Estimation of monthly bulk nitrate deposition in China based on satellite NO$_2$ measurement by the Ozone Monitoring Instrument

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**Abstract**

Remote sensing technology has great potential to expand the observation of ground-level nitrogen deposition from local monitoring sites to a regional scale, with high spatial and temporal resolutions. A new methodology is developed to estimate the spatial distribution of monthly bulk nitrogen deposition on a regional scale, based on precipitation amounts and HNO$_3$ and aerosol nitrate (NO$_3^-$) columns, derived from OMI NO$_2$ columns and the relationship of NO$_2$, HNO$_3$ and NO$_3^-$ from MOZART. The accuracy assessment shows that the proposed model has achieved a reasonably high predictive power for monthly NO$_3^-$-N deposition (slope = 0.96, intercept = 0.35, R = 0.83, RMSE = 0.72) across China. The spatial NO$_3^-$-N deposition shows a significant gradient from industrial areas to undeveloped regions, ranging from 0.01 to 26.76 kg N ha$^{-1}$ y$^{-1}$ with an average of 5.77 kg N ha$^{-1}$ y$^{-1}$ over China during 2010–2012. The bulk NO$_3^-$-N deposition shows a clear seasonal variation, with high depositions occurring in the warm season (March–November) and peaking in July and August, and low bulk NO$_3^-$-N deposition appearing in winter (December–February). This study proves for the first time that the atmospheric boundary layer (ABL) HNO$_3$ and NO$_3^-$ columns and precipitation are powerful to predict the bulk nitrate deposition.

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1. Introduction

Nitrogen (N) deposition (N$_{dep}$) is a worldwide problem (Sutton and Bleeker, 2013; Van Damme et al., 2015), leading to N saturation (Phoenix et al., 2012), eutrophication (BERGSTROM and Jansson, 2006; Horswill et al., 2008), loss of biomass productivity and vegetation cover (Bassin et al., 2007; Reich, 2009) and soil acidification (Hoegberg et al., 2006; Stevens et al., 2009), China has been one of the hotspots of the N deposition (Jia et al., 2014; Liu et al., 2013; Pan et al., 2012), resulting from human activities such as industrial development, fertilizer application, biomass burning and agriculture expansion (Gu et al., 2012; Lee et al., 2011b). Therefore, it is essential to estimate N$_{dep}$ on the land surface and establish control measurements for improving environmental quality.

Many studies concerned bulk nitrate deposition in precipitation (containing wet and dry depositions through particles and/or gas) based on ground measurements. The bulk nitrate deposition over China was estimated in our previous work (Liu et al., 2016), based on the data from papers published during 2003–2014. However, large uncertainties still existed due to the errors of measurements from different studies and the large span of the measurements. China Agricultural University has organized a Nationwide Nitrogen Deposition Monitoring Network (NNDMN) since 2004, consisting of 43 monitoring sites across China (Liu et al., 2011; Xu et al., 2015). They reported the ground bulk nitrate depositions based on 43 NNDMN observation sites throughout China, providing a great potential for understanding the temporal change of the ground bulk nitrate depositions on a national scale (Xu et al., 2015). However, it is not easy to obtain the spatial distribution of the nitrate depositions across China only based on the ground measurements, due to the limited number of the monitoring sites and their ununiform distribution. This study tries to expand the ground bulk nitrate depositions at the monitoring sites in NNDMN to a national scale.

The spatial variation of N$_{dep}$ is influenced by energy consumption (E), N fertilizer use (F$_{N}$) and precipitation amount (P). Based on previous studies on estimating N$_{dep}$ on a regional scale, the N$_{dep}$ has linear or logarithmical relationships with P, F$_{N}$ and E (Jia et al., 2014; Liu et al., 2016; Zhan et al., 2015; Zhu et al., 2015), confirming that these factors could be used to estimate the spatial variations of N$_{dep}$ on a regional
scale. The studies mentioned above were based on statistical data (F9 and E) from the China Statistical Yearbook on a provincial scale, which may not reflect the spatial variations of N emissions due to the influence of atmospheric transmission and complex air flows. Thus, it is very difficult to estimate \( N_{\text{dep}} \) with high spatial or temporal resolutions using such coarse datasets.

The remote sensing technology provides a new means to indicate the temporal and spatial variations of \( \text{NO}_2 \) concentrations in the atmosphere due to its advantages of high temporal and spatial resolutions. The \( \text{NO}_2 \) columns retrieved from Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY), Global Ozone Monitoring Experiment (GOME) and GOME-2 and Ozone Monitoring Instrument (OMI) indicate the spatial and temporal variations of \( \text{NO}_2 \) in the atmosphere (Ma et al., 2013). In recent years, the satellite data have been widely used to calculate pollutant concentrations due to its high spatial and temporal resolutions. The tropospheric \( \text{NO}_2 \) vertical column densities (VCDs) have been employed to study the \( \text{NO}_2 \) issues (Fig. 1) have complete monitoring data, and the ground measured HNO3 and NO3\(^+\) model is established based on measured bulk nitrate depositions, the spatial and temporal variations of \( \text{NO}_2 \) in the atmosphere (Lee and Koutrakis, 2014). Column densities (VCDs) have been employed to study the \( \text{NO}_2 \) issues (Fig. 1). Satellite data have been used to estimate the temporal and spatial variations of \( \text{NO}_2 \) concentration predictions (Lee and Koutrakis, 2014). The detailed information on the description of the monitoring sites and the observation timespan of the sites are shown in the Supplementary Table S2 in Xu et al. (2015). The detailed information on measuring bulk \( \text{NO}_3^- \) -N deposition can be found in Xu et al. (2015) and Liu et al. (2011).

The monthly ground-based \( \text{NO}_3^- \) -N depositions at 7 sites (Fig. 1) from the Acid Deposition Monitoring Network in East Asia (EANET) were also used to examine the predictive performance of the constructed model in this study, which are considered as the independent monitoring network for model validation. Compared with the NNDMN, the EANET sites are mainly located in less polluted area, and the bulk/wet nitrate depositions are reasonably lower than those in NNDMN (Xu et al., 2015). The details of the monitoring techniques including sampling, chemical analysis, definitions of data completeness, quality control and quality assurance, were documented in the EANET monitoring manual (http://www.eanet.asia/product/index.html).

2.2. Tropospheric vertical column density (VCD) of \( \text{NO}_2 \)

The tropospheric vertical column density (VCD) of \( \text{NO}_2 \) is retrieved from the Ozone Monitoring Instrument (OMI), boarded on NASA’s EOS Aura satellite. The DOMINO (Dutch Finnish Ozone Monitoring Instrument) product (v2.0) is used in this study (http://www.temis.nl). The algorithm on retrieving \( \text{NO}_2 \) columns is described in the manuscript (Boersma et al., 2007). The recently updated version can be tracked from the DOMINO Product Specification Document. We use individual pixel clear sky (cloud radiance fraction < 0.5) Level 2 OMI data. The OMI \( \text{NO}_2 \) columns have been well validated, with a bias of +25% to 30% accounting for different regions (Boersma et al., 2008; Irie et al., 2008; Irie et al., 2009), and have also been widely applied in environmental-related studies and for the support of emission control policy (Russell et al., 2012; Zhao and Wang, 2009). We found some grid cells with a very small percentage (≥0.003%) had outlier values (“NULL” or “tropospheric \( \text{NO}_2 \) VCD <0 molecules cm\(^{-2}\)”), which should be removed before the usage for estimating bulk deposition. To generate continuous maps, we performed the Kriging interpolation (Geostatistical tool in ArcGIS) to estimate the values at these cells with outlier values. The cross validation of Kriging interpolation (0.125° latitude × 0.125° longitude) showed that the average relative error by month ranged from −2.97% to 4.17%. Notably, the resolution of interpolation maps is consistent with the original resolution of DOMINO \( \text{NO}_2 \) (0.125° latitude × 0.125° longitude), indicating that this interpolation procedure mainly produces uncertainty at the grid cells (with outlier values).

2.3. MOZART-4 output of the \( \text{NO}_2 \), \( \text{NO}_3^- \) and HNO3 data

In this study the gaseous \( \text{NO}_2 \), \( \text{NO}_3^- \) and HNO3 data outputted from the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4) during 2010–2012 were used. The MOZART-4 has been widely used as a global chemical transport model, which can be run at any resolution, relying on the input meteorological fields and the computer memory limitations (Emmons et al., 2010). The standard MOZART-4 mechanism contains 39 photolysis, 12 bulk aerosol compounds, 85 gas-phase species and 157 gas-phase reactions. The MOZART-4 output of the \( \text{NO}_2 \), \( \text{NO}_3^- \) and HNO3 data was temporally varying (6 h) with 1.9 latitude × 2.5 longitude horizontal resolution and 56 vertical levels from the ground. Detailed descriptions on the MOZART simulations of \( \text{NO}_2 \), HNO3 and \( \text{NO}_3^- \) data can be found in previous studies (Emmons et al., 2010; Emmons et al., 2012; Tie et al., 2007).

2.4. Atmospheric boundary layer (ABL) height

The monthly average of atmospheric boundary layer (ABL) height, obtained from ERA-Interim (http://www.ecmwf.int/services/archive), is used in this study. The ERA-Interim Archive is a part of ECMWF’s (European Centre for Medium-Range Weather Forecasts) Meteorological
Archive and Retrieval System (MARS). A comprehensive documentation of the ERA-Interim reanalysis system has been published as an open-access article in the Quarterly Journal of the Royal Meteorological Society (Dee et al., 2011).

2.5. Monthly precipitation

The monthly precipitation data from 2010 to 2012 throughout China is supplied by Centre for Atmosphere Watch and Services (CAWAS), China Meteorological Administration (CMA). The original gridded precipitation data from CAWAS were used directly in the present work (http://data.cma.cn/), which are considered to be the most accurate dataset in China among similar products such as the National Centers for Environmental Prediction (NCEP) and European Centre for Medium-Range Weather Forecasts (ECMWF). The CAWAS precipitation data were produced by two dimensional thin plate smoothing splines with the degree of data smoothing determined by minimizing the generalized cross validation (Hutchinson, 1998; Wan et al., 2011; Yan, 2004). The detailed discussion on the data set and processing can be found at China Meteorological Data Sharing Service System (http://data.cma.cn/).

2.6. Land use map

In this study, 30 m digital land-use data is obtained from the Landsat Thematic Mapper (TM) and Enhanced Thematic Mapper Plus (ETM+) data in 2010. The land cover types used in this study refer to the Tsinghua University 30 m resolution global land cover product of 2010 (http://data.ess.tsinghua.edu.cn). Those land-cover classes are grouped further into seven aggregated classes of land cover in this study: water area, grassland, cropland, forestry land, built-up land, permanent wetland and barren valeted land. The detailed description and accuracy control and assessment of this data can be found in the manuscripts (Gong et al., 2013; Yu et al., 2013).

3. Methodology

3.1. N compounds in the atmosphere

There are many N species including NO2, NO, N2O, N2O5, HNO3, HONO and NO3− in the atmosphere. The contribution of NO2 to dissolved N in precipitation is small as this gas is not very soluble relative to HNO3 or NO3− (Mentel et al., 1996). We firstly derived the HNO3 or NO3− columns based on OMI NO2 columns and their relationship from MOZART. Notably, we used the OMI NO2 columns with local time between 13:00 and 14:00 whereas the MOZART output NO2 data used in the current work are temporally varying 6 h every day (00, 06, 12 and 18). We have two steps to derive the HNO3 or NO3− columns. First, we established the relationship between monthly NO2 columns (at 12:00) and the average HNO3 columns \(\frac{\text{HNO3}(00)+\text{HNO3}(6)+\text{HNO3}(12)+\text{HNO3}(18)}{4}\) as well as the average NO3− columns \(\frac{\text{NO3}(00)+\text{NO3}(6)+\text{NO3}(12)+\text{NO3}(18)}{4}\) from MOZART. NO2 columns are significantly \((p < 0.01)\) correlated with both HNO3 and NO3− columns from MOZART, as shown in Fig. 2 and Fig. S2. Second, we derived the monthly mean HNO3 or NO3− columns based on the OMI NO2 columns and the relationship established in the first step.

3.2. Atmospheric boundary layer (ABL) HNO3 and NO3− columns

To calculate bulk nitrate deposition in the form of precipitation, it is more reasonable to use the HNO3 and NO3− columns below the precipitation height instead of the tropospheric HNO3 and NO3− columns (Fig. 3a) because the scavenging effect on N compounds is from the top precipitation height rather than the top troposphere height (Racette et al., 2009), which is much higher than that of the production of cloud water (Garratt, 1994). However, it is not feasible to model the precipitation height because the precipitation height depends on the status of the cloud which is extremely ephemeral and variable in both space and time (Bruintjes et al., 2010). Alternatively, we use ABL height as it is well modeled and validated (Dee et al., 2011). There are two major reasons supporting this alternative. First, the precipitation height

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**Fig. 1.** Spatial locations of ground measurements of wet/bulk nitrate depositions during 2010–2012. NNDMN was used for model construction and cross validation while EANET was used for independent model validation. The GDP (gross domestic product) data were obtained from China National Earth System Science Data Sharing Infrastructure (http://www.geodata.cn).
(commonly below 2–3 km) is higher than but close to ABL height (commonly below 2 km, Fig. 3b) (relative to the top of the troposphere, commonly 10–20 km). Second, more importantly, the HNO3 and NO3− columns, are mainly within ABL from the profile shapes (Rozanov et al., 2005; Russell et al., 2011), indicating there is no large difference between the HNO3 and NO3− columns under precipitation height and under ABL height. Thus, the N compounds within the ABL contribute to the dominated percentage of bulk nitrate depositions by precipitation scavenging effects, and the tropospheric HNO3 and NO3− columns were converted to ABL HNO3 and NO3− columns to calculate the nitrate deposition.

Atmospheric chemistry transport model (CTM) can produce profiles for aerosol (Liu et al., 2004; Van Donkelaar et al., 2010; Van Donkelaar et al., 2006), NO2 (Hudman et al., 2007; Lamsal et al., 2008; Nowlan et al., 2014) and SO2 (Lee et al., 2011a; Nowlan et al., 2014). We used the relationship between the tropospheric HNO3/NO3− columns and ABL HNO3/NO3− columns in MOZART-4 to convert the satellite-derived tropospheric HNO3/NO3− columns to ABL HNO3/NO3− columns.

The MOZART-4 output of HNO3 and NO3− includes 56 vertical levels from the ground and the vertical HNO3 and NO3− profiles from MOZART are simulated in every grid cell by Gauss function:

$$f(x) = \sum_{i=1}^{n} a_i e^{-\frac{(x-b_i)^2}{c_i^2}}$$

where \(n = 2, 3, 4, 5 \text{ or } 6\); \(x\) represents the height from the surface; \(f(x)\) represents the HNO3 or NO3− concentration at a height of \(x\) (the HNO3 or NO3− profiles). \(a_i, b_i \text{ and } c_i\) represent the constants of Gauss function. As
measures of accuracy and precision of the five models \((n = 2, 3, 4, 5 \text{ or } 6)\), we use the coefficient of determination \((R^2)\) and root mean square error (RMSE) to determine the best simulation function.

The tropospheric HNO\(_3\) or NO\(_3^-\) columns from MOZART are calculated according to the vertical profiles as:

\[
F(h_{\text{trop}}) = \int_0^{h_{\text{trop}}} f(x) \, dx
\]

where \(F(h_{\text{trop}})\) is MOZART tropospheric HNO\(_3\) or NO\(_3^-\) columns; \(h_{\text{trop}}\) represents the height of troposphere; \(f(x)\) represents the HNO\(_3\) or NO\(_3^-\) profiles.

The satellite-derived ABL HNO\(_3\) or NO\(_3^-\) columns are calculated as:

\[
S_{\text{ABL}} = S_{\text{tmp}} \times \frac{F(h_{\text{ABL}})}{F(h_{\text{trop}})}
\]

where \(S_{\text{tmp}}\) represents the tropospheric HNO\(_3\) or NO\(_3^-\) columns (described in Section 3.1); \(F(h_{\text{ABL}})\) is the ABL HNO\(_3\) or NO\(_3^-\) columns from MOZART; \(h_{\text{ABL}}\) represents the height of atmospheric boundary layer.

3.3. Statistical model of estimating bulk nitrate depositions

The statistical model tries to estimate bulk nitrate deposition from ABL HNO\(_3\) or NO\(_3^-\) columns and precipitation on a monthly scale at each site, which is summarized by the following equations:

\[
N_{\text{mn}} = \alpha_{\text{fn}} + \beta_{\text{fn}} (S_{\text{mn}} - [\varepsilon_n + \varepsilon_{\text{fn}}])
\]

where

\[
S_{\text{mn}} = P_{\text{mn}} \times (S_{\text{ABL}})_{\text{mn}}
\]

\(N_{\text{mn}}\) is the measured NO\(_3^-\)-N deposition in month \(m\), at site \(n\); \((S_{\text{ABL}})_{\text{mn}}\) is an indicator of combining effect of HNO\(_3\) and NO\(_3^-\); \((\text{HNO}3)_{\text{ABL}})_{\text{mn}}\) and \((\text{NO}3)_{\text{ABL}})_{\text{mn}}\) are the ABL HNO\(_3\) and NO\(_3^-\) columns in month \(m\), at site \(n\), respectively; \(\gamma\) and \(\delta\) are the constants; \(P_{\text{mn}}\) is the precipitation in month \(m\), at site \(n\); \(S_{\text{mn}}\) is an indicator of a combining effect of precipitation and N compounds in the atmosphere; \(\varepsilon_{\text{fn}}\) and \(\alpha_{\text{fn}}\) are the slope and intercept; \(\varepsilon_n\) indicates random error or site bias for site \(n\); \(\varepsilon_{\text{fn}}\) indicates the fixed error derived from the long term measurements of \(S_{\text{mn}}\) at sites, indicating the average effect of \(S_{\text{mn}}\) on the NO\(_3^-\)-N measurements; In addition, the site bias represents the monthly random error in the \(S_{\text{mn}}\)-NO\(_3^-\)-N relationship because the NO\(_3^-\)-N measured at a site may not be representative of a \(S_{\text{mn}}\) value in a 0.125° latitude \(\times\) 0.125° longitude grid cell. In brief, the bias may result from their land use, spatial locations or meteorological condition (Lee et al., 2011b; Yap and Hashim, 2013).

If all the independent variables including \((\text{HNO}3)_{\text{ABL}})_{\text{mn}}\), \((\text{NO}3)_{\text{ABL}})_{\text{mn}}\) and \(P_{\text{mn}}\) and the dependent variable \(N_{\text{mn}}\) are taken into Eq. (4), the constants include \(\gamma\), \(\delta\), \(\alpha\), \(\beta\) as well as site bias \(\varepsilon_n\). All the constants are fixed and can be easily gained except the \(\varepsilon_n\), which is variable geographically. We use the controlling covariant \((S_{\text{mn}})\) combining the ground \(\varepsilon_n\) to generate the continuous \(\varepsilon_n\) map by the Co-Kriging method, where the relationship between \(\varepsilon_n\) and \(S_{\text{mn}}\) is statistically significant with slope \(-3 \times 10^{-7}\) and intercept \(2 \times 10^{-7} (p < 0.001)\). Once the \(\varepsilon_n\) map is generated, we can gain the continuous monthly bulk nitrate depositions using the established model.

3.4. Model validation

The statistical model of estimating bulk nitrate deposition was validated by a widely used cross validation (CV) technique, known as Monte Carlo cross-validation, in evaluating the statistical model performance (Dubitzky et al., 2007; Lee et al., 2011b; Lee and Koutrakis, 2014; Varma and Simon, 2006). This technique randomly splits the dataset into validation and training data. The model is established using the training data and the accuracy of the model performance is evaluated using the validation data (Varma and Simon, 2006).

In k-fold cross-validation, the original dataset is randomly divided into \(k\) equal sized subgroups. Of the \(k\) subgroups, one subgroup is treated as the validation data for evaluating the performance of the statistical model, and the remaining \(k-1\) subgroups are used as training data. In this study, the 5-fold cross validation technique is used to validate the statistical model of estimating nitrate deposition. The observation data are divided into 5 randomly subgroups, among which 4 subgroups (training set) are used to construct a model, and 1 subgroup (test set) is used to evaluate the estimation performance. The process of 5-fold cross validation is then repeated 5 times, with each of the 5 subgroups used exactly once. The CV method over repeated random subgroups ensures that all observation data are used for both validation and training, and every observation data is exactly once used for model validation (Varma and Simon, 2006). To evaluate the relationship between the measured and predicted NO\(_3^-\)-N, the Pearson correlation coefficients and the coefficient of determination \((R^2)\) are used. Also, the root mean square error (RMSE) is applied to evaluate the accuracy. The validation is very important to assess the spatial accuracy of the predicted bulk NO\(_3^-\)-N depositions.

3.5. Clarifications on methodology thought

Given the aforementioned explanations, figures, associated concepts and method descriptions, the implementation seems not easy. We aim to generate accurate datasets of bulk nitrate depositions over China, and hence will provide basic input parameters for process-based models of N biogeochemistry in agricultural or other ecosystems to determine or quantify their effects on ecosystem health, biological diversity and greenhouse gas balances. Thus, the national ground measurements of bulk nitrate depositions (NNDMN) were used for model constructions to make this estimation less biased with the real status of bulk nitrate depositions. Due to limited spatial representatives of ground measurements, satellite observations with high spatial and temporal resolutions, and an atmospheric chemistry transport model (from MOZART in this study) with detailed vertical profiles for N compounds (HNO\(_3\) or NO\(_3^-\)), were combined to expand the ground measurements to a national scale. The thought of this study can also be tracked in some studies in estimating particular matter (PM) (Kloog et al., 2015; Yap and Hashim, 2013) or some pollution gases (Lee and Koutrakis, 2014). In such methods, three steps are generally included: (1) as many as ground measurements of target objects should be prepared for both model construction and validation; (2) the most related factors influencing the target objects should be selected, and the most important point is that selected factors should be equipped with characters of high spatiotemporal resolutions; (3) these ground measurements of target objects and selected factors are then used for model construction and retrieval of high spatiotemporal target objects on a regional scale.

On the analogy of this, the methodology also includes three similar steps. For the first step, this study selected the national ground measurements of bulk nitrate depositions (NNDMN) over China for model construction and validation. Second, N compounds (HNO\(_3\) and NO\(_3^-\)) as well as precipitation were selected as the most important factors influencing the nitrate depositions. By this step, HNO\(_3\) and NO\(_3^-\) columns were generated by OMI NO\(_2\) columns and their relationship with HNO\(_3\) and NO\(_3^-\) from MOZART. Third, a statistical model was constructed for estimating nitrate depositions combining generated HNO\(_3\) and NO\(_3^-\) columns and precipitation. Key procedures of this study are given in Fig. 4, and detailed procedures step by step have been described in Section 2 in the Supplementary material.
3.6. Sensitivity analysis by Monte Carlo

The analysis of the uncertainty degree due to the errors or uncertainty coming from the input data to drive the model, which is in particular associated with the regional or large scale modeling where the inputs are usually derived from simulations (such as the precipitation data) or satellite observations (such as NO2 columns data in the present work). The Monte Carlo simulations have the ability to quantify the sensitivity of these input factors, in which several possible scenarios are considered for every input parameter by using the random values within an acceptable specific range. Therefore, the corresponding estimated dependent values can be generated, and then the statistically possible distributions and range of the model simulations with the change of independent input variables can be gained. Actually, the Most Significant Factor (MSF) simplified by Monte Carlo simulations (due to expensive computation) is widely used in many large scale simulations (Giltrap et al., 2010; Kiese et al., 2005; Li et al., 1996), in which the extreme values of the input parameters are used to producing the variations of the target estimated object. In this study, we also used the MSF simulations to explore the sensitive parameters on estimating the bulk nitrate depositions in the constructed model.

We referred to the methods in a previous study (Li et al., 1996) by varying a single input parameter and keeping other input parameters unchanged to explore the impact of the input parameters on the bulk nitrate depositions. We set the single varying parameter by 10%, 20% and 30% (the extreme value in MSF) higher than the actual data to drive the model, and gained three additional estimated bulk nitrate depositions to compare with the baseline (using the actual data to drive the model). After repeating the same procedures one by one for all input parameters, variations of the bulk nitrate depositions can be quantified, which will be used to determine which parameter is the most sensitive factor.

4. Results and discussions

4.1. NO3−-N prediction and accuracy assessment

HNO3 and NO3− columns were firstly derived from OMI NO2 columns based on their relationship from MOZART (Fig. 2 and S2). Then, tropospheric HNO3 or NO3− columns were converted to ABL HNO3 or NO3− columns based on their vertical profiles from MOZART. The vertical profiles were well simulated by Gauss function in each grid cell for HNO3 (Fig. 5) or NO3− (Fig. S3).

The spatial pattern of the random errors (εn) across China was generated from 2010 to 2012 in the mixed effects models (Fig. 6). The εn map was generated using Co-Kriging method constrained by Smn as stated in Section 3.3. We used the mean predictive error (MPE) and root mean square standardized error (RMSSE) to assess the interpolation performance. The MPE indicates the degree of predictive bias and the predictive values are unbiased if this value is equal to 0, while the RMSSE close to 1 represents accurate error distribution (Jia et al., 2014). The MPE and RMSSE of εn were 0.03 and 0.98, respectively (Table S2), showing the interpolation performed well and the εn map was normally distributed. The developed areas have a high negative site bias and the southeastern and northwestern China have a high positive site bias, showing that densely developed areas have underestimated NO3−-N and the developing areas have an overestimated NO3−-N. Thus, it is essential to add the site bias into the mixed effect model to do the adjustment. The spatial pattern of the site bias indicates the influence of the land uses over China. Land use partly explains the NO3−-N variability because there are different emission sources in different developed areas, suggesting the simulated NO3−-N deposition is sensitive to emission estimates. The negative regions, corresponding to the cropland or Natural Vegetation Mosaic land, denote underestimated values from Smn, so that enhancement is needed. This is mainly due to the fact that these regions are being
surrounded by intensive anthropogenic activities and rapid developments along with urbanization, which shorten the transport distance of NOx emission from fossil fuel combustion (Xu et al., 2015). Similarly, the positive regions, corresponding to Grasslands, Forests or Barren or Sparsely Vegetated land, indicate an overestimation in values from $S_{\text{nn}}$ that need to be trimmed down.

The monthly bulk NO$_3^-$-N depositions were generated over China during the period 2010–2012 based on the constructed statistical model. Based on the NNDMN measurements, the 5-fold cross validation results are shown in Fig. 7, explaining the variability in monthly NO$_3^-$-N depositions (slope = 0.96, intercept = 0.35, R = 0.83, RMSE = 0.72) for a period of three years (i.e. 2010 to 2012) in China. Moreover, 7 site in EANET representing the independent measurements were also compared with the estimation (slope = 0.98, intercept = 0.02, R = 0.85, RMSE = 0.17) during 2010–2012 in China (Fig. 8). This indicated that the ABL HNO$_3$, NO$_3^-$ columns and precipitation amounts are powerful to predict the bulk nitrate depositions, and the constructed model could be used to estimate the bulk nitrate deposition on a regional scale.

**Fig. 5.** $R^2$ and RMSE (molec. cm$^{-2}$) simulated by Gauss function (68–142°E, 5–55°N) for HNO$_3$ vertical profiles from MOZART in each grid cell in 2012.
4.2. Spatial patterns of bulk NO$_3^-\text{N}$ deposition

This study expanded the ground-level NNDMN measurements to a national scale and obtained a reliable estimation of bulk NO$_3^-\text{N}$ deposition for three years, with the aid of the HNO$_3$, NO$_3^-$ columns and precipitation. To our knowledge, this is the first time to obtain the bulk NO$_3^-\text{N}$ deposition with such high spatial and temporal resolutions throughout China.

The monthly bulk NO$_3^-\text{N}$ deposition from January to December during 2010–2012 is shown in Fig. 9, and the annual bulk NO$_3^-\text{N}$ deposition over China during 2010–2012 was also demonstrated in Fig. 10. The bulk NO$_3^-\text{N}$ deposition map showed an obvious gradient from the developed regions to undeveloped regions in China, ranging from 0.01 to 26.76 kg N ha$^{-1}$ y$^{-1}$ with an average of 5.77 kg N ha$^{-1}$ y$^{-1}$ during 2010–2012 (Fig. 10a). Based on the measurements in NNDMN, in spite of some dry deposition (e.g. dust and/or particulates) included, the wet (-only) deposition is the major part (78–90%) of bulk deposition according to a previous study (Zhang et al., 2008).

From the monthly spatial maps (Fig. 9), we clearly found the bulk NO$_3^-\text{N}$ deposition by month (month$^{-1}$) exceeding 1.5 kg N ha$^{-1}$ m$^{-1}$ mostly occurred in Northern China (in July and August) including Beijing, Shandong, Shaanxi, Henan and Liaoning provinces, as well as Southern China (especially in December, January, February and March) including the Jiangsu, Anhui, Zhejiang, Jiangxi, Hunan, Sichuan and Guangdong provinces. From the annual spatial map (Fig. 10), high bulk nitrate deposition occurred in three main regions: (1) North China, including Hebei, Liaoning, Shandong, Tianjin, Henan and Beijing provinces; (2) Yangtze delta region, including Jiangsu, Anhui, Zhejiang, Shanghai, Jiangxi, Hunan and Hubei provinces; (3) Sichuan Basin, including Sichuan and Chongqing provinces. It is not surprising that

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**Fig. 6.** Spatial distribution of random error (a) and land use (b) in China. Note: The land use (b) could partly explain the random error (a); positive values in (a) corresponding to the Barren and Sparsely Vegetated and Grasslands; the negative values in (a) corresponding to the croplands and forests.

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**Fig. 7.** Accuracy assessment of the monthly estimated bulk nitrate depositions (kg N ha$^{-1}$ m$^{-1}$) in NNDMN using 5-fold cross-validation. For detailed steps for this validation can be found in Section 2 in the Supplementary material.
North China Plain, Yangtze delta region, and Sichuan Basin had high bulk nitrate deposition due to high NO\textsubscript{x} emissions, which can be clearly seen from the HNO\textsubscript{3} map (Fig. 10c). High HNO\textsubscript{3} (as a highly soluble N compound) columns occur in these regions, and hence largely be scavenged by precipitation. In some regions in South China, such as Hunan and Jiangxi provinces, small areas of high HNO\textsubscript{3} columns were found, while large areas of bulk nitrate depositions were found in these regions. This is mainly because the precipitation amounts in these regions were much higher than those in other regions (Fig. 10b, annual precipitation is 1.4–6.5 times than that in other geographical areas).

The Western China, including Tibetan plateau (TP) and Northwest China (NW), had low bulk nitrate depositions compared with the other areas of China, with the bulk NO\textsubscript{3}\textsuperscript{−} -N deposition below 0.5 kg N ha\textsuperscript{−1} m\textsuperscript{−1} even for all months (Fig. 9). This comes from two reasons. First, NW and TP were much less populated (Fig. 10d) and industrialized, and natural emissions were supposed to dominate the N compounds (e.g., soil emissions and lighting), while, in central and eastern coastal regions, HNO\textsubscript{3} columns (Fig. 10c) are mainly distributed with dense population and high industrialization level. Second, more importantly, the precipitation amounts in Western China (annual precipitation was about 200–300 mm) were much lower than that in other regions, which were about 1/2–1/6 times than that in other geographical regions.

4.3. Seasonal variations of the bulk NO\textsubscript{3}\textsuperscript{−} -N depositions

The monthly average bulk NO\textsubscript{3}\textsuperscript{−} -N deposition from 2010 to 2012 is shown in Fig. 11a, which is consistent with the temporal changes of precipitation amounts over China (Fig. 11b). Higher bulk NO\textsubscript{3}\textsuperscript{−} -N deposition occurred in summer, when China received on average 330.51 mm of rain during the summer, accounting for 51.29% of total annual precipitation. The minimum bulk NO\textsubscript{3}\textsuperscript{−} -N deposition occurred in winter, which was attributable to the low precipitation (<50.00 mm, about 1/7 of the precipitation amounts in summer). This indicates that the precipitation was an important controlling effect on the temporal change of bulk NO\textsubscript{3}\textsuperscript{−} -N deposition. The consistent effects of precipitation on the bulk nitrate deposition have also been reported by other studies (Pan et al., 2012; Xu et al., 2015).

The seasonal trend of bulk nitrate deposition can also be influenced by the N compounds in the atmosphere, which can be seen from the temporal change of ABL HNO\textsubscript{3} columns (Fig. 11c), as an indicator of highly soluble N compounds (N\textsubscript{2}O\textsubscript{5}, HNO\textsubscript{3}, or NO\textsubscript{3}\textsuperscript{−}) in the atmosphere. The scatter plots of precipitation versus the ABL HNO\textsubscript{3} columns are
illustrated in Fig. 12. A log model was created to simulate the relationship between precipitation and N compounds in the atmosphere. This showed that when the rainfall was low, the soluble N compounds (such as N$_2$O$_5$, HNO$_3$, or NO$_3^-$) in the atmosphere decreased with increasing precipitation, mainly because of the scavenging of pollutants. The scavenging of N compounds by precipitation is an important process influencing the seasonal change of bulk NO$_3^-$-N depositions (Liu et al., 2015). Thus, the seasonal trends of bulk NO$_3^-$-N deposition are caused by a combination of precipitation and the ABL HNO$_3$ columns, which can explain the seasonal variation of the bulk NO$_3^-$-N depositions with correlation coefficients of 0.91 (Fig. 12b).

It should be noted here that this analysis ignored the spatial variations of the bulk NO$_3^-$-N depositions, precipitation and ABL HNO$_3$ columns. We used the average bulk NO$_3^-$-N depositions, precipitation and ABL HNO$_3$ columns throughout China by month to do the analysis of the seasonal variations. There is no doubt that the spatial variations of the bulk NO$_3^-$-N depositions result from combining effects of the precipitation and the ABL HNO$_3$ columns.

4.4 Different methods to estimate bulk nitrate depositions

Generally, there were three methods to quantify atmospheric bulk nitrate/wet deposition on the national scale: atmospheric chemistry transport model (CTM) simulations (Appel et al., 2011; Dentener et al., 2006; Ge et al., 2014; Zhang et al., 2012; Zhao et al., 2017), geostatistical methods (such as Kriging interpolation) (Jia et al., 2014; Lü and Tian, 2007; Liu et al., 2016; Zhu et al., 2015) and average methods based on long-term monitoring networks (Liu et al., 2013; Pan et al., 2012; Xu et al., 2015). The average method is the simplest method, and the national nitrate deposition can be easily gained by averaging the observation data at the monitoring sites. There was no doubt that the average method at the site scale in the long-term monitoring networks such as the Chinese Nationwide Nitrogen Deposition Monitoring Network (NNDMN), Chinese Ecosystem Research Network (CERN), Acid Deposition Monitoring Network in East Asia (EANET), European Monitoring and Evaluation Programme, Europe (EMEP), Clean Air Status and Trends Network/the National Atmospheric Deposition Program, United States (CASTNET/NADP) and Canadian Air and Precipitation Monitoring Network, Canada (CAPMoN) were the most accurate and valuable datasets, which have been widely used to validate the modeling bulk/wet nitrate deposition by CTMs (Appel et al., 2011; Dentener et al., 2006; Ge et al., 2014; Zhang et al., 2012). At the national scale, the average method used to estimate the bulk/wet nitrate deposition by averaging the observation data at the monitoring sites possibly should be careful and may cause large uncertainties due to ignoring the relatively unbalanced levels of economic development in different regions and the inhomogeneous distribution of observation sites (Fig. 1).

Geostatistical methods (such as Kriging interpolation) can generate relatively more accurate results than average method because of
considering the surrounding area around observation sites as long as we can derive the bulk/wet nitrate deposition data with a relatively sufficient number of ground sites which are distributed throughout China (Jia et al., 2014; Lü and Tian, 2007; Liu et al., 2016; Zhu et al., 2015). Jia et al. (2014) used the Kriging methods to obtain the spatial distributions of yearly bulk nitrate depositions based on published papers between 1980s and 2010s; Liu et al. (2016) summarized the existing spatial distributions of yearly bulk nitrate deposition since 2003, and explored the potential influencing factors. However, the above studies are constrained by different sampling procedures and standards of measured bulk nitrate depositions resulting from different studies. Lack of standards for sampling procedures and concept of atmospheric bulk nitrate depositions led to incomparable results by different studies, and worsens the existed difficulties related to data integration. The geostatistical methods can hardly estimate the long-term nitrate deposition due to the limited continuous monitoring sites (43 sites in NNDMN, 41 sites in CERN) in China.

CTM methods can be used to estimate the bulk/wet nitrate deposition, and the nitrate deposition maps on a national or global scale have been generated (Appel et al., 2011; Brasseur et al., 1998; Lu and

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**Fig. 11.** Monthly bulk NO$_3^-$-N deposition (kg N ha$^{-1}$ m$^{-1}$), precipitation (mm) and ABL HNO$_3$ (10$^{13}$ molec./cm$^2$) for the time period 2010–2012 in China. The vertical bars represent the error of monthly bulk NO$_3^-$-N deposition, precipitation and ABL NO$_2$ for the three years of values. (a), (b) and (c) shows the monthly bulk nitrate deposition, precipitation and ABL HNO$_3$ columns. J, F, M, A, M, J, A, S, O, N, D represent the months from January to December.

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**Fig. 12.** The relationship between precipitation (mm), ABL HNO$_3$ (10$^{13}$ molec./cm$^2$) and bulk NO$_3^-$-N deposition (kg N ha$^{-1}$ m$^{-1}$) on a monthly scale in China from 2010 to 2012. (a) shows the relationship between precipitation (mm) and ABL HNO$_3$ (10$^{13}$ molec./cm$^2$). (b) shows the combination effect of precipitation and ABL HNO$_3$ columns on the bulk nitrate deposition on a monthly scale.
the underestimation of emission, which has been suggested by previous studies (Amos et al., 2012; Liu et al., 2001; Mari et al., 2000). Wet/bulk nitrate depositions from CTMs have large spatial resolutions. Resolutions of different CTMs are varying from 1° latitude × 1° longitude to 5° latitude × 4° longitude, and further to be improved to <1° latitude × 1° longitude in recent years (Appel et al., 2011; Dentener et al., 2006; Vet et al., 2014; Zhang et al., 2012). Liu and Tian (2007) found the CTM modeling results during the year of 1993 (Dentener, 2006) significantly underestimated the real nitrate depositions by 71.3% of modeled values within ±50% of the ground measurements of nitrate deposition. Vet et al. (2014) also found that moderate underestimation (the modeling results accounting for 70% of the measured) in Asia, implying that the CTMs were not completely effective in deriving the spatiotemporal nitrate deposition throughout the country. The reason for the underestimation in Asia may be due to the underestimate of emission, which has been suggested by previous studies (Wang et al., 2012; Wang et al., 2007b; Zhang et al., 2007). In addition, many chemical transport processes are simplified and parameterized in CTMs (uncertainties in chemistry schemes and errors of the emission data), and consequently CTMs cannot provide all the information of reality (Du and Liu, 2014). The operational performance of atmospheric chemistry model in predicting nitrate deposition needs to be further validated by comparison with field measurements. Further improvement of CTM methods in predicting the bulk/wet nitrate deposition need to be corrected or modified by as many as possible observation data of nitrate deposition. In recent years, the spatial resolutions of CTM in estimating bulk/wet nitrate depositions has been improved such as 1° × 1° resolution in the globe (note that the emission resolution are larger than 1° × 1°) by Dentener et al. (2006) and Vet et al. (2014), 1/2° × 2/3° resolution in the USA by Zhang et al. (2012) and 30 km by 30 km in China by Ge et al. (2014). Ge et al. (2014) assessed the accuracy of an improved CTM named as the Nested Air Quality Prediction Modeling System (NAQPMs), improved the spatial resolutions into 30 km by 30 km (note that the emission data at 0.5° × 0.5° resolution and the precipitation at 0.25° × 0.25°), and found the overall correlation (R) between the modeling and observation were about 0.74 across China (slightly lower than the accuracy with R = 0.81 in this study).

We are supposed to clarify in particular that we do not aim at improving the scheme of CTM using the traditional way including in-cloud and below-cloud scavenging to estimate the bulk/wet nitrate deposition, but enhancing the methods proposed by the recent studies (Jia et al., 2014; Zhan et al., 2015; Zhu et al., 2015) from the statistical perspective. Jia et al. (2014) found that FN, E and P combined contributed 79% of the spatial variation of Ndep. Zhan et al. (2015) concluded that FN, E, and P jointly explained 84.3% of the spatial pattern of Ndep, in which FN (27.2%) was the most important, followed by E (24.8%) and P (9.3%). Zhu et al. (2015) also found P and FN could explain 80–91% of the spatial variation of Ndep. These studies confirmed that these factors could be used to estimate the spatial variations of Ndep on a regional scale, but were confined effectively to provincial, municipal or county-level scale due to the limited statistical data from the China Statistical Yearbook, which may not denote the real status of spatial distribution of N species resulting from the impact of the complicated air atmospheric transport. Facing this problem, we applied the satellite-derived columns with high spatial and temporal resolutions to replace the statistical data in estimating the bulk nitrate deposition over China, and test whether the NO2 columns retrieved from remotely-sensed techniques could be used to estimate the bulk/wet NO3-N on a monthly scale. The bulk nitrate deposition estimated from the proposed method were compared with the ground measurements during 2010–2012 in China. The results showed this method is powerful to estimate the spatial distribution of bulk nitrate deposition with high-resolution on national and regional scales in China. We consider that the methodology will be promising in investigating and measuring the bulk/wet deposition from a satellite perspective on a regional scale.

4.5. Model uncertainty

We conducted both 5-fold cross validation using NNDMN measurements and independent validation using the EANET measurements between the estimated and measured bulk nitrate depositions, showing the modeling simulations can still generate estimations with uncertainties. This may result from both the input dataset used for running the model and the constructed model itself. The estimation may produce relatively enormous uncertainty with inaccurate input data, indicating it is critically to conduct a sensitive analysis on how the different input data impact the estimation of bulk nitrate depositions. We presented here the sensitive analysis by using the MSF method to better understand the key influencing factors on the model performance for the regional simulations.

As described in Section 3 on the methodology, the key input parameters are NO2 columns, precipitation and ABL height (NO2 columns and ABL height are key inputs to derive the process variables of ABL HNO3 and NO2- ). To examine the sensitivity of each parameters to the bulk nitrate depositions, we took a month (July in 2012) as a case study by controlling a single parameter varying and other input parameters unchanging to drive the model in a single simulation. Based on the MSF method by setting the extreme value as 10%, 20% and 30% higher than the actual data for each parameter, we found the precipitation is the most sensitive parameter to the bulk nitrate depositions as shown in Fig. 13. A 30% increase in precipitation led to 19.6% increase in bulk nitrate deposition. Varying NO2 columns had moderate impact on

![Fig. 13. Sensitivity of bulk nitrate depositions (kg N ha-1 m-1) to NO2 columns (1015 molec. cm-2), precipitation (mm) and ABL height (m) in July 2012. The single varying parameter was set 10%, 20% and 30% (the extreme value in MSF) higher than the actual data to drive the model in a simulation.](image-url)
the bulk nitrate deposition. A 30% increase in NO2 columns produced a 13.73% increase in bulk nitrate deposition. Compared with precipitation and NO2 columns, ABL had less effect on the bulk nitrate deposition, and a 30% increase in ABL height generated a 3.92% increase in bulk nitrate deposition.

In addition to the uncertainty coming from the input data, the constructed model itself with multiple assumptions may also arouse uncertainty in estimating bulk nitrate depositions. First, we used ABL height instead of the top precipitation height to calculate HNO3 and NO3 columns scavenged by precipitation due to the difficulty in modeling the top precipitation height. Second, the discrepancy of resolutions between OMI and MOZART as well as the relationship of MOZART NO2 columns vs. HNO3 columns, and NO2 columns vs. NO3 columns may also lead to uncertainty in estimating the bulk nitrate depositions. Third, our constructed model was not only based on satellite NO2 columns, MOZART simulations but also measured NNDMN sites, indicating that in general more continuous monitoring sites with uniform monitoring methods should be enhanced in future.

5. Conclusion

In order to better estimate long-term monthly NO3−N deposition, we have developed and validated a model to estimate the monthly bulk NO3−N deposition with a 0.125° latitudes × 0.125° longitudes across China. A good model performance has been shown across the wide range of geo-climatic characteristics of China. The 5-fold cross validation in NNDMN shows that the monthly estimated and measured NO3−N deposition are generally correlated with a slope = 0.96 and R = 0.83, and the independent validation in EANET denotes the monthly estimated and measured NO3−N deposition are also significantly correlated with a slope = 0.98 and R = 0.85.

The NO3−N deposition map indicated a significant gradient from east to west in China, ranging from 0.01 to 26.76 kg N ha−1 y−1 with an average of 5.77 kg N ha−1 y−1. The spatial pattern of NO3−N deposition by province showed that Beijing, Hebei, Shandong, Jiangsu, Guangdong and Zhejiang, were the largest contributors, while the undeveloped areas in the west had little contribution to national NO3−N deposition. Also, high bulk NO3−N deposition occurred in summer, followed in order by spring, autumn and winter.

The generated bulk nitrate deposition is able to reflect the status of bulk nitrate deposition in China, and to provide basic information for assessing the influence of N enrichment on regional biogeochemical cycles, water resources and climate. The satellite-retrieved bulk nitrate deposition is particularly helpful in assessing the status of nitrate deposition. ABL had less effect on the bulk nitrate deposition, and the results support the demonstration of the Community Multiscale Air Quality (CMAQ) model v4.7 wet deposition estimates for 2002–2006. Geosci. Model Dev. 4, 357–371.


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