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Estimating NH_3 emissions from agricultural fertilizer application in China using the bi-directional CMAQ model coupled to an agro-ecosystem model

X. Fu[1,2], S. X. Wang[1,2], L. M. Ran[3], J. E. Pleim[4], E. Cooter[4], J. O. Bash[4], V. Benson[5], and J. M. Hao[1,6]

[1]State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China
[2]State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China
[3]University of North Carolina, Institute for the Environment, Chapel Hill, North Carolina, USA
[4]US Environmental Protection Agency, Research Triangle Park, North Carolina, USA
[5]Benson Consulting, Columbia, Missouri, USA
[6]Collaborative Innovation Center for Regional Environmental Quality, Tsinghua University, Beijing 100084, China

Correspondence to: S. X. Wang (shxwang@tsinghua.edu.cn)

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Abstract. Atmospheric ammonia (NH_3) plays an important role in atmospheric aerosol chemistry. China is one of the largest NH_3 emitting countries with the majority of NH_3 emissions coming from agricultural practices, such as fertilizer application and livestock production. The current NH_3 emission estimates in China are mainly based on pre-defined emission factors that lack temporal or spatial details, which are needed to accurately predict NH_3 emissions. This study provides the first online estimate of NH_3 emissions from agricultural fertilizer application in China, using an agricultural fertilizer modeling system which couples a regional air quality model (the Community Multi-scale Air Quality model, or CMAQ) and an agro-ecosystem model (the Environmental Policy Integrated Climate model, or EPIC). This method improves the spatial and temporal resolution of NH_3 emissions from this sector.

We combined the cropland area data of 14 crops from 2710 counties with the Moderate Resolution Imaging Spectroradiometer (MODIS) land use data to determine the crop distribution. The fertilizer application rates and methods for different crops were collected at provincial or agricultural region levels. The EPIC outputs of daily fertilizer application and soil characteristics were input into the CMAQ model and the hourly NH_3 emissions were calculated online with CMAQ running. The estimated agricultural fertilizer NH_3 emissions in this study were approximately 3 Tg in 2011. The regions with the highest modeled emission rates are located in the North China Plain. Seasonally, peak ammonia emissions occur from April to July. Compared with previous researches, this study considers an increased number of influencing factors, such as meteorological fields, soil and fertilizer application, and provides improved NH_3 emissions with higher spatial and temporal resolution.

1 Introduction

Ammonia (NH_3) is the most important and abundant alkaline constituent in the atmosphere, with a wide range of impacts. It plays a key role in atmospheric chemistry and ambient particle formation. NH_3 partitions to sulfate (SO_4^{2-}), and nitrate (NO_3^-) aerosol, adding to the concentration of secondary inorganic aerosol (SIA), including sulfate, nitrate, and ammonium. Field measurements indicate that SIA is a major contributing factor during haze days in China (He et al., 2014; Wang et al., 2012; K. Huang et al., 2012). Ye et al. (2011) observed a strong correlation between peak levels of fine particles and large increases in NH_3 concentrations. High aerosol concentrations also have a significant effect on visibility range, climate forcing, and human

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health (Cheng et al., 2013; Ding et al., 2013; Pope III et al., 2011). In addition, the deposition of ammonium particles (NH_4^+) and gaseous ammonia can cause soil acidification, water eutrophication, loss of biodiversity, and perturbation of ecosystems (Lepori and Keck, 2012; Stevens et al., 2004; Zhu et al., 2013). As one of the largest agricultural and meat producers in the world (FAO, 2013), China is a significant source of NH_3 emissions. Previous studies have indicated that China's ammonia emissions contribute 23 % of the global NH_3 budget (EDGARv4.1 2015; http://edgar.jrc.ec.europa.eu/datasets_list.php?v=41) and present a continuously increasing trend (Dong et al., 2010).

Nitrogen fertilizer use is one of the largest sources of NH_3 emissions in China, accounting for 35–55 % of the national total (X. Huang et al., 2012; Zhao et al., 2013). There are many studies focusing on NH_3 emissions from agricultural fertilizer in China, but they are mostly based on traditional "emission factors" (EFs) methods. Some of them (Klimont, 2001; Streets et al., 2003; Dong et al., 2010; Zhao et al., 2013) use nationally averaged EFs for the whole of China. However, ammonia volatilization from nitrogen fertilizer application depends strongly on localized environmental parameters, such as ambient temperature and soil acidity (Roelle and Aneja, 2002; Corstanje et al., 2008). In addition, fertilizer application dates and application amounts vary by geographical regions and crop types. Therefore, these estimates are subject to high uncertainties, especially in their temporal and spatial distributions. Zhang et al. (2011) and X. Huang et al. (2012) use some relative correction factors to introduce the impacts of temperature, soil properties, and fertilization method, which somewhat reduce temporal and spatial uncertainties. In recent years, some scientists from outside China have begun to focus on estimating NH_3 emissions based on a bi-directional surface flux model (Cooter et al., 2010; Wichink Kruit et al., 2012). For example, a group at the U.S. Environmental Protection Agency (US EPA) (Cooter et al., 2012; Bash et al., 2013; Pleim et al., 2013) has modified the Community Multi-scale Air Quality (CMAQ) model to include a bi-directional NH_3 exchange module. It is coupled to the Fertilizer Emission Scenario Tool for CMAQ (FEST-C) system (Ran et al., 2010; CMAS, 2014), which contains the Environmental Policy Integrated Climate (EPIC) model (Williams et al., 1984). This system includes the influences of meteorology, air–surface exchange, and human agricultural activity. It has been used to simulate the bi-directional exchange of NH_3 in the United States. Compared with a traditional emission inventory, the model performances for NO_3^- concentration and N deposition in the USA are improved (Bash et al., 2013). However, until now this method has not yet been used to estimate the agricultural fertilizer NH_3 emission in China.

For the first time in this study, we estimate China's NH_3 emission from agricultural fertilizer use in 2011, based on the CMAQ model with a bi-directional NH_3 exchange module coupled to the FEST-C system with the EPIC agro-ecosystem model. The structure of this modeling system and input data processing are described in detail in the next section. The results of the fertilizer use and NH_3 emissions simulation, along with a comparison to other studies, are discussed in Sect. 3. The results of CMAQ modeling are also discussed and compared with field measurements. Finally, the uncertainties of this method are discussed in detail at the end of the section.

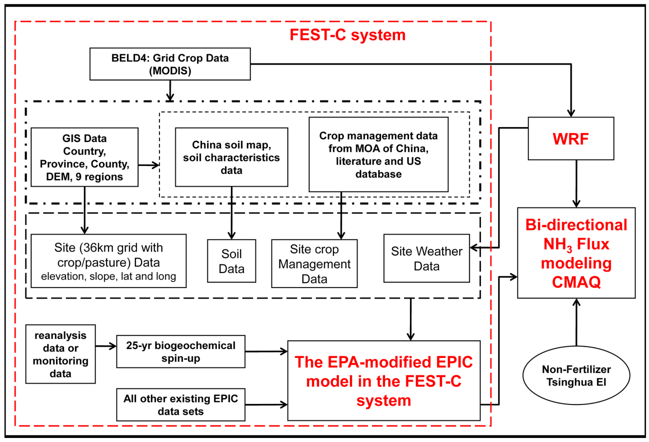

Figure 1. The modeling system of agricultural fertilizer NH_3 emission for China.

2 Methodology and inputs

2.1 General description of the modeling system

Figure 1 shows the structure of the modeling system, which contains three main components: (1) the FEST-C system containing the EPIC model, (2) the mesoscale meteorology Weather Research and Forecasting (WRF) model, and (3) the CMAQ air quality model with bi-directional ammonia fluxes. A detailed description of the bi-directional module can be found in Bash et al. (2013). Soil NH_4^+ content and agricultural activity data were simulated by the EPIC model in the FEST-C system. In order to run the EPIC model for this study, we collected and processed local Chinese agricultural information, such as crop distribution, soil characteristics, climate patterns, and fertilizer use characteristics. The details regarding these data sources and processing methods are described in Sect. 2.2. In addition to agricultural activity and soil information, this system also considers the influence of WRF-simulated weather on NH_3 emissions. The tools in the FEST-C system can be used to process the EPIC input data and also extract the EPIC daily output data required for CMAQ (CMAS, 2014).

The CMAQ simulation domain, as shown in Fig. 2, is based on a Lambert projection with two true latitudes of 25 and 40° N and covers most of East Asia with a grid resolu-

Figure 2. The modeling domain. The black points represent the locations of the nitrate observations.

tion of 36 km × 36 km. EPIC data and micrometeorological parameters are estimated for each modeled CMAQ grid cell.

2.2 EPIC modeling in the FEST-C system

The EPIC model is a semi-empirical agro-ecosystem model which is designed to simulate agricultural fields that are characterized by soil, landscape, weather, and crop management (Williams et al., 1984). A wide range of vegetative systems, tillage systems, and other crop management practices can be simulated in this model (Gassman et al., 2005). Additionally, soil nitrogen (N), carbon (C), and phosphorus (P) biogeochemical process models are incorporated into EPIC. Therefore, it is well suited for simulation of fertilizer management and soil nitrogen content in agricultural systems. The input information required by EPIC includes crop site information, soil characteristics, weather, and crop management, which are described in detail in the next section. All data are processed to a 36 km × 36 km grid for integration with the air quality model, CMAQ.

2.2.1 Crops

Fourteen crop types are modeled in this study: early rice, middle rice, late rice, winter wheat, spring wheat, corn, sorghum, barley, soybean, potato, peanuts, canola, cotton and other crops. The "other crops" category represents all remaining crops. Data on the cropland area[1] for each crop grown in the 2710 counties studied was collected and processed based on province-level or city-level statistical yearbooks. The Moderate Resolution Imaging Spectroradiometer (MODIS; https://lpdaac.usgs.gov/products/modis_products_table/mcd12q1) was used to provide finer-level land use information. The MODIS land use product provides annual 500 m pixel-scale information for 20 land use categories. MODIS classes 12 (cropland) and 14 (cropland/natural vegetation mosaic) are of particular interest in this study. In addition, irrigation is an important factor for crop growth and soil characteristics. Here, we used the global irrigated area map (GIAM) at 1 km resolution (Thenkabail et al., 2008) to divide each crop into irrigated and non-irrigated classes. The BELD4 tool in FEST-C system was used to process these data into 36 km × 36 km grid cell (CMAS, 2014).

2.2.2 Soil information

The dominant soil type in each grid was taken from the Harmonized World Soil Database (HWSD; http://webarchive.iiasa.ac.at/Research/LUC/External-World-soil-database/HTML/), which gives soil distribution with 30 arc-second resolution (about 1 km × 1 km maximally) in China. We matched the soil in each grid with a specific soil profile in a US database (Cooter et al., 2012) based on soil type, ecological region, and latitude. Soil characteristics of the matched soil were extracted as soil input for the corresponding grid, including layer depth, soil texture, soil carbon content, carbonate content, bulk density, cation exchange capacity, pH, etc. The assumption taken is that the characteristics of same soil types in similar eco-regions and latitudes between China and the US are similar. These soil characteristics were used as initial input data for EPIC because they were for general soil, not specially for agriculture soil. A spin-up run allowed the soil characteristics to adjust to agriculture management. For example, the EPIC model applied lime to maintain the soil pH at levels that reduce crop stress due to low pH. Besides, the soil characteristics are also updated with CMAQ running.

2.2.3 Weather

The weather parameters required by EPIC for this simulation included maximum and minimum temperature, radiation, precipitation, relative humidity, and 10 m wind speed. For the spin-up run, these variables were extracted from the NASA Modern Era Reanalysis for Research and Applications (MERRA; http://disc.sci.gsfc.nasa.gov/mdisc/overview/index.shtml) data, which provides weather information from 1979 to the present with 0.5° × 0.667° grid resolution (approximately 55 km × 75 km maximally). The climatological characteristics of the closest grid cell in MERRA to each EPIC model grid cell were selected as the weather input for the EPIC spin-up simulation run in each grid. For the year-specific EPIC run, the output of the WRF was processed to generate the gridded weather conditions on the CMAQ 36 km × 36 km grid using the *WRF/CMAQ to EPIC* tool in the FEST-C system (CMAS, 2014).

[1]Please contact the corresponding author for the data set.

2.2.4 Crop management

In the EPIC model, the timing of crop management can be prescribed or scheduled based on a heat-unit (HU) method, as described in Cooter et al. (2012). In this study, a combination of prescribed and HU scheduled timing was used. The HU scheduled timing allowed for adaptation to inter-annual and interregional temperature variability and more realistically represents a farmer's dynamic decision-making. At the same time, the timing was also limited to a fixed range based on available information from the Chinese planting information network (http://www.zzys.moa.gov.cn/) and unpublished research about crop management from the Chinese Academy of Agriculture Sciences.[2] This allowed the timing to be adjusted to Chinese agriculture.

Nitrogen fertilizer application information is necessary to accurately estimate NH_3 emissions in this study. The application rates for specific fertilizer type, crop, and province were extracted from Chinese statistical material (National Bureau of Statistics of China or NBSC, 2012b). The fertilizer types included urea, ammonium bicarbonate (ABC), diammonium phosphate (DAP), N–P–K compound fertilizer (NPK), and others (e.g., ammonium nitrate and ammonium sulfate). Table 1 shows the national average application rates for some major crops. We can see that the nitrogen fertilizer application rates for different crops are varied. The largest nitrogen amount is required for cotton and wheat, which are 228.11 and 196.22 $kg\,N\,ha^{-1}$, respectively. However, nitrogen-fixing crops (e.g., soybean and peanuts) require much less nitrogen input. Among all the fertilizer types, urea and ammonium bicarbonate are dominant.

Besides application rates, the ratio of basal and topdressing fertilizer is also important for ammonia volatilization. Basal fertilizer is used before crops are planted and topdressing fertilizer is used during crop growth. Figure 3 presents the Chinese agriculture regions used to characterize these management practices. Each region is a geographic area where crop management practices are assumed to be similar. Based on the results of previous field investigations (Wang et al., 2008; Zhang, 2008), the ratios of basal and topdressing fertilizer for different crops in each agriculture region are identified. Table 2 shows the fertilizer ratios used on three major crops in China and a clear geographical divergence can be observed. For example, the ratio of fertilizer used on wheat in the middle and lower Yangtze River region is 1.39, but only 0.33 in the southwest region. In general, the ratio of fertilizer used on corn is the highest of the three major crops. A greater amount of fertilizer is applied to corn just prior to or at planting than is applied to the crop later in the growing season. The information in Tables 1 and 2 was combined for this study to determine the amount of fertilizer applied to each crop in each grid cell during basal and topdressing activities.

[2]Please contact ylbai@caas.ac.cn for the data

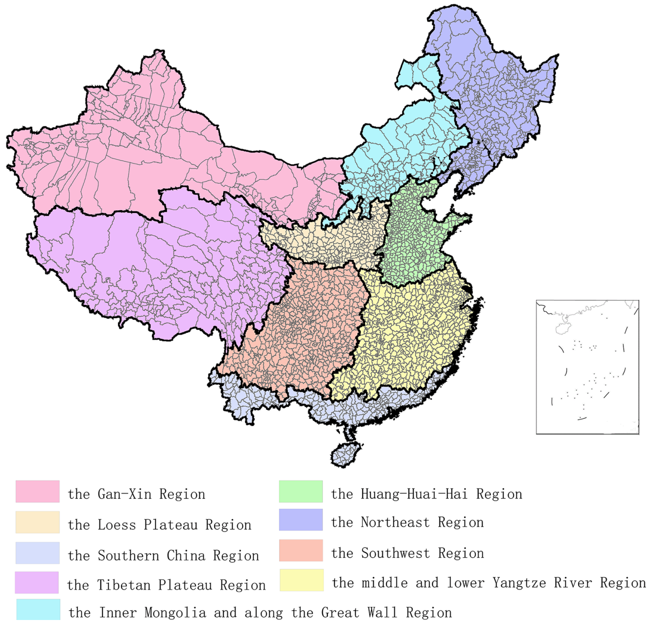

Figure 3. The nine agriculture regions in China. The thin black line represents the county boundary and the small insert represents the South China Sea and its islands.

2.3 The bi-directional CMAQ model system

Direct flux measurements have shown that the air–surface flux of NH_3 is bi-directional, and vegetation and soil can be either a sink or a source of atmospheric NH_3 (Fowler et al., 2009; Sutton et al., 1995). The direction and magnitude of the flux depend on the concentration gradient between canopy or soil and the atmosphere. Bash et al. (2013) has implemented a bi-directional ammonia flux module in CMAQv5.0.1 to represent this process. This module is based on the two-layer (soil and vegetation canopy) resistance model described by Pleim et al. (2013), which is similar to the model presented by Nemitz et al. (2001). The NH_3 air–surface flux (F_t) is calculated by the following formula

$$F_t = \frac{1}{R_a + 0.5R_{inc}} (C_c - C_a), \quad (1)$$

where the aerodynamic resistance (R_a) and the in-canopy aerodynamic resistance (R_{inc}) are calculated following Pleim et al. (2013). C_a is the atmospheric NH_3 concentration. C_c is a function of C_a, the soil compensation point (C_g) and the stomatal compensation point (C_{st}).

$$C_c = \frac{\frac{C_a}{R_a+0.5R_{inc}} + \frac{C_{st}}{R_b+R_{st}} + \frac{C_g}{0.5R_{inc}+R_{bg}+R_{soil}}}{(R_a+0.5R_{inc})^{-1} + (R_b+R_{st})^{-1} + (R_b+R_w)^{-1} + (0.5R_{inc}+R_{bg}+R_{soil})^{-1}}, \quad (2)$$

where the quasi-laminar boundary-layer resistance of leaf surface (R_b), the stomatal resistance (R_{st}) and the quasi-laminar boundary-layer resistance of ground surface (R_{bg})

Table 1. The 2011 national-average fertilizer application rate for major crops in China ($kg\,N\,ha^{-1}$).

	Total	Urea	ABC[a]	DAP[b]	NPK[c]	Others
Early rice	183.48	125.03	20.03	4.00	21.87	12.55
Middle rice	185.62	117.38	33.15	4.04	18.69	12.36
Late rice	181.14	124.20	19.13	4.02	21.63	12.17
Wheat	196.22	123.90	19.05	16.14	29.98	7.16
Corn	186.75	123.45	19.05	12.63	18.85	12.77
Soybean	45.92	19.50	1.65	10.48	11.51	2.77
Peanuts	95.14	36.30	11.70	3.43	29.03	14.68
Canola	128.14	75.90	30.90	2.35	11.02	7.97
Cotton	228.11	152.40	9.45	24.34	27.45	14.46

[a] ammonium bicarbonate (ABC); [b] diammonium phosphate (DAP); [c] N–P–K compound fertilizer (NPK)

Table 2. Ratio of basal and topdressing fertilizer for major crops in each agriculture region.

Region	Wheat		Corn		Rice	
	basal	topdressing	basal	topdressing	basal	topdressing
The northeast region	1.00	0.80	1.00	1.23	1.00	0.88
The Gan-Xin region	1.00	0.44	1.00	3.50	1.00	1.00
The southern China region	1.00	1.00	1.00	2.98	1.00	2.91
The Huang-Huai-Hai region	1.00	0.80	1.00	2.07	1.00	1.29
The Loess Plateau region	1.00	0.44	1.00	3.50	1.00	1.00
The Inner Mongolia and along the Great Wall region	1.00	0.44	1.00	3.50	1.00	1.00
The Tibetan Plateau region	1.00	0.44	1.00	3.50	1.00	1.00
The southwest region	1.00	0.33	1.00	2.33	1.00	1.88
The middle and lower Yangtze River region	1.00	1.39	1.00	1.66	1.00	1.29

are calculated following Pleim et al. (2013). The cuticular resistance (R_w) is a function of C_c similar to Jones et al. (2007). C_{st} and C_g are calculated as follows:

$$C_{st} = M_n/V_m \frac{161\ 500}{T_c} e^{\left(-\frac{10\ 380}{T_c}\right)} \Gamma_s, \quad (3)$$

$$C_g = M_n/V_m \frac{161\ 500}{T_s} e^{\left(-\frac{10\ 380}{T_s}\right)} \Gamma_g, \quad (4)$$

where M_n is the molar mass of NH_3, V_m is the conversion factor of L to m^3, and T_s and T_c are the soil and canopy temperature in K. The apoplast gamma (Γ_s) is modeled with a function similar to Zhang et al. (2010). The soil gamma (Γ_g) is defined as soil $[NH_4^+]/[H^+]$, and the soil NH_4^+ budget in CMAQ is parameterized following the method in EPIC (Williams et al., 1984). The soil NH_4^+ would increase due to N deposition, and decrease due to NH_3 evasion and soil nitrification. When fertilizer is used, Γ_g is calculated by the following function:

$$\Gamma_g = \frac{N_{app}/(\theta_s M_N d_s)}{10^{-pH}}, \quad (5)$$

where N_{app} is the fertilizer application rate ($g\,N\,m^{-2}$), θ_s is the soil volumetric water content ($m^3\,m^{-3}$), M_N is the molar mass of nitrogen ($14\,g\,mol^{-1}$), d_s is the depth of soil layer (m), and pH is soil pH. The initial soil NH_4^+, θ_s and pH are taken from the EPIC output and then calculated in CMAQ hourly.

In addition to the inputs of soil condition and fertilizer use, other input data used were the same as those in the traditional CMAQ model. WRF version 3.5.1 was used to generate the meteorological input. The configuration options used in WRF and CMAQ were the same as those described by Fu et al. (2014).

In order to evaluate the performance of this method, two simulations – a base case and a bi-directional case (bidi case) – were conducted in this study using different methods to estimate ammonia emissions from fertilizer use. For the base case, the emission inventory from Zhao et al. (2013) was used, which is estimated by the traditional “emission factors”

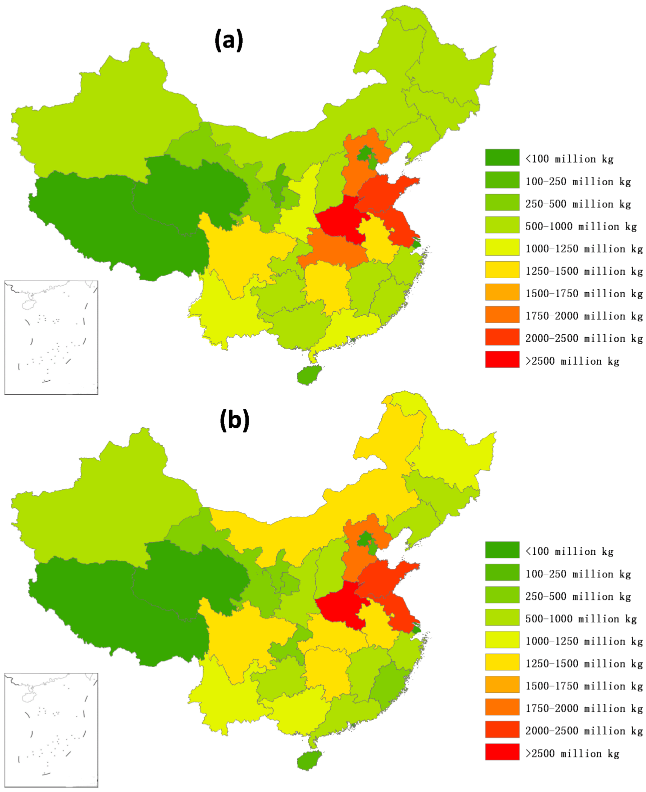

Figure 4. Comparison of annual N fertilizer use at province level between existing statistical data **(a)** and EPIC output **(b)**. The small insert represents the South China Sea and its islands.

method. This case did not include the bi-directional flux algorithm in CMAQ. For the bidi case, NH_3 emissions were estimated online using the bi-directional module in CMAQ. The emissions of ammonia from other sectors and the emissions of other pollutants were taken from Zhao et al. (2013) for both cases.

3 Results and discussion

3.1 Nitrogen fertilizer application

Nitrogen fertilizer application was a key aspect in this study, explored through a comparison of the EPIC results to existing statistical data. The N use in each grid cell per day is calculated by the following formula

$$\mathrm{USE}_i = \sum_{j=1}^{\mathrm{crop}} \left(N_{ij} \times f_{ij}\right) \times 129\,600, \tag{6}$$

where USE_i (kg) is the N application in grid cell i; N_{ij} ($\mathrm{kg\,ha^{-1}}$) is the N application rate in the grid cell i for crop j; f_{ij} is the fraction of cell used for crop j in grid cell i; and $129\,600\,\mathrm{ha\,grid^{-1}}$ is a conversion factor accounting for the area of the grid cell.

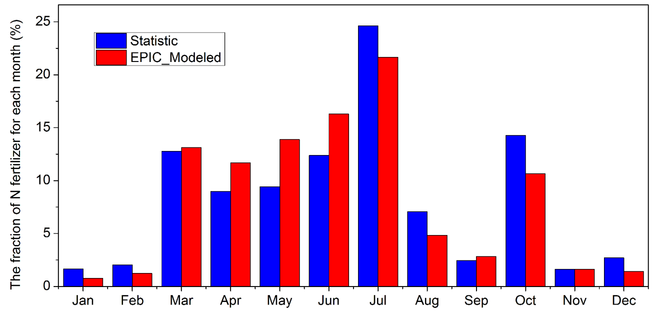

Figure 5. Comparison of the fraction of N fertilizer use by each month between statistics and EPIC output.

Figure 4a and b show the patterns of annual fertilizer use at province-level between the statistical data from NBSC (2012a) and the EPIC output. We can see that EPIC results captured the general pattern, especially for the provinces with the largest fertilizer use (> 1750 million kg), such as Henan, Shandong, Jiangsu, and Hebei provinces, where the biases were −9.7, −5.1, −1, and −0.6 %, respectively. At the same time, relatively large biases existed for some provinces, such as Hunan province (−20.6 %) and Heilongjiang province (19.2 %). This may be due to uncertainty in the statistical data. Additionally, the 36 km grid is relatively coarse and uncertainty exists for the gridded crop areas calculated according to the county-level statistical crop data and MODIS crop data. Because the provinces with a larger bias applied relatively small amounts of fertilizer, these modeled biases are not expected to lead to large biases in the simulations.

Figure 5 shows a comparison of the fraction of N fertilizer use each month between existing statistics and EPIC output. The statistical data is derived from the field investigation from Zhang et al. (2008) for 2004 and the model results capture the temporal characteristics. The fertilizer amounts used from March to July and in October dominated the model, which closely relates to the timing of crop fertilization in China. For example, the North China Plain is the most important agricultural production region in the country, where the major crop planting system is the winter wheat–summer corn rotation. Winter wheat is usually planted in October with an application of basal fertilizer, followed by the topdressing fertilizer in March and April of the next year. Basal fertilizer for summer corn is usually applied in June and topdressing fertilizer in July. The Northeast Plain, another major agricultural region, rice is the dominant crop. Due to temperature limitations, rice is usually seeded in April and May and the topdressing fertilizer is applied in June and July.

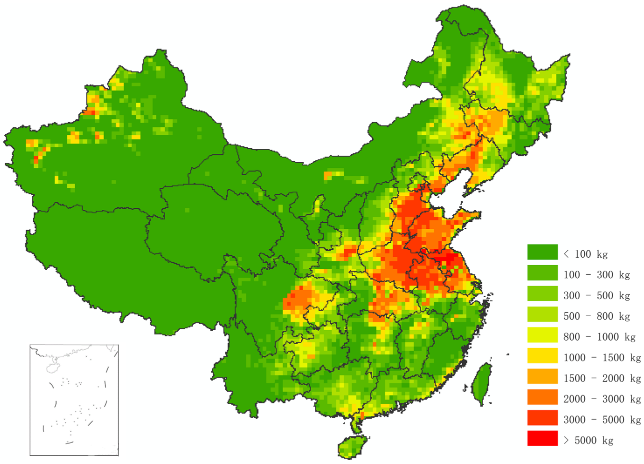

Figure 6. Spatial distribution of NH_3 emissions from N fertilizer use in $36\,km \times 36\,km$ grid cell ($kg\,yr^{-1}$). The small insert represents the South China Sea and its islands.

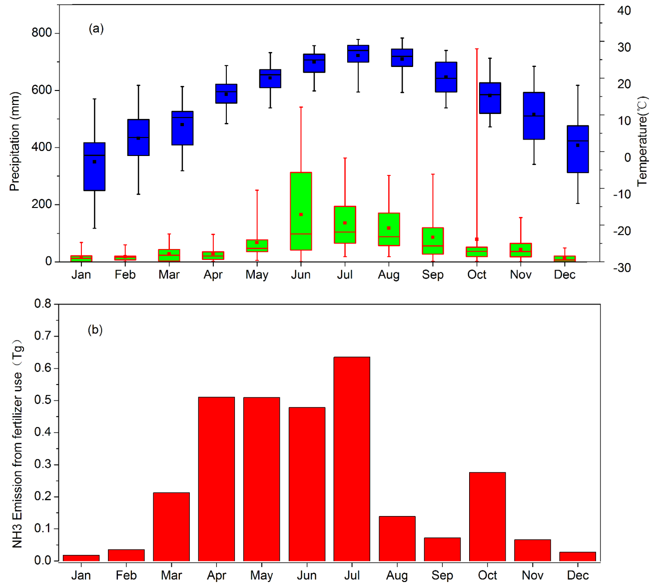

Figure 7. (a) The variation of monthly precipitation (green) and temperature (blue) in 31 provinces. In the box-and-whisker plots, the boxes and whiskers indicate the 100th (max), 75th, 50th (median), 25th and 0th (min) percentiles, respectively. The point represents the average value. **(b)** Monthly NH_3 emissions from N fertilizer use.

3.2 NH_3 emissions

3.2.1 Spatial and temporal distribution

The NH_3 emissions from N fertilizer application in 2011 estimated in this study were approximately 3.0 Tg. The spatial distribution of annual NH_3 emission in a $36\,km \times 36\,km$ grid is presented in Fig. 6 and shows that NH_3 volatilization was concentrated in Henan, Shandong, Hebei, Jiangsu, and Anhui provinces, accounting for 11.1, 9.9, 8.8, 6.7, and 7.1 % of total emissions, respectively. The highest NH_3 emissions in this region were above $386\,kg\,ha^{-1}$. The crop production here is the most intense in China and the total crop area in these five provinces accounts for about 31.4 % of China's total. These five provinces consumed approximately 37.3 % of the nitrogen fertilizer for the whole country in 2011 (NBSC, 2012b). Elevated emissions were also due to the high fertilizer application rate. For example, the rate of N fertilizer use for rice in Jiangsu province was above $300\,kg\,ha^{-1}$, which is twice the national average. The smaller contributors to NH_3 emission were primarily located in western China, in Tibet, Qinghai, and Gansu province, where the amount of arable land and N fertilizer use was small.

Figure 7b shows the monthly distribution of ammonia emissions, which were dominant from March to July, and in October, accounting for 88.7 % of the annual total. This agrees with the pattern of N fertilizer usage described in Sect. 3.1. Besides N fertilizer use, weather parameters, like temperature and precipitation, also affected the temporal and spatial distribution of emissions. For example, the emissions in March were much smaller than April and May due to lower temperatures (as shown in Fig. 7a), even though the amount of consumed fertilizer was nearly equivalent. Similarly, the emissions in June were slightly less than in April and May. A possible reason is that precipitation in June is greater than that in the previous 2 months. Based on the statistical data of major Chinese cities (NBSC, 2012a), the total precipitation in June 2011 was 165.1 mm, while in April and May, it was 28.5 and 67.4 mm, respectively (as shown in Fig. 7a). Figure S1 in the Supplement presents the spatial distribution for each month. Some differences for the months with larger emissions can be seen. For example, in the North China Plain, like Hebei, Henan, and Shandong provinces, NH_3 emissions were relatively small in May due to lower amounts of fertilizer application. In northeast China, including Liaoning, Jilin, and Heilongjiang provinces, the NH_3 emissions in May, June and July were dominant. In November, major NH_3 emissions occurred in Jiangsu, Hubei and Anhui provinces, when winter canola basal fertilizer was applied.

3.2.2 Comparison with other studies

The ammonia emissions from N fertilizer use in China were estimated for different base years by different methods. The results of comparisons between this study and some previous studies are listed in Table 3. In order to make the inventories comparable, we updated the emissions from different years to 2011 based on changes in fertilizer use, temperature, and precipitation, as described in the supplementary materials. As presented, the results of this study are generally equivalent and comparable to the research of Zhang et al. (2011) and X. Huang et al. (2012), which is 60–70 %

lower compared with other studies. The discrepancies are mostly caused by the various estimating methods and EFs employed. Streets et al. (2003), Dong et al. (2010) and Zhao et al. (2013) used averaged emission factors for all agriculture in China and did not consider the impacts of environmental parameters, e.g., soil pH, or precipitation. For example, the EFs for urea used by Streets et al. (2003), Dong et al. (2010), and Zhao et al. (2013) are 15–20 % (temperate and tropical ozone). However, the basic emission factors for urea used by X. Huang et al. (2012) are 8.8 % for acid soil and 30.1 % for alkaline soil. The agricultural regions in China are dominated by acidic soil (http://www.soil.csdb.cn/), so this value is nearly 50 % lower compared with averaged EFs. In addition to soil pH, precipitation can also decrease NH_3 emissions, because precipitation can increase the water content in soil and fertilizer N can be leached to a deeper soil layer by water (Wang et al., 2004). Zhang et al. (2011) adjusted the EFs by 0.75, 0.80, 0.85, 0.90, 0.95, and 1.0 for significant rainfall events (> 5 mm in 24 h) within 24, 24–48, 48–72, 72–96, 96–120, and > 120 h of fertilizer application. In this study, the impacts of soil pH and precipitation on NH_3 emissions were considered by impacting soil gamma and resistances, as shown in Sect. 2.3. In addition, our study and Zhang et al. (2011) included the impacts of irrigation. The experiments of Wang et al. (2004) in Beijing for the winter wheat–summer maize cycle show that NH_3 volatilization is reduced after irrigation and reveal a low EF value of 2.1–9.5 %.

Figures S4 and S5 represent the comparisons of provincial distributions and seasonal variations of these different NH_3 emission inventories. The provincial distributions are similar, and the emissions from Henan, Shandong, Jiangsu, Hebei, and Anhui provinces dominate the country's annual total emissions. At the same time, some discrepancy also exists for the specific provinces among the different studies, which may be caused by distinct fertilizer consumptions and emission rates employed. For example, for Henan province, the estimation of X. Huang et al. (2012) is the highest among these studies. A possible reason for this difference is that alkaline soil is dominant in Henan province and X. Huang et al. (2012) set a uniform high emission factor for alkaline soil, which is twice as high as that in Dong et al. (2010). Compared with provincial distributions, the difference of seasonal variations among these studies is larger. The seasonal profile in Zhao et al. (2013) is based on temperature variations. In addition to temperature, others also considered the impacts of fertilizer application timing. It is indeed difficult to capture the exact date of fertilization for all of China, which may have created this large discrepancy amongst studies. For example, X. Huang et al. (2012) states that the basal fertilizer and topdressing fertilizer of winter wheat are conducted in September and November. However, basal fertilizer was applied in October in our study and in the Zhang et al. (2011), and the topdressing fertilizer is mainly used in March of the next year. The diversity of seasonal fertilization among different studies reflects that the large uncertainties still exist for the temporal distribution of NH_3 emissions and shows that continued local research is needed.

Table 3. Comparison of NH_3 emissions from fertilizer use in our study with other published results.

Reference	Year	Original NH_3 Emission ($Tg\,yr^{-1}$)	Revised to 2011 ($Tg\,yr^{-1}$)
Streets et al. (2003)	2000	6.7	7.0
Zhang et al. (2011)	2005	3.6	3.8
X. Huang et al. (2012)	2006	3.2	3.2
Dong et al. (2010)	2006	8.7	8.9
Zhao et al. (2013)	2010	9.8	9.8
This study	2011	3	3

3.3 Evaluation of the CMAQ results by ground observations

NH_3 is the most important and abundant alkaline constituent in the atmosphere, and NH_3 emission estimates can affect the simulation of the inorganic gas-particle system (Schiferl et al., 2014). As the dominant positive ion in the atmosphere, NH_4^+ preferentially partitions to SO_4^{2-} and then partitions to NO_3^-. In NH_3-rich regions, the NO_3^- concentration is sensitive to NH_3 changes, but NH_3 changes do not lead to large differences in SO_4^{2-} concentration (Wang et al., 2011). In order to evaluate the reliability of this NH_3 emissions estimate, we compared the CMAQ-modeled NO_3^- concentrations using different NH_3 emissions against actual observations. In China, observation data on chemical components of fine particulates is very limited and not publicly available. For this study, we collected the observation data at three monitoring sites: Shanghai station (121.5° E, 31.2° N), Suzhou station (120.6° E, 31.3° N), and Nanjing station (118.7° E, 32.1° N). Ion chromatography (Dionex-3000, Dionex Corp,CA, USA) was used to measure daily NO_3^- concentration in $PM_{2.5}$ particles (Cheng et al., 2014). Some statistical indices, including mean observation (mean obs.), mean prediction (mean pred.), bias, normalized mean bias (NMB), normalized mean error (NME) and correlation coefficient (R) were calculated for the base case and bidi case in June, August, and November, as shown in Table 4. For the base case, the emission inventory from Zhao et al. (2013) was used. For the bidi case, the NH_3 emission from fertilizer use was calculated online using CMAQ, while other emissions were also from Zhao et al. (2013). The model performance from the bidi case is comparable to or better in general than the base case. For August and November, the NMBs and NMEs were improved by 3.29–66.85 % and 0.22–46.32 %, respectively. The correlation coefficients for the bidi case were also comparable or better than the base case. Though the bias for the bidi case is a little larger in June, other statistical indices were acceptable. For example, the NME decreased from 57.3 to 45.1 % and the correlation coefficient increased from 0.83 to 0.91 % at

Shanghai station. The correlation coefficient at Suzhou station and the NME at Nanjing station were comparable for these two cases.

3.4 Uncertainty analysis

This is a pilot study to apply this model system to estimate NH_3 emissions in China and therefore, large uncertainties still exist in some aspects of this method. The quality of input data, mathematical algorithm, and parameters applied in EPIC and the bi-directional model may be associated with uncertainties in the model output.

Fertilizer application rates for each crop are important input data for the estimation of NH_3 emissions from agricultural fertilizers and were obtained from agricultural statistics. These statistical data have some level of uncertainty, because the number of samples in the census are limited. Beusen et al. (2008) has employed an uncertainty of $\pm 10\,\%$ for the statistical data of fertilizer use based on expert judgments when estimating the global NH_3 emission. A June 2006 sensitivity run of this bi-directional model in the USA shows that a 50 % increase of crop fertilizer use would result in a 31 % increase in NH_3 emissions (Dennis et al., 2013). In addition, the spatial distribution of NH_3 emissions from agricultural fertilizer is strongly related to cropland area and its distribution, which are achieved from the MODIS data. Friedl et al. (2010) mentions that the producer's and user's accuracies are 83.3 and 92.8 % for MODIS class 12 (cropland) and 60.5 and 27.5 % for class 14 (cropland/natural vegetation mosaic) in MODIS collection 5 product. This leads to the uncertainties in spatial distribution. Additionally, due to the limited data available, the initial characteristics of the dominant soil in each grid were acquired from a US data set. Although we have matched the soil based on soil type, eco-region, and latitude, uncertainties still existed due to different long-term agriculture management.

Based on the algorithm described in Sect. 2.3, the EPIC outputs, including soil NH_4^+ concentration, soil volumetric water content (θ_s) and soil pH, are important inputs of the bi-directional module. EPIC has been used and evaluated world wide to simulate the nitrogen cycle and soil water content. Some validation studies have found favorable results for soil nitrogen and/or crop nitrogen uptake levels (Cavero et al., 1998, 1999; Wang et al., 2013). However, less accurate simulation results have also been reported (Chung et al., 2002). Li et al. (2004) found that the EPIC model could catch the variation of soil volumetric water content in different years accurately, with a relative bias of 11.7 %. The research conducted by Huang et al. (2006) also showed that the EPIC-simulated long-term average θ_s values were not significantly different from the measured values in the Loess Plateau of China. For soil pH, the normal growth pH range of three dominant crops (rice, corn, and wheat) is 6.0–7.0[3]. The 95 % confidence interval of EPIC-simulated values is 6.3–7.6, which is reasonable and acceptable although uncertainties still exist.

The bi-directional ammonia flux module in CMAQ is the core of this model system. The uncertainties of the bi-directional exchange parameterization would bring uncertainties to NH_3 emission estimates. Pleim et al. (2013) has compared the simulated NH_3 flux from the box model of this ammonia bi-directional flux algorithm with observations in three periods. The results showed that the model generally reproduced the observed series and significantly correlated with the observations ($p < 0.001$). The mean normalized biases were 78.6, −49, and 1 % for soybeans (18 June–24 August 2002), corn (21–29 June 2007), and corn (11–19 July 2007), respectively. The soil gamma (Γ_g) and apoplast gamma (Γ_s) are two important parameters in this ammonia bi-directional flux algorithm (Bash et al., 2013) and their parameterization remains uncertain (Massad et al., 2010). The field measurements of Γ_g and Γ_s are limited, and measured values are scattered, owing to complex impact factors (Massad et al., 2010, and reference therein). Dennis et al. (2013) assessed the effects of these uncertainties. A 50 % increase of Γ_g would result in a 42.3 % increase in NH_3 emission. Two different parameterization methods of Bash et al. (2013) and Massad et al. (2010) could lead to a 17 % change in NH_3 emissions.

In order to reduce the uncertainty in emission estimates, work is needed to improve the quality of input data and record additional local measurements of soil and vegetation chemistry. Ambient NH_3 concentration and flux data are also needed to enhance and evaluate the parameterizations of EPIC model and bi-directional module.

4 Conclusions

This study provides the first estimates of 2011 NH_3 emissions from N fertilizer use in China using the bi-directional CMAQ model rather than the traditional "emission factors" method. Hourly NH_3 emissions can be calculated online with CMAQ. Compared with previous researches, this method considers more influencing factors, such as meteorological fields, soil and fertilizer application, and provides improved spatial and temporal resolution. The higher resolution of NH_3 emissions is beneficial for modeling and exploring the impacts of NH_3 emission on air quality. In addition, the results can be used for a better comparison of novel and traditional methods of emission estimation. This is an important contribution to scientific literature on this topic.

China's NH_3 emissions from N fertilizer application were approximately 3.0 Tg in 2011. The major contributors were Henan, Shandong, Hebei, Jiangsu, and Anhui provinces, accounting for 11.1, 9.9, 8.8, 6.7, and 7.1 % of total emis-

[3]http://njzx.mianxian.gov.cn/xxgk/ccpf/20804.htm; http://nmsp.cals.cornell.edu/publications/factsheets/factsheet5.pdf

Table 4. The performance statistics of CMAQ-modeled daily NO_3^- concentrations for base case and bidi case, compared to the observations at three monitoring stations.

			Shanghai station	Suzhou station	Nanjing station
June (1–30 Jun 2011)	base case	mean obs. ($\mu g\,m^{-3}$)	7.27	13.43	12.81
		mean pred. ($\mu g\,m^{-3}$)	8.41	9.32	13.44
		bias ($\mu g\,m^{-3}$)	1.14	−4.10	0.63
		NMB (%)	15.65	−30.56	4.90
		NME (%)	57.34	40.71	59.93
		R	0.83	0.81	0.24
	bidi case	mean pred. ($\mu g\,m^{-3}$)	8.60	7.16	7.59
		bias ($\mu g\,m^{-3}$)	1.32	−6.26	−5.23
		NMB (%)	18.21	−46.63	−40.81
		NME (%)	45.07	50.63	60.40
		R	0.91	0.83	0.14
August (20 Jul–20 Aug 2011)	base case	mean obs. ($\mu g\,m^{-3}$)	2.99	7.04	6.24
		mean pred. ($\mu g\,m^{-3}$)	6.42	14.51	12.02
		bias ($\mu g\,m^{-3}$)	3.43	7.46	5.78
		NMB (%)	114.84	105.95	92.68
		NME (%)	142.48	115.89	97.18
		R	0.62	0.28	0.87
	bidi case	mean pred. ($\mu g\,m^{-3}$)	4.42	10.36	8.85
		bias ($\mu g\,m^{-3}$)	1.43	3.31	2.62
		NMB (%)	47.99	47.01	41.92
		NME (%)	96.16	79.43	62.64
		R	0.64	0.24	0.90
November (1–30 Nov 2011)	base case	mean obs. ($\mu g\,m^{-3}$)	9.42	11.59	14.57
		mean pred. ($\mu g\,m^{-3}$)	12.59	16.72	22.62
		bias ($\mu g\,m^{-3}$)	3.17	5.14	8.05
		NMB (%)	33.68	44.32	55.24
		NME (%)	83.85	53.68	74.81
		R	0.71	0.72	0.68
	bidi case	mean pred. ($\mu g\,m^{-3}$)	12.28	12.41	12.88
		bias ($\mu g\,m^{-3}$)	2.86	0.82	−1.68
		NMB (%)	30.39	7.05	−11.56
		NME (%)	65.33	53.46	43.35
		R	0.78	0.72	0.79

sions, respectively. The monthly distribution of these ammonia emissions is in line with the pattern of N fertilizer consumption. The emissions are dominant from March to July and in October, accounting for 88.7 % of the whole year. Compared to other NH_3 sources, nitrogen fertilizer application is the second largest contributor to NH_3 emissions in China. It is important to reduce the use of N fertilizer to control ammonia emissions.

This is a pilot study to apply this model system to estimate NH_3 emissions in China and gaps still exist for this method due to the uncertainties of model parameterization and input data. Much work is still needed to improve this model system when applied to China in the future. For example, it is important to build the initial soil input file for EPIC based on Chinese soil profile data instead of US data. In addition, Chinese farmers' logic of agriculture management must be explored and an automatic management algorithm in the EPIC model for China shall be designed. This model system can be improved with additional local measurements of soil and vegetation chemistry, ambient NH_3 concentration and flux data to enhance and evaluate the parameterizations of the EPIC model and bi-directional module.

Although uncertainties still exist in the NH_3 emission estimation, the CMAQ-EPIC modeling system allows for some interesting future research. This system is a combination of air quality and agro-ecosystem models and couples the processes and impacts that human activity has on air quality through food production. The model could be applied at finer grid resolutions for China in order to more accurately capture spatial gradients in NH_3 emissions and the resulting impacts on air quality. Secondly, this system reflects the impacts of weather and climate on NH_3 emissions. Therefore, it can be coupled with climate models to explore the interaction of climate change and NH_3 emission. When it is linked to a water quality and transport model, the impacts of atmospheric nitrogen deposition from CMAQ and nutrient run off from EPIC on water eutrophication are estimated. This study is the first attempt to apply this model system to China, and it is also the foundation for future scientific research.

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