (Clarisse et al., 2009; Van Damme et al., 2014).  
267 Several emissions hotspots are observed in the Tarim basin, the North China Plain and  
268 western Heilongjiang province and Jilin province by the IASI sensor, emission density  
269 is 4.2, 7.4, 5.2 and 9.6 tNH<sub>3</sub> km<sup>-2</sup> yr<sup>-1</sup>, respectively. This result demonstrated excellent  
270 qualitative consistent with our estimated emissions. However, the higher emission  
271 areas were not observed by satellite monitoring because of clouds, water vapor, the  
272 surface temperature, high SO<sub>2</sub> emissions (Kharol et al., 2013; Wang et al., 2013; Garcia  
273 et al., 2008), land surface variation and the retrieval methods of NH<sub>3</sub> total columns  
274 (Xu et al., 2015). Higher plenty of cloud cover and precipitation could generate some  
275 uncertainties in the Sichuan Basin and Lianghu Plain. Additionally, NH<sub>3</sub> concentration  
276 distribution might not be always in agreement with emission pattern due to its high  
277 reactive ability, solubility and short-lived in the atmosphere (Huang et al., 2012);  
278 Higher surface temperature and humidity could speed up NH<sub>3</sub> consumption  
279 simultaneously. And Sichuan Basin is high SO<sub>2</sub> pollution district where NH<sub>3</sub> gas could  
280 easily react with SO<sub>2</sub> (Zhang et al., 2009). Therefore, these factors lead the  
281 inconsistent between satellite monitoring and our inventory.

282 To test the sensitivity of the NH<sub>3</sub> emissions spatial patterns to input activity data, an  
283 emissions inventory (PRO-NH<sub>3</sub>(China)) was developed using the same methods that  
284 were employed to create CAF\_NH<sub>3</sub> except county-level activity data for provincial  
285 disaggregation using regression models (Zhang et al., 2007; Zhou et al., 2014). The  
286  $E_{\text{total}}$  of PRO-NH<sub>3</sub> is 7.3 TgNH<sub>3</sub> yr<sup>-1</sup>, which is 12.5% less than the CAF\_NH<sub>3</sub> value.

287 For a more detailed comparison, the relative difference was defined as  $RD = (E_1 - E_2)$   
288  $/ ((E_1 + E_2)/2)$  (Wang et al., 2012), where  $E_1$  and  $E_2$  are the  $E_{total}$  for agricultural  
289 fertilizer of the counties for CAF-NH<sub>3</sub> and for PRO-NH<sub>3</sub> for each county, respectively.  
290 Fig. 3 shows all counties' frequency and spatial distributions of the RDs. The spatial  
291 bias of the provincial disaggregation increases as the absolute RDs. A negative  
292 (positive) RD suggests an overestimation (underestimation) of a county's emissions  
293 by utilizing the provincial disaggregation approach (PRO-NH<sub>3</sub>). The mean absolute  
294 RD was 48.7% for all counties. In 37% of the countries, the absolute RDs were found  
295 higher than 50%. In addition, the PRO-NH<sub>3</sub> emission pattern is lowly correlated with  
296 the CAF-NH<sub>3</sub> pattern ( $R = 0.49$ ,  $p < 0.01$ ). These results indicate that spatial bias can  
297 be substantially reduced using the county-level activity data and that provincial  
298 disaggregation using regression models cannot determine the county-scale structure of  
299 the spatial distribution of activity data within provinces. Large RDs were often  
300 observed in provinces and regions in which the development status significantly  
301 varies, such as Sichuan, Qinghai, Inner Mongolia and Tibet.

302 By comparing nitrogen fertilizer, compound fertilizer, rural population, rice, wheat,  
303 maize, cattle, sheep and pigs activity data (1978-2007) which are the major NH<sub>3</sub>  
304 emission sources in this study from NBSC provincial statistics (sums of the provincial  
305 data), IFA and FAO (national data), it was found that 64.8% IFA and FAO statistics  
306 underestimated the above activity data from 1978 to 2007 because of the difference  
307 statistical criteria, especially rural population and sheep attained 100% and 80.0%  
308 respectively (Fig. S3). The possible underestimation of national emission statistics has  
309 been demonstrated by NH<sub>3</sub> emission trends based on the per capita livestock that can  
310 cover all the NH<sub>3</sub> emission during the whole lifespan of livestock in Gu et al. (2012),  
311 and this fact may support our conclusion. Considering the information presented here  
312 and the limit of county-level activity data availability in 1978-2007, province-level  
313 activity data from 1978 to 2007 was used in our study in order to develop high  
314 resolution inventory.

315 Fig. 4 shows the monthly NH<sub>3</sub> emissions in 2008 from various sources, which are  
316 generally in agreement with the local climate, planting time and cultivation practices.  
317 Higher emissions occurred during the summer (June to August) and accounted for  
318 39.7% of the annual total emissions. These higher emissions are virtually identical  
319 with several in situ data sets (Ianniello et al., 2010; Meng et al., 2011). In addition, the  
320 seasonality of emissions from IASI and Tropospheric Emission Spectrometer (TES)  
321 satellite observations demonstrated excellent consistent with the temporal distribution  
322 of our inventory which is a summer maximum of NH<sub>3</sub> emissions in China (Shephard  
323 et al., 2011; Van Damme et al., 2015). The peak value was found for July (1.2  
324 TgNH<sub>3</sub> yr<sup>-1</sup>). This value was approximately 3.1 times larger than the smallest value  
325 (January). Regarding synthetic fertilizer sources, NH<sub>3</sub> emissions significantly  
326 increased in April, peaked in July, and then decreased. This pattern could be partly  
327 attributed to an increased application of synthetic fertilizer and higher temperatures.  
328 In China, winter wheat and oilseed rape are typically seeded in late September and  
329 early October with the base fertilizer application. The basal dressing and topdressing  
330 of summer maize occur in June and August. In addition, early rice sowing, late rice  
331 sowing and transplanting typically occur in April and July and are accompanied by  
332 base fertilization. For these crops, topdressing is performed in late June and late  
333 September, respectively. A total of 50~80% of the synthetic fertilizer is applied at or  
334 around planting (Zhang et al., 2011). The largest livestock manure spreading  
335 emissions also occurred in summer and accounted for nearly 28.8% of livestock  
336 manure spreading emissions. This result might be explained by larger EFs related to  
337 the substantial increase in ambient temperature and little variation in the livestock  
338 population among the different months (Huang et al., 2012). The NH<sub>3</sub> emissions in  
339 winter (December to February) were lower due to the relatively lower temperature  
340 and infrequent agricultural activities. The spatial distributions of CAF NH<sub>3</sub> for  
341 January, April, July and October are shown in Fig. S4. In western China, rural  
342 excrement's monthly contribution proportions were higher than in eastern China,

343 particularly during winter (1.6 times); In central China, synthetic fertilizer's monthly  
344 contribution proportions began to exceed livestock manure in April (Fig. S5),  
345 however, this condition occurred in May in eastern and western China because of  
346 temperature rebounded significantly. In addition, NH<sub>3</sub> emissions in central China (i.e.,  
347 in Guangdong, Guangxi and Hainan) were typically more stable than in eastern China  
348 (i.e., in Jilin, Liaoning and Heilongjiang) because of less dramatic temperature  
349 fluctuations and less intensive agricultural activities.

350

### 351 **3.3 Historical Time Trend for NH<sub>3</sub> Emissions in China**

352 Annual CAF NH<sub>3</sub> emissions were estimated based on the activity data, the EFs and  
353 related parameters as described in the Methodology section for 1978 to 2008. Fig. 5  
354 shows the annual variations in  $E_{total}$  and the distributions of each sector during the  
355 study years. The emissions increased from 3.2 to 8.4 Tg (2.6 times) during the period  
356 1978-2008. Fertilizer has been promoted as an important means to improve crop  
357 yields because the overall grain response to fertilizer and to technological and  
358 institutional changes is viewed as crucial to Chinese agricultural production (Wang et  
359 al., 1996). In addition, because of the initiation of reform and opening-up in 1978, the  
360 government has implemented a subsidy policy with respect to fertilizer and urged  
361 farmers to apply additional fertilizer to increase grain yields. From 1978 to 2008,  $E_{total}$   
362 fluctuated, with peaks in 1987, 1996 and 2005. The NH<sub>3</sub> emissions growth rates in  
363 1978-1987 and 1988-1996 were 41.7% and 51.3%, respectively, primarily as a result  
364 of the improvement of the unified food price in 1979 to increase the enthusiasm of  
365 farmers after the establishment of the Householder's Responsibility System. The  
366 system enhanced China's agricultural intensification degree and continuously  
367 increased the intensity of fertilizer use. In 1988, NH<sub>3</sub> emissions appeared to decrease.  
368 The primary reason for this decrease was the shortage and/or inflated price of supplies  
369 and equipment required for agricultural production, particularly the substantially  
370 higher prices of synthetic fertilizer and fodder, which increased agricultural

371 production costs and thus affected production output. In addition, a severe drought  
372 occurred during the entire year, which seriously affected agricultural production (Ma  
373 and Zhao, 1989). In 1997-2005, the NH<sub>3</sub> emission growth rate was 17.4%. This rate  
374 reflects a steady growth trend although one that was slower than that of the first two  
375 periods because following the grain yield peak in 1998 (512.3 Tg, NBSC, 2009a)  
376 grain prices decreased as a result of oversupply. These events sharply reduced the  
377 enthusiasm of farmers engaged in agricultural production. In addition, with China's  
378 accession to the World Trade Organization in 2001, lower overseas grain prices  
379 restrained the increase of domestic grain prices, which encouraged the rural  
380 population transfer to non-agricultural production. The national government did not  
381 recognize the problem's severity until the end of 2003 and then issued a series of  
382 favorable and preferential agricultural policies, including the repeal of the agriculture  
383 tax. This policy approach reversed the damaging decline of crop yields. However,  
384 influenced by the Asian financial crisis and El Nino, in 1997, emissions decreased.  
385 Since 2005, grain yields have continuously increased, and the quantity of synthetic  
386 fertilizer applied has decreased overall as a result of the dissemination of new  
387 technologies for soil testing and fertilizer formulation.  $E_{\text{total}}$  decreased in 2007 and  
388 then increased. Natural disasters and livestock and poultry disease caused a marked  
389 decline in livestock breeding stock, which is the primary reason for the sudden  
390 decrease in NH<sub>3</sub> emissions in 2007. That is, livestock manure emissions decreased  
391 18.8% compared with 2006.

392 Regarding the contribution by each sector in China, the contribution of livestock  
393 manure spreading increased from 37.0% in 1978 to 45.5% in 2008 because  
394 fertilization practices changed from organic to inorganic fertilizer and then to a  
395 combination of these types. To encourage farmers to use more organic fertilizer and to  
396 spur the development of organic fertilizer resources across the country, in 1988, the  
397 Chinese State Council published "With respect to instruction of valuing and  
398 reinforcing organic fertilizer." Subsequently, farmers realized that organic fertilizer

399 could play a significant role in water conservation, soil fertilization and soil  
400 improvement. In addition, livestock and poultry breeding techniques were improved  
401 as a result of the rapid increase in egg, milk and meat consumption. The contribution  
402 of livestock manure spreading (from pigs, poultry and dairy cattle) has been  
403 increasing during the past 31 years, others (from cattle, sheep, horses, donkeys and  
404 mules) have observed the opposite trend. However, the largest contributors are cattle  
405 and pigs (46.6% and 23.3%, respectively, on average) (Table S4). The average  
406 contribution of synthetic fertilizer to  $E_{total}$  is approximately 38.3% during the past 31  
407 years, and the minimum and maximum is 33.4% and 42.7% respectively. Generally,  
408 synthetic fertilizer application exhibits a strong positive correlation with crop yields  
409 ( $R^2=0.89$ ) (Fig. S6). In addition, because of the growth effect of synthetic fertilizer in  
410 agriculture, the high demand for synthetic fertilizer will not change. Synthetic  
411 fertilizer application will continue to increase as the optimization of the domestic  
412 agricultural planting structure and the cash crop planting area increase. The  
413 contribution of the rural excrement sector substantially decreased from 20.3% in 1978  
414 to 8.5% in 2008 as a result of the decline in China's rural population that accompanied  
415 rapid urbanization. The contributions of cake fertilizer and straw returning were small  
416 and remained stable during the study period. Their average contributions were  
417 approximately 3.8% and 4.5%, respectively. Collectively, these findings support the  
418 hypothesis that in addition to the limitation of climate conditions, agricultural  
419 production suffered as a consequence of the co-ordination and control of the country's  
420 agricultural policy, which directly affected the  $NH_3$  emissions of fertilizers used in  
421 agricultural production. That is, to a certain extent, the  $NH_3$  emissions attributable to  
422 agricultural fertilizer reflect the country's agricultural policy. Overall, our findings are  
423 in substantial qualitative agreement with the analysis of China's fertilizer policies by  
424 Li et al (Li et al., 2013).

425

#### 426 **4. Discussion**

#### 427 **4.1 Differences with Previous NH<sub>3</sub> Emissions Inventories**

428 Table 1 presents a comparison of the 2004-2008 NH<sub>3</sub> emission inventories for China  
429 of this study with other inventories that investigated the same emission sources. Our  
430 estimate is 22.8% less than that of EDGAR v.4.2 (2013), 20.4% less than that of Cao  
431 et al. (2010), and 43.1% less than that of Dong et al. (2010). These differences  
432 primarily result from differences in synthetic fertilizer emissions. The previous  
433 estimates employed uniform EFs for the entire country, which were derived from  
434 foreign expert evaluations or European rather than local data. However, despite using  
435 corrected EFs (Zhang et al., 2011), our estimate is 23.3% lower than that of Zhang et  
436 al. (2011). This difference can be partly attributed to the choice of parameters used in  
437 the EF corrections. Our estimate is completely based on local measurements, whereas  
438 the results of Zhang et al. (2011) were primarily based on measurements performed in  
439 Europe. Our estimate is 23.8% higher than that of Huang et al. (2012), 14.5% higher  
440 than that of Paulot et al. (2014), 19.2% higher than that of Wang et al. (2009), and 7.7%  
441 higher than that of Li et al. (2012). These differences are explained by the differences  
442 in base year and by the use of regional EFs as well as local and high-resolution  
443 activity data. The annual NH<sub>3</sub> emissions calculated in this study were compared with  
444 previous estimates (Wang et al., 2009; Dong et al., 2010), and the results are shown in  
445 Fig. 5 (a). A year-by-year comparison of the findings of EDGAR v.4.2 (2013) or  
446 Wang et al. (2009) with the findings of this study indicates that the growth trends  
447 compare well for 1980-2005. Our estimates for 1994 to 2006 are approximately 1.8  
448 times lower than those of Dong et al. (2010) for each year. We compared our monthly  
449 variation of synthetic fertilizer application to the findings of Paulot et al. (2014),  
450 Huang et al. (2012) and Zhang et al. (2011). Our estimates agree well with the above  
451 three inventories for the monthly variation tendency. However, in our study and that  
452 of Zhang et al. (2011), emissions peaked in July, whereas in Huang et al. (2012), the  
453 emissions peaked in August, and the maximum emission occurred during summer,  
454 this phenomenon could be primarily attributed to the local climate conditions, which



455 affected the EFs for the base year, but in Paulot et al. (2014), the emissions peaked in  
456 April because erroneous planting dates were used in the crop model such as the winter  
457 wheat-summer corn rotation, corn sown in June instead of April in China (Huang et al.  
458 2012). This study assumes that 60% of the synthetic fertilizer is used in planting, 20%  
459 in growth and 20% in harvest. Regarding livestock manure, our estimates are  
460 approximately 1.6 times larger than the monthly results of Huang et al. because of  
461 different base years, EF selection and differences in livestock population. In our study,  
462 emissions for livestock manure spreading peaked in June-August, which was similar  
463 to the corresponding findings of Paulot et al. (2014), whereas the monthly emission in  
464 winter in our study was nearly 2.2-fold higher than in Paulot et al. (2014). The reason  
465 is that in Paulot et al. (2014) the timing of livestock manure spreading is presumed to  
466 be identical with synthetic fertilizer application and the crops hardly need synthetic  
467 fertilizer application in winter, however, in this study the number of livestock is same  
468 during each month of the year and the EFs for the same season of different months are  
469 equivalent.

470

#### 471 **4.2 Impacts of NH<sub>3</sub> Emissions on Urban Air pollution**

472 A key research and policy question is how NH<sub>3</sub> emissions affect China's urban air  
473 pollution (in terms of PM<sub>2.5</sub> and its precursors, e.g., NO<sub>x</sub>, SO<sub>2</sub> and NH<sub>3</sub>). Because  
474 China is a large agricultural country, CAF is the nation's largest emitter of NH<sub>3</sub>.  
475 However, China is in the midst of an urban expansion necessary to becoming an  
476 economic superpower. The nation's urbanization rate (the urbanization rate equals the  
477 proportion of the urban population and the total population, <http://www.stats.gov.cn/>)  
478 rapidly increased from 17.9% in 1978 to 47.0% in 2008 (NBSC, 2009a). In addition  
479 to urbanization, the difference between CAF NH<sub>3</sub> emissions and NO<sub>x</sub> and SO<sub>2</sub>  
480 emissions from fossil-fuel combustion is being effaced by the development of  
481 intensive agricultural and livestock production in marginal zones between rural and  
482 urban areas, which results in PM<sub>2.5</sub> that exacerbates urban air quality because the

483 pollutants react more easily (Gu et al., 2014). Additionally, the high PM<sub>2.5</sub> levels of  
484 2014 in China occurred in areas that overlap with agricultural areas (Fig. S7).  
485 Apparently, the CAF NH<sub>3</sub> emissions cause urban air pollution by aerial transformation.  
486 Using a response surface modeling technique, Wang et al. (Wang et al., 2011) revealed  
487 that approximately 50-60% of the increases in NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> aerosol concentrations  
488 were caused by the 90% increase in NH<sub>3</sub> emissions from 1990-2005 in East China.  
489 Wang et al.(Wang et al., 2013) utilized GEOS-Chem to examine the impact of  
490 precursors of changes in anthropogenic emissions on the change in  
491 sulfate-nitrate-ammonium aerosols over China during 2000-2015, and found that the  
492 advantage of SO<sub>2</sub> reduction would be totally neutralized if NH<sub>3</sub> emissions increased  
493 by 16% from 2006 to 2015, as anticipated based on China's recent growth rate.  
494 Therefore, to decrease PM<sub>2.5</sub> concentrations and improve urban air quality in China, a  
495 more effective approach would be to simultaneously decrease NO<sub>x</sub>, SO<sub>2</sub> and NH<sub>3</sub>  
496 emissions. However, the determination of the degree to which CAF NH<sub>3</sub> contributes  
497 to the urban PM<sub>2.5</sub> concentration is a topic for future research. Our high resolution  
498 inventory can be applied to simulate atmospheric aerosol formation in air quality  
499 models with a bidirectional NH<sub>3</sub> exchange module, and then explore the effects of  
500 NH<sub>3</sub> emissions on China's urban air pollution.

501

## 502 **5. Implications for NH<sub>3</sub> Emissions**

503 With the local high-resolution data, spatially and temporally precise EF<sub>NH3</sub> and related  
504 parameters, times series of CAF\_NH<sub>3</sub> emissions were developed, which provide the  
505 high-resolution maps of NH<sub>3</sub> emission densities, the source apportionment, and the  
506 spatial and temporal pattern for 2008 as well as a historical time trend analysis of total  
507 NH<sub>3</sub> emissions from 1978 to 2008. Additionally, we could distinguish NH<sub>3</sub> emissions  
508 hotspots and their spatial and temporal variations as well as identify the influence of  
509 national agricultural policy changes on NH<sub>3</sub> emissions because the initiation of reform  
510 and opening-up. Fortunately, the rate of NH<sub>3</sub> emissions during the last decade has

511 increased slowly compared with 1978-1996. Because of their high volatility, urea and  
512 ABC have been gradually replaced by compound nitrogen-phosphorous-potassium  
513 and organic fertilizers in the wake of the country attaching greater importance to the  
514 food security problem. Although an increasing portion of the rural population has  
515 moved to cities in the current period of rapid urbanization, a large rural population  
516 will continue to exist in the next decades (Wang et al., 2012). Agricultural fertilizer  
517 will continue to be required to meet the increasing demand for food, and fertilizer  
518 application technology will slowly improve (Sutton et al., 2011). To decrease the NH<sub>3</sub>  
519 emissions from agricultural fertilizers, it is necessary to enhance the efficient use of  
520 agricultural fertilizer, reduce the intensity of agricultural fertilizer use, improve  
521 environmental factors and accelerate abatement strategy development. Liu et al. (2013,  
522 2010a) noted that the accuracy as well as the temporal and spatial resolution of  
523 CAF\_NH<sub>3</sub> inventories is essential to better quantify atmospheric N deposition and  
524 more accurately assess nitrogen flows in cropland (Liu et al., 2013;Liu et al., 2010a).  
525 Nevertheless, our inventory still exist several uncertainties especially in the emissions  
526 from synthetic fertilizer application and livestock manure spreading due to the  
527 exceedingly high values and large amount of parameters related to the emission  
528 factors adjustment. It has been demonstrated that a dependable data-driven approach  
529 and local experiments or process-based models can substantially help increase the  
530 spatial and temporal resolution and decrease the uncertainties of emissions inventories.  
531 Therefore, they should be implemented in the future research.

532

### 533 **Supporting Information**

534 Additional Supporting Information may be found in the online version of this article:

535 Appendix S1: Methodology

536 Appendix S2: Data on activity data, EFs, and RPs

537 Appendix S3: Supplement results

538 Appendix S4: Supporting references

539 Number of figures: 7

540 Number of tables: 4

541

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545

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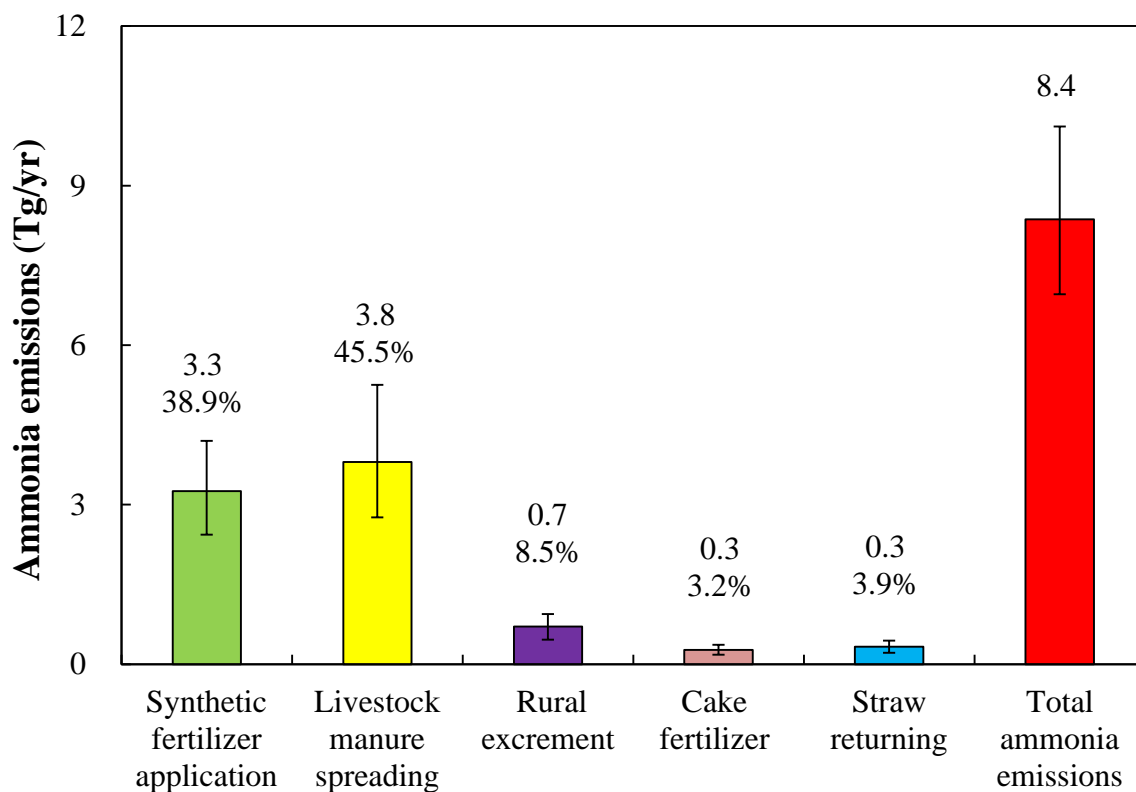
783 Table 1 Total NH<sub>3</sub> Emissions (TgNH<sub>3</sub> yr<sup>-1</sup>); source profile by sector after 2004 and  
784 their comparisons with previous studies; Note: SF = Synthetic fertilizer application;  
785 LS = Livestock manure spreading; RE = Rural excrement; CF = Cake fertilizer; SR =  
786 Straw returning. The gray shaded segments represent the sum of LS and RE.

787

References	Base year	EFs	SF	LS	RE	CF	SR	total
This study	2008	Correction EFs	3.3	3.8	0.7	0.3	0.3	8.4
Paulot et al., 2014	2005-2008	Region-specific EFs	3.6	2.6				6.2
EDGAR, 2013	2008	IPCC	8.1	1.1				9.2

Cao et al., 2010	2007	EEA	3.6	6.2				9.8
Huang et al., 2012	2006	Correction EFs	3.2	2.4	0.2	0.3	0.3	6.4
Dong et al., 2010	2006	EEA	8.7	4.3	0.7			13.7
Wang et al., 2009	2005	Region-specific EFs	3.5	2.8				6.3
Zhang et al., 2011	2005	Correction EFs	4.3					4.3
Li and Li, 2012	2004	Region-specific EFs	1.8	3.7	1.7			7.2

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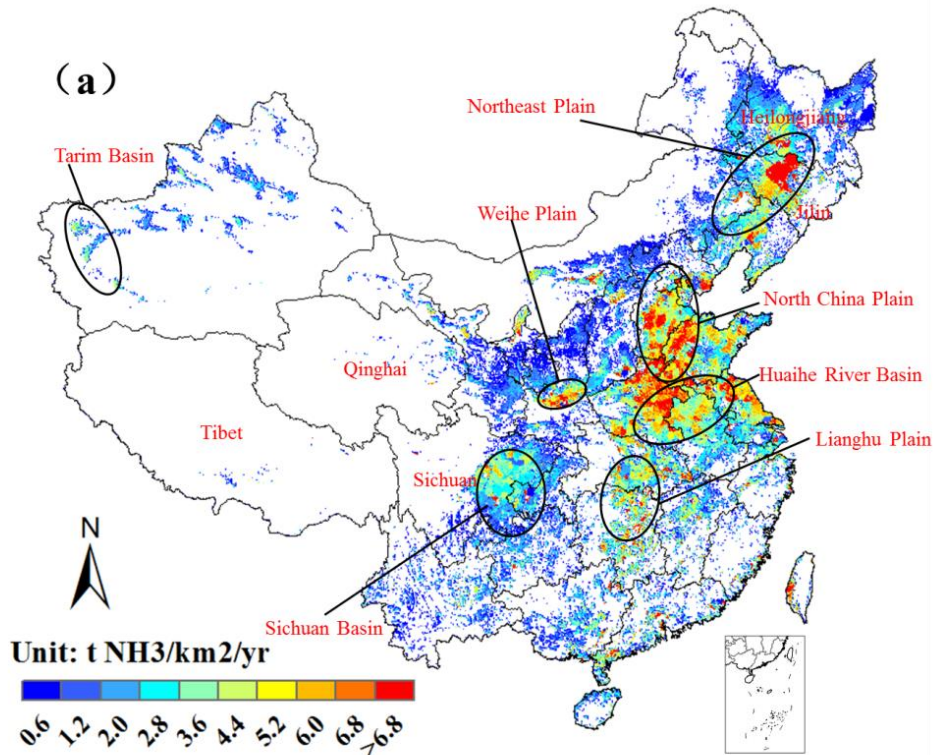


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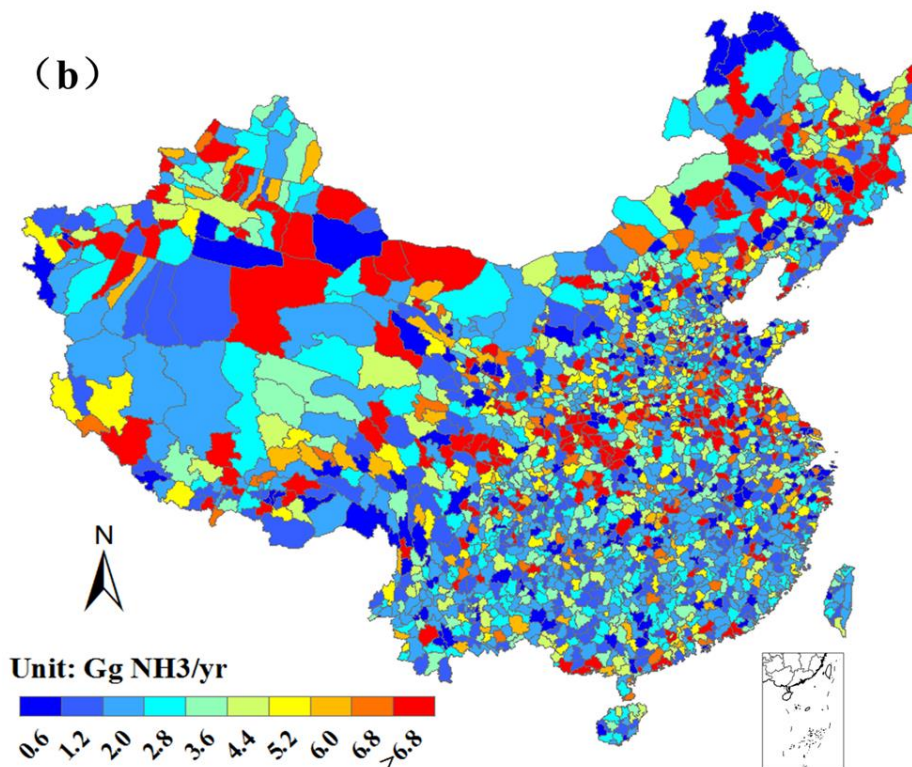
790 Figure.1 NH<sub>3</sub> emissions from CAF for 2008 by source, and the associated

791 uncertainties.

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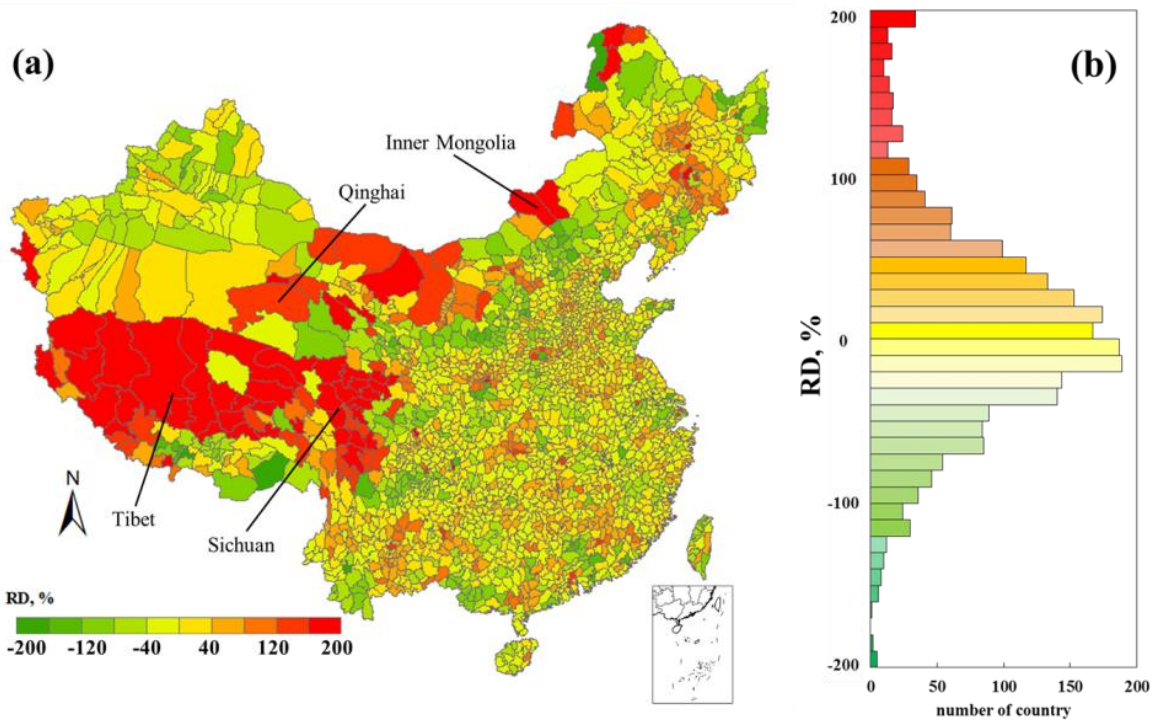


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795 Figure.2 NH<sub>3</sub> emission map of China's agricultural fertilizer at 1 km × 1 km (a) and

796 the county level (b) for 2008. Major emission areas are circled.

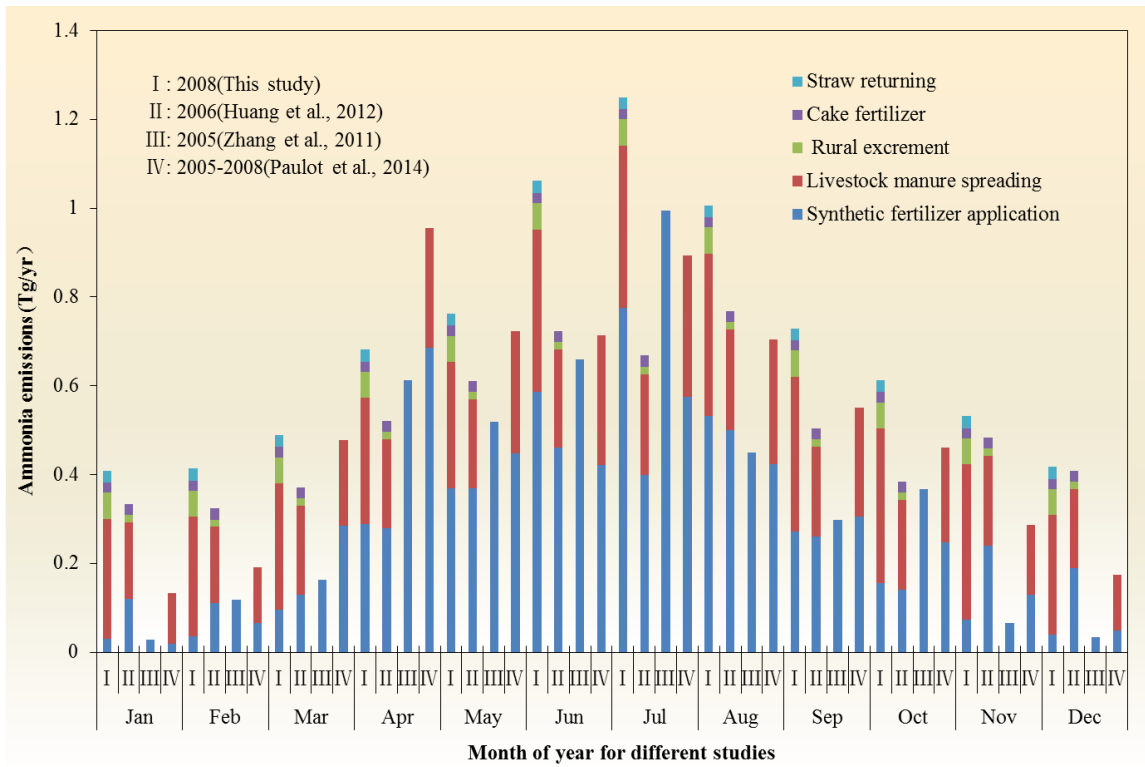
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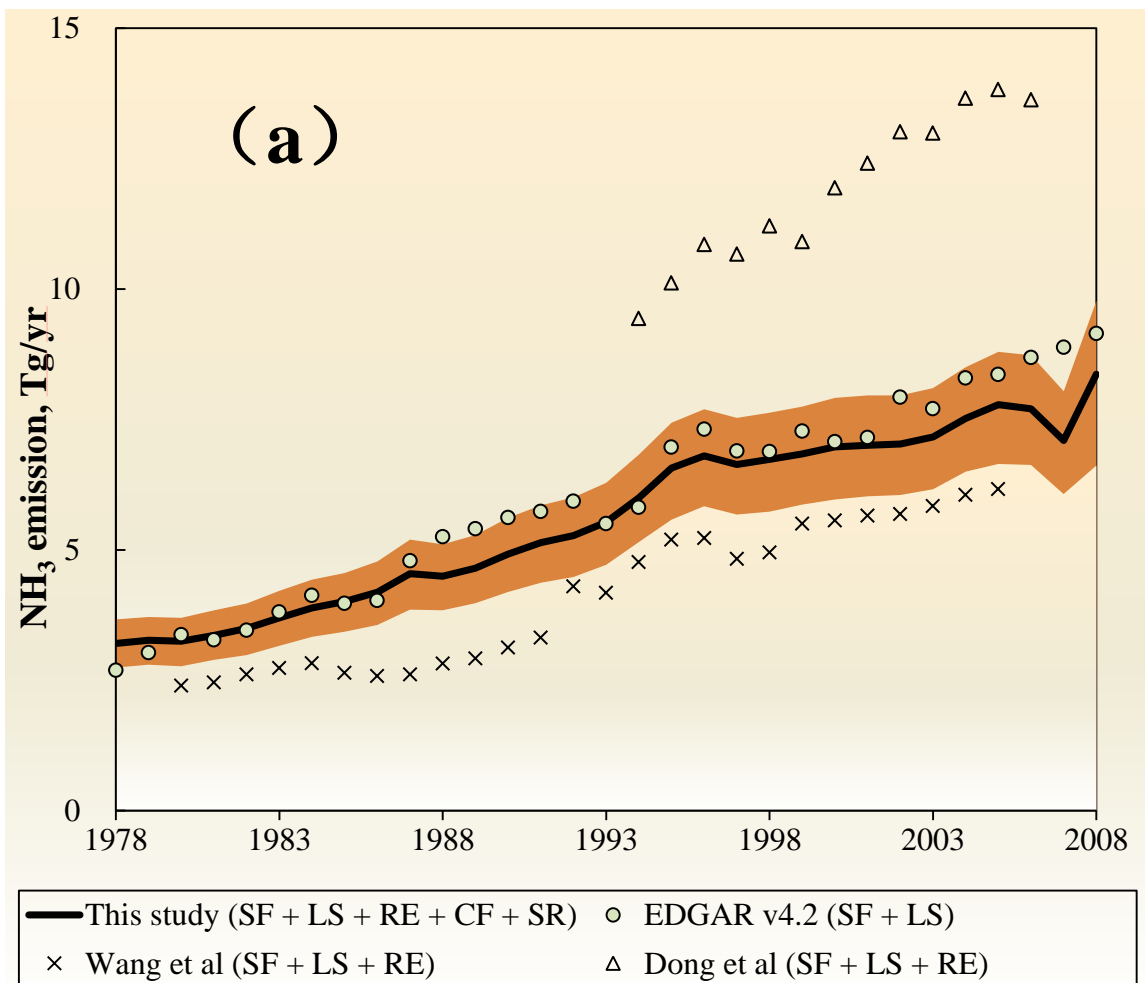
799 Figure.3 Geographic (a) and frequency (b) distributions of RDs of total NH<sub>3</sub>  
 800 emissions in 2008 between CAF\_NH<sub>3</sub> and PRO-NH<sub>3</sub>.  $RD = (E_1 - E_2) / ((E_1 + E_2)/2)$ ,  
 801 where  $E_1$  and  $E_2$  are the  $E_{total}$  for agricultural fertilizer of the counties for CAF\_NH<sub>3</sub>  
 802 and for PRO-NH<sub>3</sub> for each county, respectively. A negative (positive) RD suggests an  
 803 overestimation (underestimation) of a county's emissions by utilizing the provincial  
 804 disaggregation approach (PRO-NH<sub>3</sub>).

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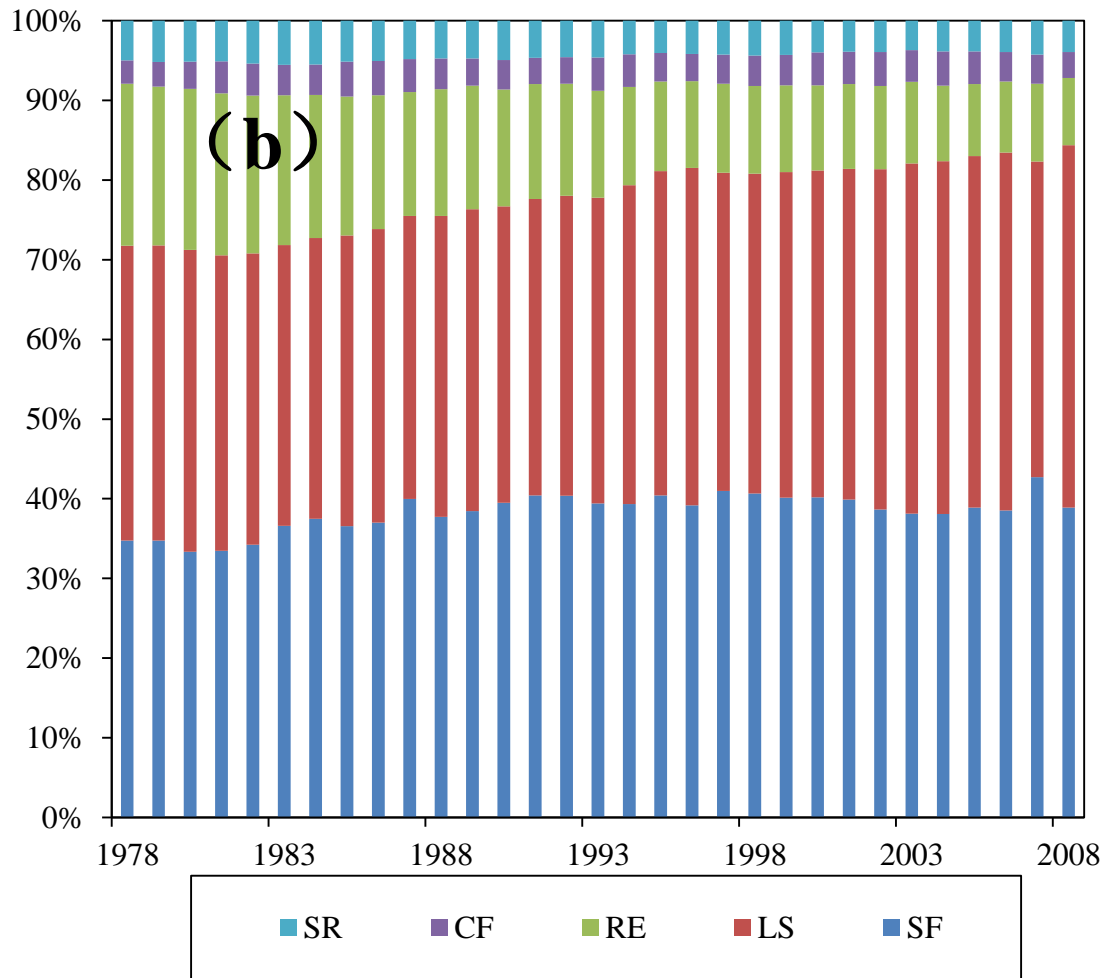
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807 Figure.4 Monthly NH<sub>3</sub> emissions in 2008 and compared with earlier studies.



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811 Figure.5 Temporal trend for agricultural fertilizer  $\text{NH}_3$  emissions for China (a) and  
 812 sector contributions between 1978 and 2008 (b). The emission estimate and the  
 813 uncertainty are provided as a median value (black curve) and the  $R_{50}$  (shaded area, for  
 814 total emissions) derived from a Monte Carlo simulation. Note: SF = Synthetic  
 815 fertilizer application; LS = Livestock manure spreading; RE = Rural excrement; CF =  
 816 Cake fertilizer; SR = Straw returning.