Improvement of atmospheric ammonia emissions combined with satellite observations

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Abstract

The increasing of atmospheric nitrogen deposition has been becoming significant due to amount of nitrogen emissions caused by human activities in regional and global areas. At present, China has become another high nitrogen deposition region besides North America and Europe. However, a major challenge in developing effective nitrogen emission control measures is necessity of accurate assess of atmospheric nitrogen emissions in these regions. In response to this scientific problem, this project uses the mainland of China as a study area to address the lack of accuracy of atmospheric nitrogen emission inventories (EIs) and construct inventory inversion models to improve the accuracy of bottom-up emission inventories using time-series remote sensing data. Firstly, the ground-based NH3 concentrations were used to assess the applicability of the long-series IASI NH3 column over the whole country. The results showed that the spatial and temporal variations of IASI NH3 column concentrations are consistent with those of the ground-observed NH3 concentrations in the study area. The NH3 EI was improved using atmospheric chemical transport models and satellite observation data based on the inverse modeling (IM) approach. The near-ground observation data were used to validate the accuracy of improved NH3 EI. In this study, for improvement of NH3 EI, corrections of acidic gas emissions as well as those of monthly profile of NH3 emissions were conducted because concentration of gaseous NH3 in the atmosphere is affected not only by its emissions, but also by concentrations of acidic gases. In order to accurately assess the uncertainties in bottom-up NH3 emissions in China, this study first corrects for the acidic gas (SO2) emissions before adjusting the NH3 emission inventory using IM combined with the near-ground SO2 observations. The simulated SO2 results using the improved SO2 emissions are in good spatial and temporal agreement with observations. After that, the monthly NH3 emission profile was improved based on satellite observations, and the validation results based on near-ground NH3 observation data showed that the reliability of the improved NH3 emission inventory in terms of spatial distribution and temporal trends. Analysis of improved NH3 emissions shows that NH3 emissions are mainly concentrated in densely populated areas such as the North China Plain, Yangtze River Delta, Pearl River Delta, and Chengdu-Chongqing region, with emissions greater than 300 kg ha\(^{-1}\) yr\(^{-1}\); in terms of recent trends, China's NH3 emissions have basically stabilized at around 10 million tons/year from 2013 to 2016. The results of this study provide a scientific and effective reference basis and technical methods for improving regional research on
atmospheric nitrogen emissions and the outcomes of this project will strengthen the utilization of satellite data on regional atmospheric nitrogen cycle.

Keywords: Ground-based observations, Spaceborne remote sensing, IASI NH\textsubscript{3} columns, emission inventories, inverse modeling

1. Introduction

In recent decades the nitrogen gas emissions significantly increased in the atmosphere mainly due to the burning of fossil fuels, the production and use of nitrogen fertilizer, plenty of livestock breeding and other human activities. The emissions, transport, chemical conversion and the subsidence process of the reactive nitrogen has migrated and redistributed in the regional and global scale. It has become a research hotspot in the field of nitrogen cycle (Galloway et al., 2008, Lu and Tian 2007, Liu et al., 2013, Zhao et al., 2015). With the intensification of human activities, the annual global nitrogen gas emissions into the atmosphere have increased from 9.9 Tg N yr\textsuperscript{-1} in 1860 to 74 Tg N yr\textsuperscript{-1} in 2010 (Fowler et al., 2013; Galloway et al., 2002), among which the total global ammonia emissions were as high as 59.3 Tg N yr\textsuperscript{-1} in 2020 (Sutton et al., 2013). China's total NH\textsubscript{3} emissions increased from 4.9 Tg N yr\textsuperscript{-1} in 1980 (Kang et al., 2016) to 17.2 Tg N yr\textsuperscript{-1} in 2010 (Gu et al., 2013), nearly three times higher than the combined annual emissions of the European Union and the United States (6.3 Tg N yr\textsuperscript{-1}) (Gu et al., 2013). Numerous studies have shown that the annual global deposition of reactive nitrogen into various ecosystems is as high as 43.5\times10\textsuperscript{6} t (Galloway and Cowling 2002, Holland et al., 1999). High nitrogen deposition not only interferes with or changes the cycling process of the regional ecosystem (Magill et al., 2000, Mo et al., 2004), but also damages the balance of the natural environment system, resulting in a series of ecological environment deterioration from the regional to the global scale (Liang et al., 2014, Liu et al., 2006). In order to relieve environmental pressure and solve the problem of high nitrogen deposition caused by human activities, accurate estimation of nitrogen gases emissions is the prerequisite and necessary basis for effective nitrogen emission reduction control measures.

There is a larger uncertainty for Chinese air pollutants emission inventories in regional and national scale, due to the incomplete coverage and complex composition of pollution sources, the rapid updating of pollution control techniques and unavailability data. The atmospheric pollutant column concentration data based on satellite remote sensing monitoring has the characteristics of wide space coverage, strong time continuity and convenient data acquisition, so as to provide a real-time and reliable reference for the improvement and update of emission inventory. Exploratory studies have been carried out to improve the accuracy of emission inventory by using satellite data (Streets et al., 2013). A number of researchers used NO\textsubscript{2} data from satellite observations to retrieve NO\textsubscript{x} emission inventories in the world (Martin et al., 2006), Europe (Zyrichidou et al., 2014) and Asia (Kurokawa et al., 2009; Zhao and Wang 2009) and achieved good results. In China, Zhang et al. (2007) calculated the NO\textsubscript{x} emission trend from 1995 to 2004 and evaluated them using NO\textsubscript{2} observed by satellite. Lin et al. (2012) used NO\textsubscript{2} data from satellite observations to invert NO\textsubscript{x} emissions from human activities, lightning and soil in eastern China in 2006. The preliminary results show that the top-down source emission inventory inversion model based on satellite observation data can well reduce the
uncertainty in the inventory and improve the accuracy and reliability of the simulation results of atmospheric nitrogen deposition. This study uses satellite remote sensing data and inversion model to improve the accuracy of NH₃ emission inventory in order to provide data support for regional atmospheric nitrogen emission management.

2. Data and Methodology

2.1 The procedures for improvement of emissions

The schematic diagram of this study as shown in Figure 1-1. As discussion above, the concentration of gaseous NH₃ in the atmosphere is affected not only by its emissions, but also by concentrations of acidic gases. Therefore, there were two steps for improving NH₃ emissions. Firstly, SO₂ emission was adjusted based on the near-ground observations using inverse model. Then spatial pattern and monthly profile of NH₃ were adjusted based on satellite data. The collected near-ground NH₃ concentrations was used to validate the simulated concentrations based on the improved emission inventory (E’

Figure 1-1. Schematic diagram of this study.

2.2 Study area

In this study, inversion of nitrogen emissions and deposition were carried out in mainland China. Considering that the monitoring of major air pollutants in China began to be routinely
monitored in 2013, in order to better verify the simulation results of the model with ground monitoring data, the simulation period of this study was selected from January 2013 to December 2016, for a total of 48 months (4 years). China's land use types and population distribution in 2010 are shown in Figure 2-1. The altitude of China has been descending from west to east. The mountainous area of China accounts for 2/3 of the total area of the country and has advantages in the development of forestry, stock farming, tourism and mining. The plain area only accounts for 1/3 of the total area of China. The Northeast Plain, the North China Plain and the Middle-Lower Yangtze plains are the three great plains in China. They are all distributed in the east of China. From the perspective of population distribution, China's population is concentrated in the east of the "Heihe-Tengchong" line proposed by Hu Huanyong (She W, 1998), presenting a multi-center of spatial and agminated pattern. The population density is generally above 500 people /km², among which the Yangtze River Delta, Pearl River Delta, Beijing-Tianjin-Hebei and Chengdu-Chongqing regions are highly densely populated areas over than 1000 people /km².

Figure 2-1. Topographic of China (a) and population distribution of 2010 (b).

2.3 Emission inventory

The initial NH₃ emission inventory from 2008 to 2016 is derived from the MEIC inventory produced by Tsinghua University. MEIC is built based on INTEX-B data set and updated based on the Technical guidelines for the compilation of emission inventories of air pollutant sources released by Ministry of ecology and environment of China (MEE) (MEE, 2015), with involving energy, industrial, residential, agriculture, road and off-road vehicles, biomass combustion sources, etc. The air pollutants of MEIC include SO₂, NOx, CO, NMVOC, PM₁₀, PM₂.₅, BC, OC, NH₃, etc (Liu et al., 2015). MEIC is considered to be the first air pollutants emission inventory in China based on a consistent methodology and widely used in national air quality improvement management (Liu et al., 2015; Cheng et al., 2017; Zheng et al, 2017). NH₃ emission inventory is developed by Peking University and constantly updated to improve the spatio-temporal resolution, which has been verified through a number of studies (Huang et al., 2012; Kang et al., 2016; Li et al., 2017). MEIC is updated every two years and provides gridded emission data with a spatial resolution of 0.25°×0.25°.

The simulation period of this study is from 2013 to 2016, and the region is in mainland China. The original data of source emission inventory is based on 2012-2016 MEIC emission inventory, and emissions in 2008 of REAS 2.1 (Kurokawa et al., 2013) was used as foreign source inventory data. The input emission inventory file for CAMx model was integrated into model grid after time profile, species allocation and grid processing. The main sources include
industry, traffic, residential sources, agriculture, power plant sources, etc. Figure 2-2 shows the distribution of annual emissions per unit area of NH$_3$ (unit: kg N ha$^{-1}$ yr$^{-1}$). It can be seen that NH$_3$ emissions are concentrated in densely populated areas such as the North China Plain, Yangtze River Delta, Pearl River Delta and Sichuan Basin, and emit more than 40 kg N ha$^{-1}$ yr$^{-1}$.

Figure 2-2. Spatial distribution of NH$_3$ emissions based on MEIC inventory of China in 2014.

2.4 Tropospheric NH$_3$ column observed by satellite

The NH$_3$ satellite observations used in this study were obtained from a new generation of ultra-high spectral Atmospheric detector — Infrared Atmospheric Detector Interferometer (IASI), which is one of the key instrument aboard MeTOP-A launched in October 2006. MeTOP-A passes from north to south over the equator at 09:30 per day and measures the infrared radiation emitted by the earth's surface and atmosphere (Clarisse et al., 2009). The detection wavelength range of the IASI is 362 nm-1550 nm, the spectral resolution is 8-70nm, and the spatial resolution in nadir is 12 km and increases to 39 km and 20 km for edges (Van Damme et al., 2015). The temporal resolution is twice a day, and the transit time is usually 09:30 and 21:30 in local time. IASI-NH$_3$ product is based on the calculation of hyperspectral range index, which is converted into NH$_3$ column through neural network algorithm and the detailed method can be seen in Whitburn et al. (2016). Some studies have found that the thermal contrast is higher in the morning of a day, and the satellite is more sensitive to NH$_3$ at the morning transit (Van Damme et al., 2017; Liu et al., 2017a, b). In this study, we will further verify the applicability of tropospheric IASI-NH$_3$ columns in China. The satellite-based NH$_3$ column concentration data product is the daily mean value of L2 data obtained from the Website IASI (https://iasi.aeris-data.fr/NH3/), with a spatial resolution of 0.25°×0.25°. The data period used in this paper is 1 January 2008 to December 31, 2016. Only the observation results with a cloud coverage of less than 25% and an absolute error of less than 5×10$^{15}$ mole cm$^{-2}$ were selected. In data processing, the daily average of observation points in each grid cell is used to calculate the monthly arithmetic average. Similarly, we calculate the annual mean by averaging the daily mean of the observation points in the grid cell throughout the year.

2.5 Near-ground verification data set

The data from Chinese Nationwide Nitrogen Deposition Monitoring Network (NNDMN) (provided by Agricultural University of China) were used to assess the applicability of IASI satellite NH$_3$ column on different land covers in China. NNDMN monitoring is in line with international standards, and monitoring sites are as far away from local direct emission sources
as possible to improve regional representation. According to their geographical location and proximity to major emission sources, they can be divided into three categories: urban stations, rural stations and background stations. A detailed description of all sites, including the surrounding environment and nearby emission sources, can be found in Xu et al. (2015, 2018). In this study, the monthly mean of NH₃ concentration over different land covers of 25 stations from 2010 to 2015 was used (Table 2-1), and its spatial distribution is shown in Figure 2-3.

Table 2-1. Station information of NH₃ concentration observation.

<table>
<thead>
<tr>
<th>Land cover types</th>
<th>Sites</th>
<th>Lon</th>
<th>Lat</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban regions</td>
<td>CAU</td>
<td>116.28°E</td>
<td>40.02°N</td>
<td>Apr.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>ZZ</td>
<td>113.63°E</td>
<td>34.75°N</td>
<td>May.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>DL</td>
<td>121.58°E</td>
<td>38.92°N</td>
<td>Sep.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>BY</td>
<td>113.27°E</td>
<td>23.16°N</td>
<td>May.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>WJ</td>
<td>103.84°E</td>
<td>30.55°N</td>
<td>Oct.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>SZ</td>
<td>116.20°E</td>
<td>40.11°N</td>
<td>Apr.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>QZ</td>
<td>114.94°E</td>
<td>36.78°N</td>
<td>Apr.2010-Dec.2015</td>
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<tr>
<td></td>
<td>YQ</td>
<td>112.89°E</td>
<td>38.05°N</td>
<td>Apr.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>YL</td>
<td>108.01°E</td>
<td>34.31°N</td>
<td>Apr.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>GZL</td>
<td>124.83°E</td>
<td>43.53°N</td>
<td>Jul.2010-Dec.2015</td>
</tr>
<tr>
<td>Rural regions</td>
<td>WX</td>
<td>115.79°E</td>
<td>30.01°N</td>
<td>Aug.2011-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>FH</td>
<td>121.53°E</td>
<td>29.61°N</td>
<td>Aug.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>ZY</td>
<td>104.63°E</td>
<td>30.13°N</td>
<td>Jul.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>JJ</td>
<td>106.18°E</td>
<td>29.06°N</td>
<td>Jan.2013-Dec.2015</td>
</tr>
<tr>
<td>Background</td>
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<td>113.41°E</td>
<td>28.52°N</td>
<td>Sep.2010-Dec.2015</td>
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<tr>
<td></td>
<td>XS</td>
<td>113.31°E</td>
<td>28.61°N</td>
<td>Sep.2010-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>LSD</td>
<td>120.18°E</td>
<td>35.77°N</td>
<td>Feb.2011-Dec.2015</td>
</tr>
<tr>
<td></td>
<td>CD</td>
<td>120.75°E</td>
<td>37.93°N</td>
<td>Sep.2010-Dec.2015</td>
</tr>
</tbody>
</table>
2.6 Description of Chemical Transport Model

We employed the WRF-CAMx model for simulating the effects of NH$_3$ emission improvement. CAMx is the third generation of three-dimensional model for air quality developed by ENVIRON company in the United States. It can simulate the emission, transport, chemical reaction and removal of pollutants in the troposphere, and apply to the comprehensive simulation study of photochemical smog and fine particulate air pollution at multiple scales. The meteorological data is provided by the Weather Research and Forecasting (WRF) model. In this study, the areas of simulation covered the whole China, Northeast Asia and parts of Southeast Asia with a horizontal grid resolution is 36 km $\times$ 36 km. The model is setup with 20 terrain-following hydrostatic vertical pressure ($\sigma$) coordinates.

2.7 Method of inversion model

Inversion model algorithm includes linear and nonlinear. Nonlinear algorithm including Kalman filter and the four-dimensional variational assimilation, the advantage of these two methods are to consider the chemical conversion process and the sensitivity analysis for different emission source contribution rate. Therefore, these two methods involve more variables and large amount of calculation and are generally used in a short time, small scale regional emissions improvement. The linear algorithm mainly refers to the method used by Martin et al. (2003, 2008) in the inversion of NO$_2$ emission inventory. Based on the principle of substance conservation, the inversion of pollutant emissions involves fewer parameters and requires less calculation. In this paper, a linear algorithm was selected to correct and improve of MEIC NH$_3$ emissions. The equation is shown as following:

\[ E' = E_b \times \frac{\Omega_s}{\Omega_m} \]  \hspace{1cm} (2.1)

Thus, $E'$ is the improved NH$_3$ emissions, $\Omega_s$ is the IASI NH$_3$ columns, $\Omega_m$ is the simulated NH$_3$ columns, $E_b$ is the initial emissions.

The method is developed based on a global model with a coarse resolution grid and assumes that the pollutants concentration in the air for each model grid is not affected by the...
emissions from the surrounding grid. However, in the regional model with relatively fine resolution grid, this assumption may not be true. When the lifetime of pollutants in the atmosphere is longer than the horizontal transmission time, there will be spatial dispersion error (Martin et al., 2003; Boersma et al., 2008; Lamsal et al., 2010; Turner et al., 2012).

3. Verification of IASI NH₃

Although the product of IASI NH₃ have been compared with the near-ground NH₃ concentration by some researchers in different spatial and temporal scale, considering that NH₃ column observed by satellite is the key data source of inverse model in this study, this part further evaluates the applicability and reliability of the newest IASI NH₃ products in a long time and nationwide scale using relatively accurate ground observation NH₃ concentration.

3.1 NH₃ satellite product selection

Now there are two products of IASI NH₃ with different algorithm: one is the NH₃ column retrieved in real time, labeled as IASI_NH₃_v1; the other is retrieved in real time, which can be further corrected based on reanalysis of temperature and relative temperature profile to obtain a more accurate NH₃ column product, labeled as IASI_NH₃_R. The spatial distribution of this two products are shown in Figure 3-1. They are basically the same, but the value of IASI_NH₃_R column is higher than IASI_NH₃_v1 in east of China.
The correlation between IASI_NH3_R and IASI_NH3_v1 products is shown in Figure 3-2. The overall correlation between them is good, with a correlation coefficient of 0.93. From the distribution of values, IASI_NH3_R product was significantly higher than IASI_NH3_v1 when it was over $12 \times 10^{15}$ mole cm$^{-2}$, and lower than IASI_NH3_v1 product when less than $12 \times 10^{15}$ mole cm$^{-2}$. It can be seen that IASI_NH3_R product has a wide range of concentration values, which can better reflect the spatio-temporal heterogeneity of atmospheric NH$_3$. 
3.2 Validation of IASI NH$_3$

As above result, IASI\_NH$_3$\_R was selected in this study to analyze the distribution characteristics of NH$_3$ in the atmosphere in China. In order to assess the accuracy of IASI\_NH$_3$\_R products, the monthly mean IASI NH$_3$ columns were compared by the near-ground monthly mean NH$_3$ concentrations on 25 NNDMN sites in eastern China.

Figure 3-3 shows the comparison of the annual mean value (Figure 3-3 a) and growth rate (Figure 3-3 b) between IASI NH$_3$ column and NNDMN NH$_3$ concentration. Figure 3-3 c, d show the corresponding scatter distribution, linear regression fitting and correlation coefficient. From 2010 to 2015, the annual average NH$_3$ concentration and its growth rate (Figure 3-3 a, b) in satellite and near-ground observations show similar spatial patterns, and the higher values appears in North China. There was a significant positive correlation between IASI NH$_3$ column and NNDMN NH$_3$ concentration ($r=0.71$, $p<0.001$, Figure 3-3 c). These results indicate that the accuracy of IASI NH$_3$ reanalysis product is consistent with that of IASI NH$_3$ product in near real-time (Van Damme et al., 2015; Xu et al., 2018), but the former is more suitable for evaluating interannual changes and trends (Van Damme et al., 2017). In addition, the annual growth rate between satellite and ground observations was significantly positive ($r=0.81$, $p<0.001$, Figure 3-3 d). The above results indicate that IASI NH$_3$ can better reflect the spatial pattern and annual variation trend of atmospheric NH$_3$ in China.
Figure 3-3. Spatial variation of atmospheric NH$_3$ in eastern China: (a) annual means of NNDMN NH$_3$ concentrations vs. IASI_NH$_3$ R columns; (b) annual growth rates of NNDMN NH$_3$ concentrations vs. reanalyzed IASI_NH$_3$ R columns; (c) relationship between annual means of NNDMN_NH$_3$ concentrations vs. IASI_NH$_3$ R columns; (d) relationship between annual growth rates of NNDMN_NH$_3$ concentrations vs. IASI_NH$_3$ R columns.

4. Results and discussions

4.1 Comparison of tropospheric NH$_3$ column based on initial EI with satellite observations

The temporal comparison between simulated troposphere NH$_3$ columns based on MEIC in China during 2013-2016 and IASI NH$_3$ observations columns is shown in Figure 4-1. Simulated NH$_3$ columns are obviously lower than IASI NH$_3$ columns. the monthly differences between them ranged from -18 $-$ $2\times10^{15}$ mole cm$^{-2}$ and have significant seasonal trend with higher in summer and lower in winter.

Figure 4-1. Difference of monthly NH$_3$ column between MEIC simulation and IASI observation.
The spatial comparison between simulated tropospheric NH$_3$ columns based on MEIC in China during 2013-2016 and IASI NH$_3$ observations columns is shown in Figure 4-2. Simulated tropospheric NH$_3$ column over China are lower than IASI NH$_3$ observations, spatially in Beijing-Tianjin-Hebei and its surrounding region (BTHs), Yangtze River Delta (YRD), Fenhe-Weihe Basin (FWB), Northeast China (NEC), South China (SC) and Xinjiang oasis agriculture area (XJO). According to the physical and chemical processes of NH$_3$ in the atmosphere, there are two possible reasons for the underestimation of simulated NH$_3$ column. One is that the underestimation of NH$_3$ emissions, and the other is that the overestimation of acidic gases emission in the atmosphere which leads to the underestimation of NH$_3$ column concentration.

![Figure 4-2. Differences of NH$_3$ column between MEIC simulation and IASI observation.](image)

4.2 Improvement of NH$_3$ emissions

As discussed in section 4.1.1, there is great uncertainty in the quantitative analysis of NH$_3$ column between simulated results based on MEIC and IASI observation. The results of several NH$_3$ emission inventories (Huang et al., 2012; Kang et al., 2016; Liu et al., 2017a, 2017b, 2019) show that amount of China's NH$_3$ emission is about 10 million tons/year. While the total emission of NH$_3$ in MEIC is consistent with the other research results, it is possible that the low simulated NH$_3$ column may be caused by the overestimated emission of acid gas (such as SO$_2$). Therefore, the method of improving NH$_3$ emission is mainly divided into two steps: firstly, the SO$_2$ emissions as a key acid gas in the air was adjusted based on near-ground observation; then, spatial and monthly profile of NH$_3$ emission will be improved based on the variation of monthly IASI NH$_3$ columns.

According to the process of atmospheric chemistry, NH$_3$ is the key alkaline gas in the atmosphere, and its emissions mainly come from agriculture such as fertilizer and livestock (Xu et al., 2016). In the atmosphere, NH$_3$ can neutralize with H$_2$SO$_4$ and HNO$_3$ to produce ammonium sulfate and ammonium nitrate (Lanniello et al., 2010). These aerosols are the main components of PM$_{2.5}$ with accounting for 20%-60% of the PM$_{2.5}$ concentrations (Shen et al., 2014; Tao et al., 2012). So, the concentration of gaseous NH$_3$ in the atmosphere is affected not only by emissions, but also by the amount of acid gases in the atmosphere. In order to accurately assess NH$_3$ emission changes in China by inversion method described in Sect. 2.7,
acidic gases and their precursors (NOx and SO2) were first corrected in this study.

Based on the linear correction method of Martin et al. (2003, 2006), NOx and SO2 emissions were corrected using the data from the Environmental Air quality monitoring Network of China Monitoring Station. The distribution of air quality monitoring stations is shown in Figure 4-3. The time resolution is the monthly average, and the time is from 2013 to 2016.

Figure 4-3. Spatial distribution of stations for air quality sites in China.

4.2.1 Validation the NOx emissions

Based on the MEIC inventory, NO2 concentrations were simulated from 2013 to 2016. The comparison between the simulated and observed monthly average NO2 concentrations was shown in Figure 4-4 in typical cities (Beijing, Tangshan, Tianjin, and Shijiazhuang). The results indicate that the simulated NO2 based on MEIC are basically consistent with the trend of the observed values, and both show obvious seasonal variation characteristics, with low summer and high winter. In terms of annual changes, both the observed and simulated NO2 concentrations decreased year by year from 2013 to 2016, with a significant decreasing trend. The uncertainty of simulated NO2 concentration in the four cities ranged from 8% to 45%.
The scatter validation result of the simulated NO$_2$ concentrations based on MEIC is shown in Figure 4-5. The simulated NO$_2$ concentrations are underestimated (43%) compared to the measured values, and the underestimation is mainly found in the values of less than 40 μg/m$^3$. In general, the simulated values are in good agreement with the observed values ($R^2=0.55$).

4.2.2 Improvement of SO$_2$ emissions

a. Correction coefficient matrix of SO$_2$
Due to the obvious spatial heterogeneity of ground monitoring sites (Figure 4-6), there are densely in eastern of China and rare in western of China. For reducing the error caused by the uneven distribution of site data, the mean of city was calculated, and then compared with the initial simulation results in order to obtain the correction coefficient matrix for spatial variability from 2013 to 2016. The results are shown in Figure 4-4. From The result shows that, except for a few cities, the SO$_2$ emission correction coefficient for most cities in China is less than 1, indicating the overestimation of the SO$_2$ emissions. The SO$_2$ correction coefficient of northeast China, Gansu Province and cities in southern China exceeds 4, indicating that the SO$_2$ emissions in these cities are underestimated.

Figure 4-6. Monthly correction coefficient matrix of SO$_2$ based on initial simulation and observation.

b. Validation of the result

Based on the above space correction factors, the 2013–2016 emissions inventories were corrected and developed using the Inverse model. Figure4-7 shows the observed SO$_2$ concentrations in Chinese cities and the spatial distribution of the annual averages of simulated SO$_2$ concentrations before and after the inventories were corrected. According to the figures, the North China Plain, the Fenhe-Weihe River Plain, Northeast China, Xinjiang and Inner Mongolia are among the regions which mainly posted high observed concentrations of SO$_2$; the concentrations decreased year by year from 2013 to 2016 with a notable downward trend. It can be seen from the pre-correction EI simulations that the spatial distribution of high SO$_2$ concentrations throughout China was similar to the observations, yet the concentrations were higher than the observations and did not change greatly year by year. The simulated spatial distribution of SO$_2$ concentrations in the post-correction EIs was roughly consistent with the observations, and the concentrations declined obviously year by year; but the SO$_2$ concentrations in Qinghai were overestimated to a degree, possibly owing to the comparatively smaller amount of observation data. On the whole, the post-correction SO$_2$ concentrations featured good temporal-spatial coherence with the observations.
Figure 4-7. Spatial distribution of SO₂ measured concentration and simulated concentration before and after inventory correction in China from 2013 to 2016.

It is found from a comparison between the simulated and the observed monthly average concentrations of SO₂ in typical cities such as Beijing, Tangshan, Tianjin and Shijiazhuang during 2013–2016 (Figure 4-8) that modified simulated results were roughly consistent with corresponding observations and both showed significant seasonal variations (low in summer and high in winter). In terms of annual changes, both the observed and the simulated concentrations of SO₂ were on a striking decline from 2013 through to 2016. With respect to absolute concentrations, the simulated SO₂ concentrations in the four cities were overestimated by 6%–44%.
The SO$_2$ EIs after correction were made much more precise, judging from the scatter plot of simulations vs observations (Figure 4-9). The annual average concentrations of SO$_2$ simulated in the original EIs were notably overestimated, while the simulated and observed concentrations had a low correlation to each other. The annual average concentrations of SO$_2$ simulated in the corrected EIs were of the same order of magnitude as the observations, and the correlation coefficient between the two reached 0.6, marking an obvious improvement and the simulations roughly in line with the observations.

Therefore, both spatial distribution and time variation justify the consistency between the post-correction SO$_2$ emissions and the actual results. On this basis, the NH$_3$ emission can be improved as the next step.
4.2.3 Correction of the monthly profiles of NH₃ emissions

Based on the relationship between monthly and annual concentrations observed by the satellites, a correction factors matrix for the 2013–2016 NH₃ emissions inventories reflecting the monthly changes was constructed. See Figure 4-10 for the results of 2014. Figure 4-8 shows the monthly profiles of NH₃ columns in China, which have obvious temporal and spatial variations. In summer months (June–August) it have the maximum percentage of NH₃ columns throughout a year, i.e. more than 10 percent in most parts of China and even over 20 percent in North China and Northeast China. However, NH₃ columns in each of all the other months contributed less than 10 percent to the annual total. Where, NH₃ columns in North China in autumn and winter made up for less than five percent in the annual total.

As discussed above, the concentration of atmospheric NH₃ is affected not only by NH₃ emissions but also by the concentration of acid gases. Considering the work above, SO₂ emission has been improved and the NOx emission is reasonable. In this step, the main reason for the uncertainty of simulated NH₃ concentrations is the NH₃ emissions. In this step, we assume that the different in observed data is the same as the difference in emissions. So the monthly value of NH₃ emission in MEIC was reassignment according to the correction factors matrix based on observed data.

![Figure 4-10. Monthly correction coefficient matrix of NH₃ emission inventory based on initial simulation and observation in 2014.](image)

4.2.4 Validation of the NH₃ simulations

See Figure 4-11 for the validation results of model-simulated monthly NH₃ concentrations during 2013-2015 and Figure 4-12 for the validation parameters. After the EIs were corrected, the simulated NH₃ concentrations of most stations fell within the range of deviations, but those of a few stations were significantly overestimated or underestimated. For example, the simulated concentrations of QZ and WW stations were significantly underestimated, even beyond the range of deviations, while the simulations of LSD, CD and DL stations were overestimated to varying degrees.
Compared with the simulations of the original emissions inventories (Figure 4-11), in spite of the differences in the simulated and observed results in a few areas at certain time intervals, the overall results were satisfying. Most stations reported the average relative deviation of simulations at a range of -37 percent to 57 percent and the average relative error at a range of 46 percent to 73 percent. Only a very few stations were outside the two ranges.

Figure 4-11. Comparison of simulated NH₃ concentration by corrected emission inventory with NNDMN station observed concentration.

<table>
<thead>
<tr>
<th>Station</th>
<th>Numbers</th>
<th>Intercept</th>
<th>Slope</th>
<th>r</th>
<th>p Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAU</td>
<td>35</td>
<td>0.81</td>
<td>0.32</td>
<td>0.72</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>ZZ</td>
<td>36</td>
<td>1.48</td>
<td>0.53</td>
<td>0.58</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>SZ</td>
<td>35</td>
<td>1.08</td>
<td>0.41</td>
<td>0.69</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>QZ</td>
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<td>2.81</td>
<td>0.12</td>
<td>0.34</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>YL</td>
<td>35</td>
<td>4.13</td>
<td>0.19</td>
<td>0.39</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>YC</td>
<td>35</td>
<td>2.62</td>
<td>0.50</td>
<td>0.61</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>WW</td>
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<td>1.48</td>
<td>0.12</td>
<td>0.53</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>WX</td>
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<td>0.91</td>
<td>0.61</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>TJ</td>
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<td>0.47</td>
<td>0.64</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>FY</td>
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<td>4.32</td>
<td>0.46</td>
<td>0.63</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>ZJ</td>
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<td>1.88</td>
<td>0.29</td>
<td>0.58</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>FZ</td>
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<td>0.31</td>
<td>0.63</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>ZY</td>
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<td>1.11</td>
<td>0.29</td>
<td>0.49</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>YT</td>
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<td>0.27</td>
<td>0.67</td>
<td>&lt;0.01</td>
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<tr>
<td>JJ</td>
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<td>&lt;0.01</td>
</tr>
<tr>
<td>LSD</td>
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<td>0.65</td>
<td>1.53</td>
<td>0.72</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>
Fig. 4-12. Comparison of simulated NH$_3$ concentration by original emission inventory with NNDMN station observed concentration.

4.3 Emission characteristics of NH$_3$ gases in China during 2013–2016

4.3.1 Comparison between original and corrected emissions inventories

When this study was conducted, emission data of MEIC were available only every two years. Therefore, emissions in 2014 and 2016 were compared in this study.

The inversion method of this study update NH$_3$ emission in monthly basis. See Figure 4-13 for the spatial changes in total monthly emissions before and after the correction. From the perspective of monthly variation, pre-correction NH$_3$ emissions did not show significant seasonal variation, with the exception of a minor increase in the North China Plain region during May–August only; but the post-correction NH$_3$ emissions varied significantly month by month, notably high in spring and summer and low in autumn and winter. Specifically, total NH$_3$ emissions in the eastern China regions including Northeast China (No.$\odot$1), North China (No.$\odot$2), the Fenhe-Weihe River Plain area (No.$\odot$3), the Yangtze River Delta (No.$\odot$4), the middle areas of the Yangtze River (No.$\odot$5), Chengdu and Chongqing (No.$\odot$6) and the Pearl River Delta (No.$\odot$7) in June and July were significantly higher (above 7.5 kg N ha$^{-1}$) than the figures in the other months. The results showed that the monthly variation characteristics of NH$_3$ emission inventory were more obvious after correction, which was consistent with the actual emission factors (such as agricultural fertilization, soil ammonia release caused by temperature rise, etc.).
Figure 4-13. Comparison spatial distribution of original and corrected NH3 emission inventory averaged in 2014 and 2016.

Figure 4-14 clearly indicates that the monthly variation of NH3 emissions in the MEIC is much smaller than those in the corrected EI which shows significant seasonal variation, i.e. high in summer and low in winter; NH3 emissions in summer in the corrected EI were approximately 2.5 times of those in the original EI. The analysis of observations shows notable seasonal variations in the concentrations of NH3 in the air, hitting highs in summer and falling to lows in autumn and winter. The seasonal variation of NH3 concentration is consistent with that of the improved NH3 emissions although the seasonality of NH3 concentration is determined not only by emissions, but also combined effects of emissions, meteorological conditions and chemical transformations in the air.
4.3.2 Characteristics of temporal changes in NH₃ gas emissions in China during 2013–2016

This section analyzes the temporal-spatial changes in the emissions of nitrogen-containing gases in China during 2013–2016 based on the corrected NH₃ emissions inventories. The corrected NH₃ emissions in China showed almost stable trend from 2013 (about 9.6 million tons) to 2016 (about 10.2 million tons) (Figure 4-15). Compared to the emission amount of MEIC, the corrected emissions were decreased by 580 thousand tons in 2014 but were increased by 100 thousand tons or so in 2016 by inversion method of this study. Generally speaking, emissions corrected by inversion model are basically in line with those in the bottom-up emission inventory MEIC.

Regarding monthly variations (Figure 4-16), monthly NH₃ emissions from 2013 to 2014 were characterized by significant seasonal variations, with highs taking place in summer (up to 1-1.5 million tons) and lows appearing in autumn and winter (basically at 0.5 million tons), and general features of the seasonality were almost the same. The updated emissions inventories showed more significant changes in monthly variation than the MEIC, with the high emission figures in spring and summer (6-56 percent larger) and the low emission figures in autumn and...
winter (1-40 percent lower). According to the features of monthly variations, the amounts of NH₃ emissions in China is stable. The reason may be that there are no efficient control measures to reduce NH₃ emissions in China.

Figure 4-16. Monthly characteristics of NH₃ emission in China from 2013 to 2016.

4.3.2 Characteristics of spatial changes in NH₃ gas emissions in China during 2013–2016

From the perspective of spatial changes in China’s NH₃ emissions during 2013–2016 (Figure 4-17), the country’s NH₃ emissions in these years were roughly consistent by spatial distribution. The high emissions, which exceeded 50 kg ha⁻¹ yr⁻¹, occurred in the North China Plain, the Yangtze River Delta, the Pearl River Delta, Chengdu and Chongqing regions with the densely populated and farmlands. The following is the northeastern and northwestern city clusters with value of 10-30 kg ha⁻¹ yr⁻¹. And the lowest NH₃ emissions (less than 10 kg ha⁻¹ yr⁻¹) appeared in the central and western regions in China with sparsely populated.

Figure 4-17. Spatial characteristics of NH₃ emission in China from 2013 to 2016.
5. Conclusions

Focusing on the Chinese mainland, the paper firstly assesses the reliability of observed temporal-spatial distribution of NH$_3$ column concentrations nationwide and the relevant trends using satellites over long time series. Then the national emission inventories of NH$_3$ were improved with the inverse model on the basis of the satellite observations. The paper draws the following conclusions mainly:

First, the reliability of the trend of temporal and spatial changes in NH$_3$ concentrations observed by satellites is examined through the NH$_3$ mass concentrations observed on the ground. According to the results, the NH$_3$ column concentrations observed by satellites feature good temporal-spatial coherence with the ground-based observations of mass concentration, and thus, are considered to reflect the temporal-spatial change characteristics of NH$_3$ concentrations in the air in China over long time series. In China, NH$_3$ concentrations in the air are characterized by significant temporal-spatial changes. In terms of spatial distribution, high NH$_3$ column concentrations in the troposphere are mainly distributed in the most developed regions such as the North China Plain region, the Yangtze River Delta, the Pearl River Delta, Chengdu and Chongqing. It can be seen that intense human activity significantly increases NH$_3$ emission in the atmosphere. In terms of the annual variation, the concentrations of Tropospheric NH$_3$ column in China showed a notable increasing trend. From the perspective of seasonal changes, NH$_3$ column concentrations have the highest value in summer and the lowest in autumn or winter.

In this study, the NH$_3$ emissions inventories were improved using atmospheric chemical transport model, satellite observations, and inverse modeling methodology. Then, the updated EI accuracy is validated by the observations at ground stations. Gaseous NH$_3$ concentrations in the air are influenced not only by its emissions but also by the content of acid gases in the air. There are two steps to improve the NH$_3$ emission inventory in this study. Firstly, SO$_2$ emission was correction before correcting the NH$_3$ emissions inventory. The bottom-up SO$_2$ emission inventories were updated by inverse modeling approach using the ground-based observation data. The simulated SO$_2$ concentrations using the corrected SO$_2$ emissions were consistent with the temporal and spatial variations of the ground-based monitoring data and thus, it is considered that SO$_2$ emissions were well corrected for the inverse modeling of NH$_3$ emissions. Then, monthly NH$_3$ emissions were improved using inverse modeling based on satellite observation. The simulated results of NH$_3$ concentrations using the updated emissions were validated using the monthly averages of data observed at NNDMN Station, and the result shows the corrected emissions inventories were improved in terms of spatial distribution and time variation characteristics. In terms of spatial distribution, according to the corrected emissions, NH$_3$ emissions were mainly seen in densely-populated areas such as the North China Plain, the Yangtze River Delta, the Pearl River Delta, Chengdu and Chongqing, with the emissions per unit area exceeding 300 kg ha$^{-1}$ yr$^{-1}$. As for annual changes, China showed almost stable trend in NH$_3$ emissions from 2013 to 2016, and nationwide NH$_3$ emissions came in at about 10 million tons in each of these years.

The research, which attempted to improve the emissions inventories of atmospheric NH$_3$ based on the satellite data and with the method of Martin et al. (2003, 2008), still has lots of limitations. This method assumes a linear relationship in the simulation grid (36 km × 36 km) when dealing with the relationship between emissions and concentrations. It does not take into
consideration the non-linear relationship between emissions and concentrations in the surrounding grids, nor the observation data and model errors. In fact, the influence of transportation between grids cannot be ignored. In addition, there are large uncertainties in satellite observations and systematic errors in the models. Furthermore, similar to influences of SO$_2$ and NO$_x$ emissions on NH$_3$ concentrations, emissions of NH$_3$ also affects concentrations of SO$_2$ and NO$_x$. These complex system of the chemical transformation in the atmosphere were not considered in the methodology of this study. Recently, the advancement of data assimilation technology has come with the introduction of Kalman filtering and four-dimensional assimilation technology into improving the air pollutant emissions inventories. These two methods give sufficient consideration to the influence of atmospheric transportation and incorporate observation and simulation errors to correct pollutant emissions data. Further efforts should be made to improve air pollutant emissions rapidly and in real time with better technologies and methods and in overall consideration of transportation and errors.

References


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