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

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Abstracts

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. In this study, we estimate, for the first time, the NH_3 emission from agricultural fertilizer application in China online using an agricultural fertilizer modeling system coupling a regional air quality model (the Community Multi-Scale Air Quality model, CMAQ) and an agro-ecosystem model (the Environmental Policy Integrated Climate model, EPIC). This method improves the spatial and temporal resolution of NH_3 emission from this sector. Cropland area data of 14 crops from 2710 counties and the Moderate Resolution Imaging Spectroradiometer (MODIS) land use data are combined to determine the crop distribution. The fertilizer application rate and method for different crop are collected at provincial or agriculture-regional level. The EPIC outputs of daily fertilizer application and soil characteristics are inputed into the CMAQ model and the hourly NH_3 emissions are calculated online with CMAQ running. The estimated agricultural fertilizer NH_3 emission in this study is about 3Tg in 2011. The regions with the highest modeled emission rates are located in the North China Plain. Seasonally, the peak ammonia emissions occur from April to July. Compared with previous research, this study considers more influencing factors, such as meteorological fields, soil and fertilizer application, and provides improved NH_3 emission with higher spatial and temporal resolution.

1 Introduction

Ammonia (NH_3) is the most important and abundant alkaline constituent in the atmosphere. It has a wide range of impacts. First, 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 (He et al, 2014; Wang et al., 2012; Huang et al., 2012a). Ye et al. (2011) observed a strong correlation between peak levels of fine particles and large increases in NH_3 concentrations. High aerosol concentrations have a significant effect on visibility range, climate forcing, and human health (Cheng et al., 2013; Ding et al., 2013; Pope 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 et al., 2012; Stevens et al., 2004; Zhu et al., 2013). China is the largest or among the largest producers of crops and meat agricultural products in the world (FAO 2013), which leads to a large amount of NH_3 emissions. Previous studies have indicated that China's ammonia emissions contribute 23% of the global NH_3 budget (EDGARv4.1,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 (Huang et al., 2012b; Zhao et al., 2013). There are many studies focusing on NH_3 emission from agricultural fertilizer in China, but they are mostly based on traditional "emission factor" (EF) methods. Some of them (Klimont, 2001; Streets et al., 2003; Dong et al., 2010; Zhao et al., 2013) use averaged emission factors (EF) for the whole China. However, ammonia volatilization from nitrogen fertilizer application depends strongly on environmental parameters, such as ambient temperature and soil acidity (Roelle et al., 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 Huang et al. (2012b) 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 of China have begun to focus on estimating NH_3 emissions based on a bidirectional surface flux model (Cooter et al., 2010; Kruit et al., 2012). For example, a group at the U.S. Environmental Protection Agency (U.S.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 bidirectional 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 (William et al., 1984). This system includes the influences of meteorology, air–surface exchange, and human agricultural activity. It has been used to simulate the bidirectional exchange of NH_3 in the United States. Compared with a traditional emission inventory, the model performances for NO_3^- concentration and N deposition are improved in the United States (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 bidirectional NH_3 exchange module coupled to the FEST-C system with an agro-ecosystem model, EPIC. The structure of this modeling system and input data processing are described in detail in the next section. The results of the simulated fertilizer use and NH_3 emission, and comparison with other studies are discussed in section 3. The results of CMAQ modeling are also discussed and compared with field measurements. Finally, the uncertainties of this method are discussed in detail.

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 EPIC model, 2) the meso-scale 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 are simulated by the EPIC model in the FEST-C system. In order to run EPIC model, local Chinese information such as crop distribution, soil characteristics, climate patterns, fertilizer use characteristics is collected and processed. The details regarding these data sources and processing methods are described in section 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 that is 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°N and 40°N and covers most of East Asia with a grid resolution of 36km×36km. EPIC data and micrometeorological parameters are estimated for each modeled CMAQ grid cell.

2.2 EPIC modeling in the FEST-C system

EPIC model is a semi-empirical agro-ecosystem model which is designed to simulate agricultural fields that are characterized by soil, landscape, weather, crop management (William 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 will be described in detail in the next section. All data are processed to a 36km×36km grid for integration with the air quality model, CMAQ.

2.2.1 Crops

Fourteen crop types are modeled in this study, including early rice, middle rice, late rice, winter wheat, spring wheat, corn, sorghum, barley, soybean, potato, peanuts, canola, cotton and other crops. "Other crops" represent all remaining crops. Data of cropland area[1] for each crop in 2710 counties is collected and processed based on province-level or city-level statistical yearbook. The Moderate Resolution Imaging Spectroradiometer (MODIS;https://lpdaac.usgs.gov/products/modis_products_table/mcd12q1) is used to provide finer level land use information. The MODIS land use product provides annual 500m 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 use the global irrigated area map (GIAM) at 1km resolution (Thenkabail et al., 2008) to divide each crop into irrigated and non-irrigated classes. The BELD4 tool in FEST-C system is used to process these data into 36km×36km grid cell (CMAS, 2014).

2.2.2 Soil information

The dominant soil type in each grid is 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 1km×1km maximally) in China. We match the soil in each grid with a specific soil profile data in a US database (Cooter et al., 2012; http://www.nrcs.usda.gov/wps/portal/nrcs/main/national/technical/nra/nri/) based on soil type (http://www.soil.csdb.cn/), ecological region and latitude. Soil characteristics of the matched soil are extracted as soil input of the corresponding grid, including layer depth, soil texture, soil carbon content, carbonate content, bulk density, cation exchange capacity and pH, etc. The assumption here is that in China and US, the soil characteristics of same soil types in the similar eco-region and latitude are similar. Here, this soil characteristics data is just an initial input for EPIC, because it is for general soil, not specifically for agriculture soil. A spin-up run will allow soil characteristics to adjust to agriculture management. For example, EPIC is set up to apply 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.

[1] Please contact the corresponding author for the dataset

2.2.3 Weather

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

2.2.4 Crop management

In 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 heat-unit scheduled timing is 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 are also limited to a fixed time range based on the information from the Chinese planting information network (http://www.zzys.moa.gov.cn/) and the unpublished research about crop management from the Chinese Academy of Agriculture Sciences[2]. This can allow the timing to be more suitable for Chinese agriculture.

Nitrogen fertilizer application information is necessary to accurately estimate NH_3 emission in this study. The application rates for specific fertilizer type, crop and province are extracted from Chinese statistical materials (National Bureau of Statistics of China (NBSC), 2012b). The fertilizer types include urea, ammonium bicarbonate(ABC), diammonium phosphate (DAP), N-P-K compound fertilizer (NPK) and others (e.g. ammonium nitrate,

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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 by cotton and wheat, which are 228.11 and 196.22 kg N/ha, 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 crops are growing. **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 some previous field investigations (Wang et al., 2008; Zhang, 2008), the ratios of basal and topdressing for different crops in each agriculture region are identified. **Table 2** shows the results for three major crops in China and the divergence can be seen. For example, the ratio for wheat in the middle and lower Yangtze river region is 1.39, but that for wheat in the southwest region is only 0.33. In general, the ratio for corn is the highest among these three major crops. Much more fertilizer is applied to corn just prior to or at planting than that is applied later in the growing season. The information in **Tables 1 and 2** is combined to determine the amount of fertilizer applied to each crop in each grid cell during basal and topdressing activities.

2.3 The bi-directional CMAQ model system

Direct flux measurements have shown that the air–surface flux of NH_3 is bidirectional, and vegetation and soil can be 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:

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

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}).

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

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}) 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:

$$C_{st} = M_n / V_m \frac{161500}{T_c} e^{\left(-\frac{10380}{T_c}\right)} \Gamma_s$$

$$C_g = M_n / V_m \frac{161500}{T_s} e^{\left(-\frac{10380}{T_s}\right)} \Gamma_g$$

where M_n is the molar mass of NH_3, V_m is the conversion factor of L to m^3, T_s and T_c are the soil and canopy temperature in K. The appoplast 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). When fertilizer is used, Γ_g is calculated by the following function:

$$\Gamma_g = \frac{N_{app} / \left(\theta_s M_N d_s\right)}{10^{-pH}}$$

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), d_s is the depth of soil layer (m), and pH is soil pH. The initial soil NH_4^+,θ_s and pH are all from the EPIC output and then calculated in CMAQ hourly.

In addition to the inputs of soil condition and fertilizer use, other input data are same as those in the traditional CMAQ model. The WRF version 3.5.1 (http://www.wrf-model.org) is used to generate the meteorological input. The configuration options used in WRF and CMAQ are same as described by Fu et al. (2014).

In order to evaluate the performance of this method, two simulations are conducted in this study, including Base-case and Bidi-case. The only difference between these two cases is the method of estimating ammonia emissions from fertilizer use. For Base-case, the emission inventory from Zhao et al. (2013) is used, which is estimated by the traditional "emission-factor" method. This case does not include the bi-directional flux algorithm in CMAQ. For Bidi-case, NH_3 emission is estimated online by the bi-directional module in the CMAQ. The emissions of ammonia from other sectors and the emissions of other pollutants are both from Zhao et al. (2013) in these two cases.

3 Results and discussion

3.1 Nitrogen fertilizer application

The nitrogen fertilizer application is a key aspect in this system. This is explored by comparison of the EPIC results to statistical data. The N use in each grid cell per day is calculated by the following formula:

$$USE_i = \sum_{j=1}^{crop} \left(N_{ij} \times f_{ij} \right) \times 129600$$

where USE_i (kg) is the N application in grid cell i ; N_{ij} (kg/ha) 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 129600 ha/grid is a conversion factor accounting for the area of the grid cell.

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

Figure 5 shows the comparison of the fraction of N fertilizer use by each month between statistics and EPIC output. The statistical data is derived from the field investigation of Zhang et al. (2008) for 2004. It can be seen that the model results well capture the temporal characteristics. The fertilizer amounts used from March to July, and October are dominant, which are closely related to the fertilizer timing of crops in China. For example, the North China Plain is the most important agriculture production region, where the winter wheat-summer corn rotation is the major crop planting system. Winter wheat is usually planted in October with the application of basal fertilizer, and the topdressing fertilizer is used in March and April of the next year. For summer corn, the timing for basal fertilizer is usually in June and that for topdressing fertilizer is in July. In another major agriculture production region, the Northeast Plain, rice is the dominant crop. Due to the temperature limitation, rice there is usually seeded in April and May and the topdressing fertilizer is applied in June and July.

3.2 NH_3 emission

3.2.1 Spatial and Temporal Distribution

The NH_3 emission from N fertilizer application in 2011 estimated in this study is approximately 3.0Tg. The spatial distribution of annual NH_3 emission in 36km×36km grid is presented in **Fig.6**. It can be seen that the NH_3 volatilization is 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 emission intensity in this region is above 386kg /ha. The crop production here is the most intense in the whole China and the total crop area in these five provinces accounts for about 31.4% of the China’s total. These five provinces consume approximately 37.3% of the nitrogen fertilizer for the whole country in 2011(NBSC, 2012b). Besides the large crop production, high emissions are also due to the high fertilizer application rate. For example, the rate of N fertilizer use for rice in Jiangsu province is above 300kg/ha, which is much higher (2 times) than the national average. The smaller contributors of NH_3 emission are located mostly in western China, such as Tibet, Qinghai and Gansu province, where the amount of arable land and N fertilizer use is small.

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

3.2.2 Comparison with other studies

The ammonia emissions from N fertilizer use in China have been 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 update the emissions in different years to the year of 2011 based on the changes of 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 researches of Zhang et al. (2011) and Huang et al. (2012b), which is 60-70% lower compared with other studies. The discrepancies are mostly caused by the various estimating methods and emission factors 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, precipitation, etc. For example, the emission factors 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 Huang et al. (2012b) are 8.8% for acid soil and 30.1% for alkaline soil. The agricultural regions in China are dominated by acid soil (http://www.soil.csdb.cn/), so this value is lower by nearly 50% compared with the averaged emission factors. 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 emission factors by 0.75, 0.80, 0.85,0.90, 0.95 and 1.0 for significant rainfall events (>5mm in 24h)within 24h, 24-48h, 48-72h, 72-96h, 96-120h and >120h of fertilizer application. In this study, the impacts of soil pH and precipitation on NH_3 emission are considered by impacting soil gamma and resistances, as shown in section 2.3. In addition, our study and Zhang et al. (2011) include the impacts of irrigation. The experiments of Wang et al. (2004) in Beijing for winter wheat-summer maize cycle have shown that NH_3 volatilization is reduced after irrigation and revealed a low emission factor value of 2.1-9.5%.

Figure 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 dominate the country annual total emissions. At the same time, some discrepancy also exists for the specific province between different studies, which may be caused by distinct fertilizer consumptions and emission rates employed. For example, for Henan province, the estimation of Huang et al. (2012b) is the highest among these studies. The possible reason is that alkaline soil is dominant in Henan and Huang et al. (2012b) 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 entirely the exact date of fertilizing for the whole China, which may bring this large diversity. For example, Huang et al. (2012) thinks that the basal-dressing and top-dressing fertilizer of winter wheat are conducted in September and November. However, the basal-dressing fertilizer is applied in October in this study and Zhang et al. (2011), and the top-dressing fertilizer is mainly used in March of the next year. The diversity of seasonal variations among different studies reflects that large uncertainties still exist for the temporal distribution of NH_3 emissions and much local research work still need to do.

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 estimation 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 don't lead to large differences in SO_4^{2-} concentration (Wang et al., 2011). In order to evaluate the reliability of this NH_3 emission estimation, we have compared the CMAQ modeled NO_3^- concentrations using different NH_3 emission with observations. In China, observation data on chemical components of fine particulates is very spare and not publicly available. Here, we collect the observation data at three monitoring sites, including Shanghai station (121.5E, 31.2N), Suzhou station (120.6E, 31.3N) and Nanjing station (118.7E, 32.1N). Ion chromatography (Dionex-3000, Dionex Corp,CA,US) is 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) are calculated for Base-case and Bidi-case in June, August and November, as shown in **Table 4**. For Base-case, the emission inventory from Zhao et al. (2013) is used. For Bidi-case, the NH_3 emission from fertilizer use is calculated online by CMAQ, while other emissions are also from Zhao et al. (2013). It can be seen that the model performance of Bidi-case is comparable or better in general compared with Base-case. For August and November, the NMBs and NMEs are improved by 3.29%-66.85% and 0.22%-46.32%, respectively. The correlation coefficients for Bidi-case are also comparable or better than base case. For June, even though the bias of Bidi-case is a little larger, some other statistical indices are acceptable. For example, the NME decreases from 57.3% to 45.1% and the correlation coefficient increases from 0.83 to 0.91 at Shanghai station. The correlation coefficient at Suzhou station and the NME at Nanjing station are comparable for these two cases.

3.4 Uncertainty analysis

This is a pilot study to apply this model system to estimate the NH_3 emission in China and large uncertainties still exist for this method at some aspects. 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. They are obtained from the agricultural statistics. These statistical data should have some level of uncertainty, because the amounts of samples in the census are limited. Beusen et al. (2008) has employed an uncertainty of ±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 US shows that a 50% increase of crop fertilizer use would result in a 31% increase in NH_3 emission (Denniset 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%/92.8% for MODIS class 12 (cropland) and 60.5%/27.5% for class 14 (Cropland/Natural Vegetation Mosaic) in MODIS Collection 5 product. This would lead to the uncertainties of spatial distribution. Additionally, due to the limit of data availability, the initial characteristics of the dominant soil in each grid are gotten from the US dataset. Although we have matched the soil based on soil type, eco-region, and latitude, uncertainties still existed due to different long-term agriculture management.

Seeing from the algorithm described in section 2.3, the EPIC outputs, including soil NH_4^+ concentration, soil volumetric water content (θ_s) and soil pH, are important inputs of the bidirectional module. EPIC has been used and evaluated world widely to simulate nitrogen cycle and soil water. Some validation studies have found favorable results for soil nitrogen or/and crop nitrogen uptake levels (Cavero et al., 1998 and 1999; Wang et al., 2014). However, less accurate simulation results are also reported (Chung et al., 2002). For soil volumetric water content, Li et al. (2004) found that EPIC model could catch the variation of soil water in different years well with the relative bias of 11.7%, and 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 (http://njzx.mianxian.gov.cn/xxgk/ccpf/20804.htm; http://nmsp.cals.cornell.edu/publications/factsheets/factsheet5.pdf). 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 the CMAQ is the core of this model system. The uncertainties of the bidirectional 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 appoplast 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 emission.

It's very difficult to give an uncertainty interval accurately for this method, because there are many factors contributing to this model system. Here, an uncertainty of about ±50% is considered appropriate based on the above analysis, which is also the upper limit of uncertainty in previous studies (Bouwman et al., 1997; Zhang et al., 2011; Zheng et al., 2012). Therefore, the NH_3 emission from agricultural fertilizer application in China of 2011 is in the range of 1.5-4.5Tg. In order to reduce the uncertainty, much work still need to do. In addition to improve the quality of input data, additional local measurements of soil and vegetation chemistry, ambient NH_3 concentration and flux data are needed to enhance and evaluate the parameterizations of EPIC model and bi-directional module.

4 Conclusions

In this study, for the first time, the NH_3 emissions of 2011 from N fertilizer use in China are estimated using the bi-directional CMAQ model rather than the traditional "emission factor" method. The hourly NH_3 emission can be calculated online with CMAQ running. 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 emission is good for modeling and exploring the impacts of NH_3 emission on air quality. In addition, the results can be utilized for a better comparison of novel and traditional method for emission estimation. This is an important contribution to the scientific literature.

The NH_3 emission of China from N fertilizer application is about 3.0Tg in 2011, with an uncertainty of ±50%. The major contributors are Henan, Shandong, Hebei, Jiangsu and Anhui, accounting for 11.1%, 9.9%, 8.8%, 6.7% and 7.1% of total emissions, respectively. The monthly distribution of ammonia emissions is in line with the pattern of N fertilizer consumption. The emissions are dominant from March to July, and October, accounting for 88.7% of the whole year. Comparing with other sources, nitrogen fertilizer application is the second largest contributor to NH_3 emissions. It's important to reduce the usage of fertilizer and control the emission.

This is a pilot study to apply this model system to estimate the NH_3 emission in China and uncertainties 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 it is applied in China in the future. For example, it is important to build the soil initial input file for EPIC based on Chinese soil profile data. In addition, Chinese farmers' logic of agriculture management shall be explored and the automatic management algorithm in the EPIC model for China shall be designed. This model system also can likely 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 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 resulting impacts on air quality. Secondly, this system reflects the impacts of weather and climate on NH_3 emission. Therefore, it can be coupled with climate models to explore the interaction of climate change and NH_3 emission. If linking it to a water quality and transport model, the impacts of atmospheric nitrogen deposition from CMAQ and nutrient run off from EPIC on the water eutrophication can be estimated. This study is the first try to apply this model system to China, and it's also the foundation to explore more scientific researches in the future.

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Tables

Table 1. Thenational-average fertilizer application rate for major crops in China, 2011 (kg N/ha)

	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 regions

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

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

Reference	Year	Original NH_3 Emission (Tg/yr)	Revised to 2011(Tg/yr)
Streets et al. (2003)	2000	6.7	7.0
Zhang et al. (2011)	2005	3.6	3.8
Huang et al.(2012b)	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

Table 4. The performance statistics of CMAQ modeled daily NO_3^- concentration for Base-case and Bidi-case compared to the observations at three monitoring stations

			Shanghai station	Suzhou station	Nanjing station
June (2011.6.1-6.30)		Mean Obs. (μg/m^3)	7.27	13.43	12.81
	Base-case	Mean Pred. (μg/m^3)	8.41	9.32	13.44
		Bias(μg/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. (μg/m^3)	8.60	7.16	7.59
		Bias(μg/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 (2011.7.20-8.20)		Mean Obs. (μg/m^3)	2.99	7.04	6.24
	Base-case	Mean Pred. (μg/m^3)	6.42	14.51	12.02
		Bias(μg/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. (μg/m^3)	4.42	10.36	8.85
		Bias(μg/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 (2011.11.1-11.30)		Mean Obs. (μg/m^3)	9.42	11.59	14.57
	Base-case	Mean Pred. (μg/m^3)	12.59	16.72	22.62
		Bias(μg/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. (μg/m^3)	12.28	12.41	12.88
		Bias(μg/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

Figure Caption

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

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

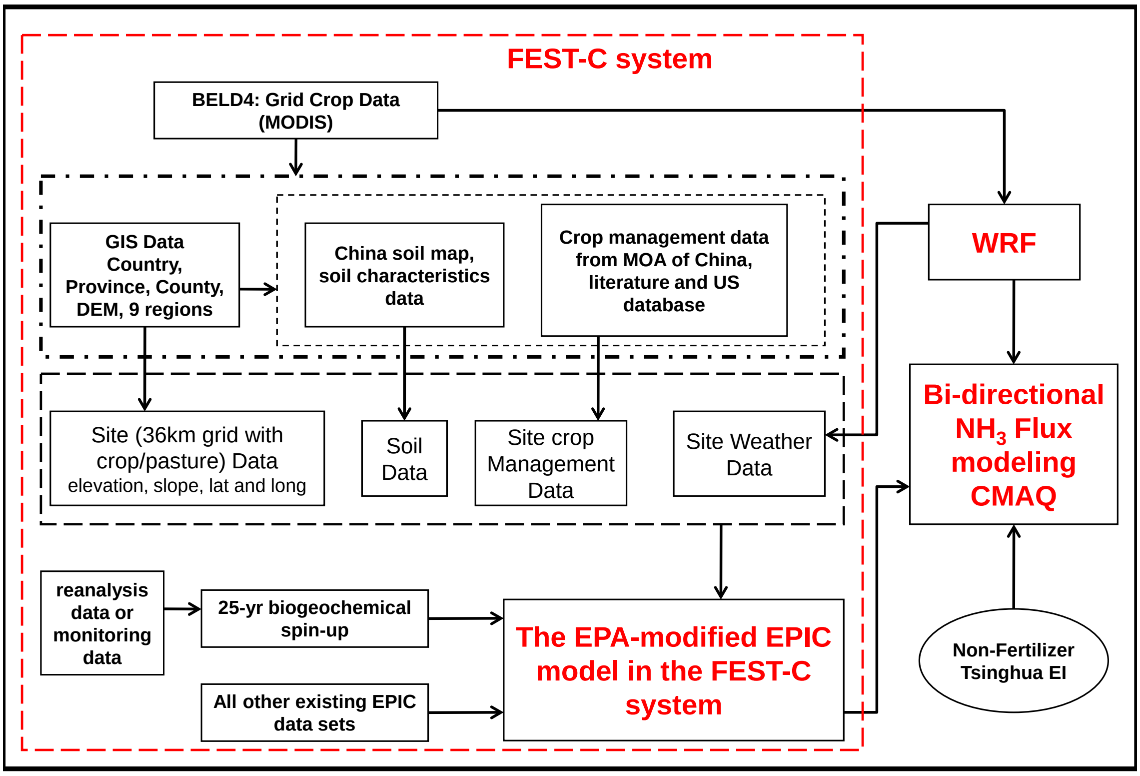
Fig.3 The nine agriculture regions in China. The thin black line represents the county boundary and the small insert represents the south China sea and its islands

Fig.4 Comparison of annual N fertilizer use at province level between statistical data (a) and EPIC output (b). The small insert represents the south China sea and its islands

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

Fig.6 Spatial distribution of NH_3 emissions from N fertilizer use in 36km×36km grid cell (kg/yr). The small insert represents the south China sea and its islands

Fig. 7 (a)The variation of monthly precipitation (green) and temperature (blue) in 31 provinces. In the box-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



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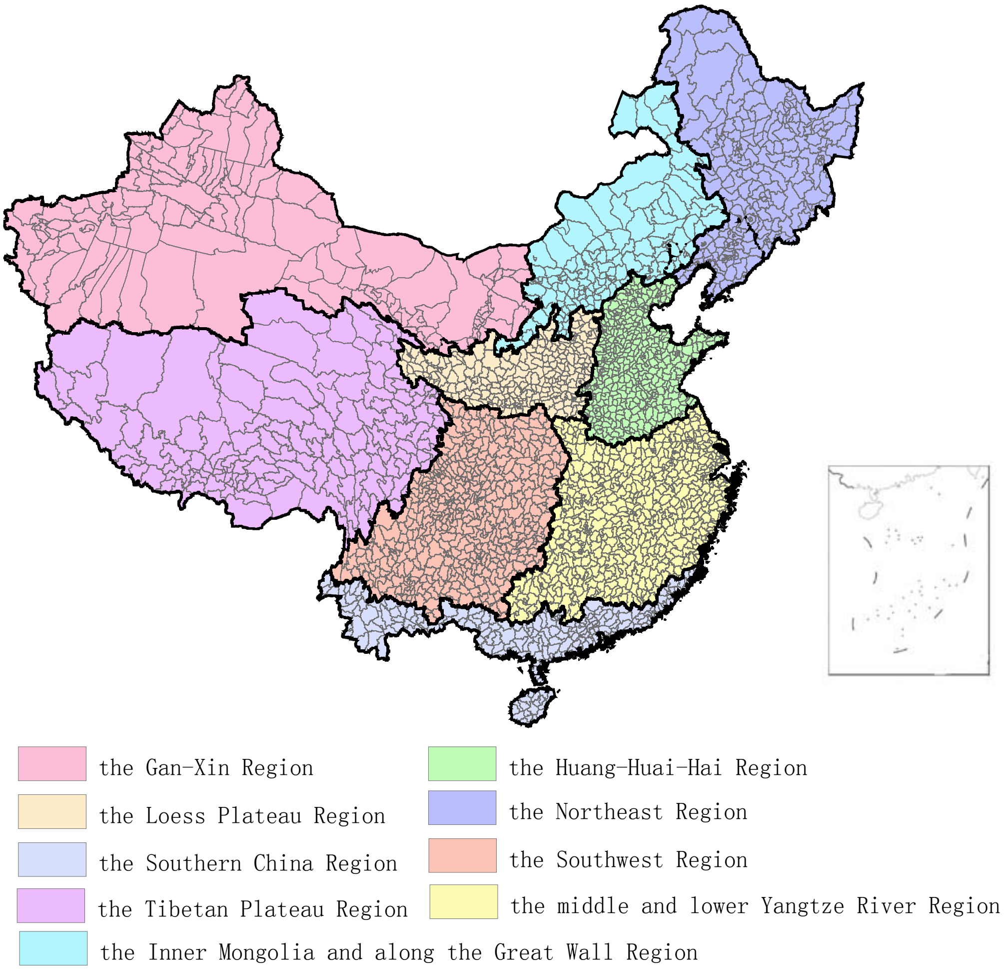

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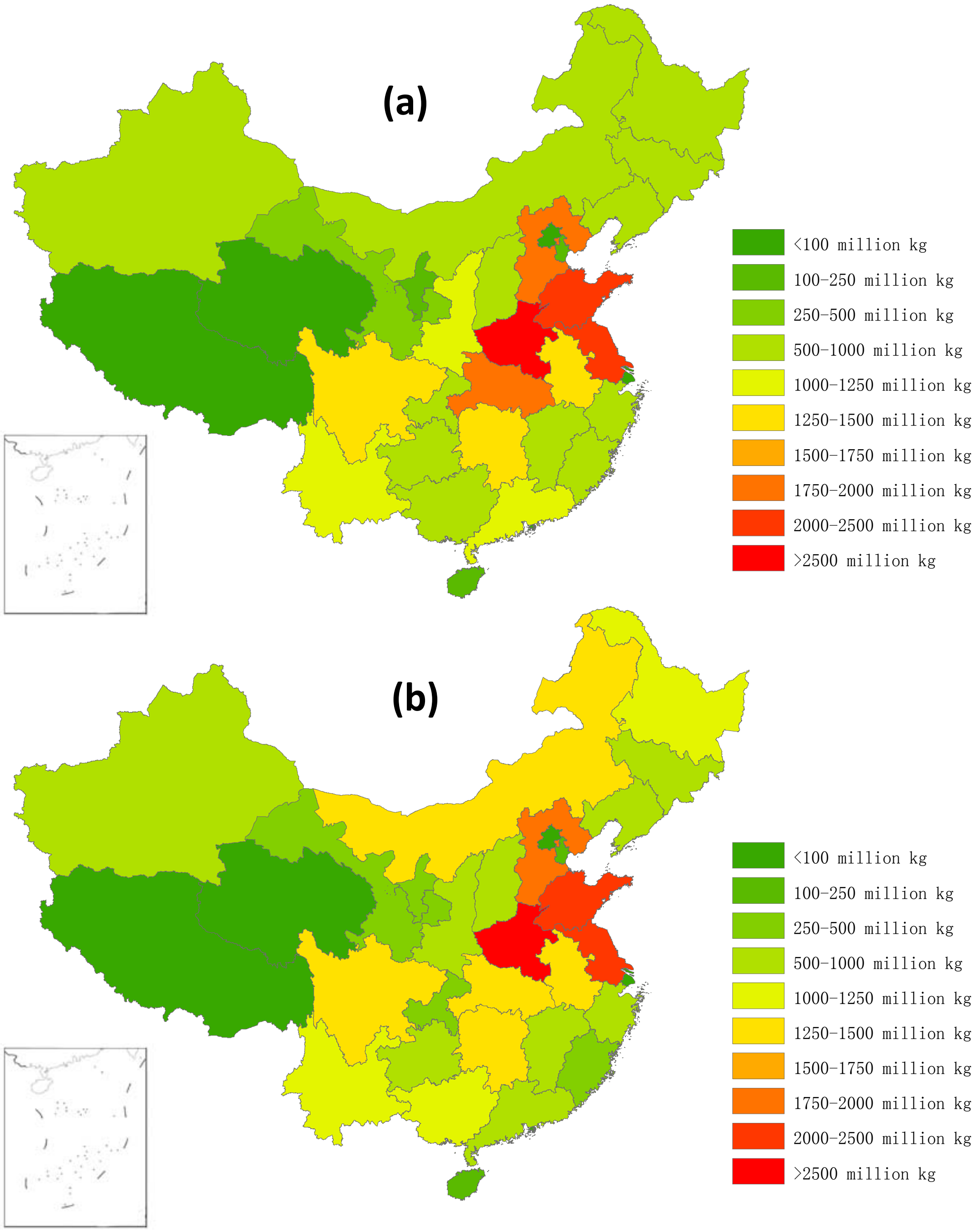

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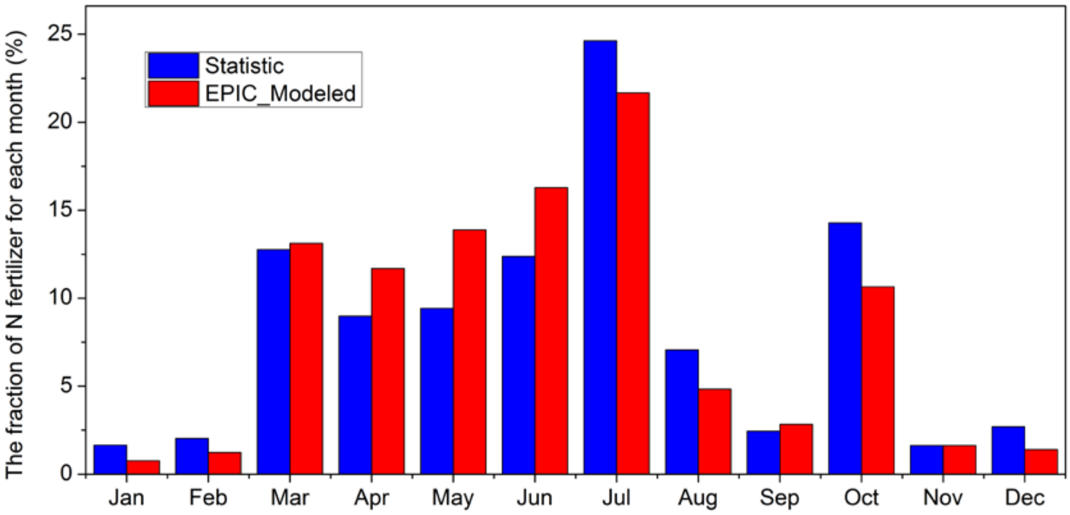

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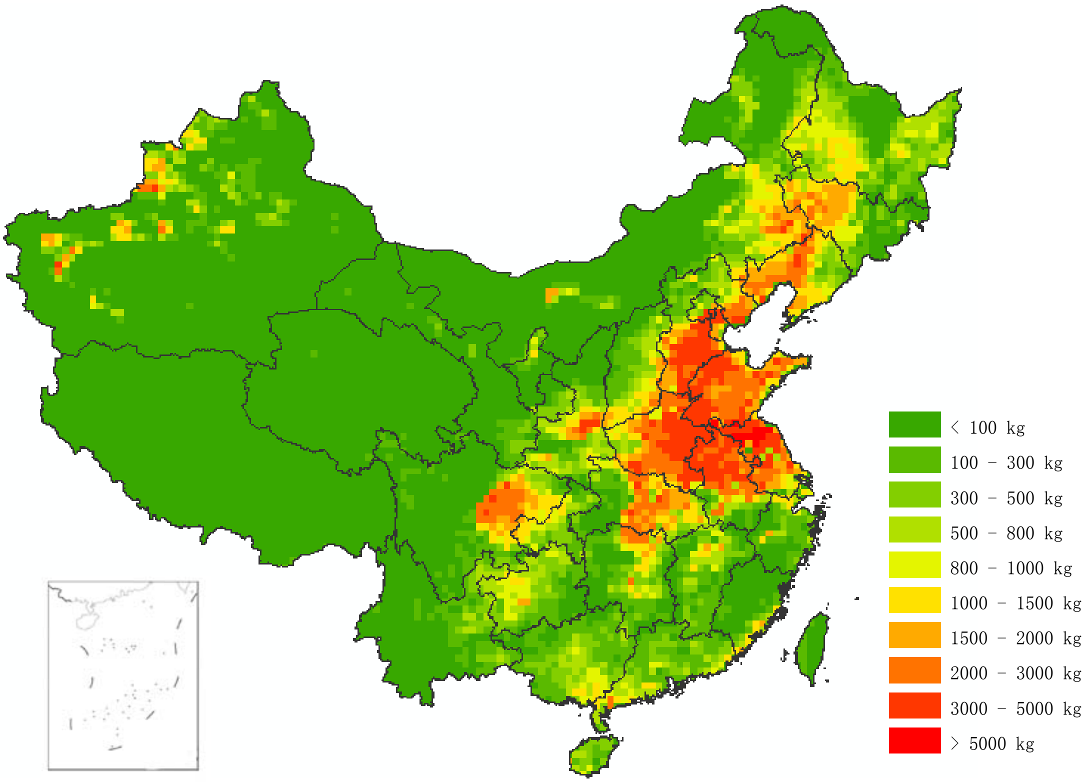

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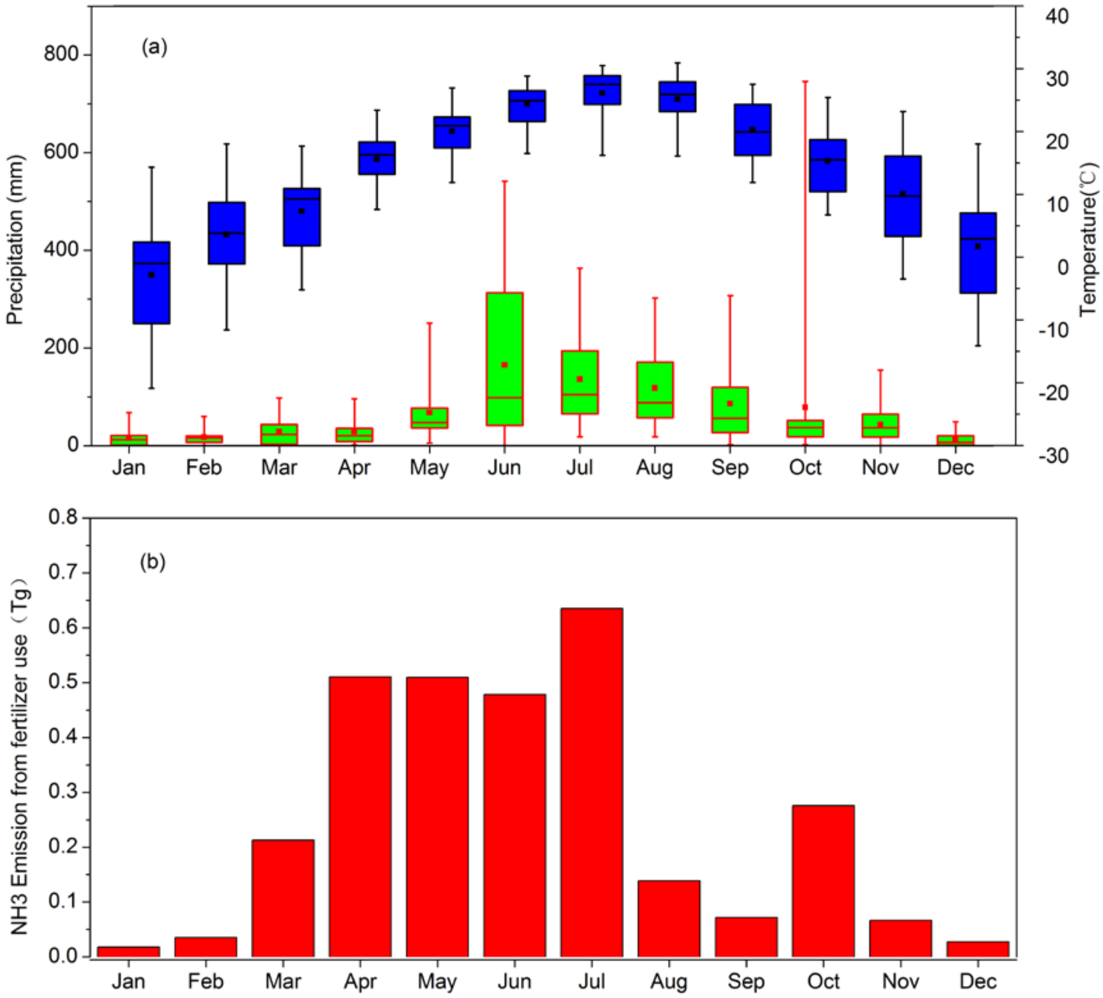

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