Simulated seasonal variations in nitrogen wet deposition over East Asia

YU Jin-Hai, ZHANG Mei-Gen and LI Jia-Lin
State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, 100083, China

ABSTRACT
The regional air quality modeling system Regional Atmospheric Modeling System–Community Multiscale Air Quality was applied to estimate the spatial distribution and seasonal variation in nitrogen wet deposition over East Asia in 2010. The simulated results were evaluated by comparing modeled precipitation rates and ion concentrations, such as ammonium (NH$_4^+$), nitrate (NO$_3^-$), and sulfate, in rainwater, against observations obtained from Acid Deposition Monitoring Network in East Asia and meteorological stations in China. Comparison of simulated and observed precipitation showed that the modeling system can reproduce seasonal precipitation patterns reasonably well. For major ion species, the simulated results in most cases were in good agreement with those observed. Analysis of the modeled wet deposition distributions indicated that China experiences noticeable variation in wet deposition patterns throughout the year. Nitrogen wet deposition (NH$_4^+$ + NO$_3^-$) during summer and spring accounted for 71% of the annual total (3.9 Tg N yr$^{-1}$), including 42.7% in summer. Precipitation plays a larger role in the seasonal variation of wet deposition; whereas, aerosol concentrations affect its distribution patterns. In China, the amount of annual nitrogen wet deposition ranged from 1 to 18 kg N ha$^{-1}$ yr$^{-1}$. Nitrogen in wet deposition was mainly in the form of NH$_4^+$, accounting for 65.76% of the total amount, and the molar ratio of NH$_4^+$/NO$_3^-$ was mostly more than 1, indicating a relatively larger effect from agricultural activities.

1. Introduction
Nitrogen wet deposition is an issue of increasing importance in China. Although nitrogen deposition can supply nutrition for plants, excessive nitrogen may induce a series of problems, including soil acidification (Bowman et al. 2008), eutrophication, loss of biodiversity, air pollution, and climate change. A major source of nitrate (NO$_3^-$) in rain are the nitrogen oxides (NO$_x$) (nitric oxide + nitrogen dioxide) emitted from fossil fuel combustion, and a major source of ammonium (NH$_4^+$) is ammonia (NH$_3$) volatilized from fertilizer and the excrement of humans and animals. Economic development and population expansion have increased the demand for chemical fertilizer and fossil fuel consumption, resulting in considerable increases in nitrogen deposition.

Since its inception in 1978, the National Atmospheric Deposition Program has monitored precipitation chemistry across the United States, and the European Monitoring and Evaluation Program was developed to measure air and precipitation quality over Europe. Systematic measures have contributed to the understanding, and in some cases reduction, of nitrogen deposition in the aforementioned regions. Numerous nitrogen deposition measurement programs have been launched in China since the 1980s (Huang et al. 2010; Pan et al. 2012; Zhao et al. 2009). However, the fluxes in nitrogen wet deposition were calculated only by using a few sites. A systematic nationwide
monitoring network to obtain nitrogen deposition distribution data is absent in China, leading to insufficient information on regional-scale nitrogen deposition.

For quantifying spatiotemporal distributions of atmospheric nitrogen deposition, modeling tools are very useful (Simpson et al. 2014; Zhang, et al. 2012). However, no such simulations have thus far been conducted with respect to the seasonal variation in nitrogen wet deposition over China. Nitrogen deposition pattern determination and the role of anthropogenic sources in China have not been clarified. Accordingly, in the present study, the seasonal variation in nitrogen wet deposition distributions over East Asia were estimated using the Regional Atmospheric Modeling System–Community Multiscale Air Quality (RAMS–CMAQ) air quality modeling system. In the remainder of the paper, the modeling system and its input data are introduced in Section 2. In Section 3, the simulated results are evaluated based on the precipitation and concentrations of major species, and the spatial and seasonal distribution patterns of nitrogen wet deposition over East Asia are discussed. Results from analyzing the role of precipitation and aerosol concentrations, and the quantification of the relative contributions to nitrogen wet deposition from NH$_4^+$ and NO$_3^-$, are also presented. Conclusions are given in Section 4.

2. Model description

RAMS–CMAQ can concurrently simulate the atmospheric and land processes affecting the transport, transformation, and deposition of air pollutants and their precursors on both regional and urban scales. It has been used successfully to simulate NO$_3^-$, NH$_4^+$, and sulfate aerosol (Han et al. 2010; Zhang et al. 2007, 2012b; Zhang, Han, and Zhu 2007; Zhang, Shen, et al. 2012), in addition to wet acidic depositions (Ge et al. 2011), over East Asia. The cloud module in the modeling system includes parameterizations for several types of clouds, including sub-grid convective (precipitating and non-precipitating) and grid-scale resolved. This module can redistribute pollutants in sub-grid clouds, calculate in-cloud and precipitation scavenging, treat aqueous chemistry, and calculate wet deposition amounts.

The model domain (Figure 1) was 6,656 km × 5,440 km with a 64 km grid cell on a rotated polar stereographic map projection centered at (35°N, 110°E), which included most of East Asia. The model height of RAMS is consistent with that of CMAQ, and the lowest seven layers in the two different models are identical. In RAMS, 25 vertical layers in the $\sigma_z$ coordinate system are unevenly distributed from ground level to approximately 23 km, with nearly nine layers in the lowest 2 km used to simulate the planetary boundary layer. CMAQ uses 15 levels, with the lowest at approximately 100 m.

RAMS was executed in a four-dimensional data assimilation mode by using analysis nudging with re-initialization every four days, in which the first 24 h was the initialization period. The background meteorological fields for RAMS were obtained from the final analysis datasets of the National Centers for Environmental Prediction, with $1^\circ \times 1^\circ$ resolution every 6 h. The boundary conditions for the RAMS calculations used weekly mean sea surface temperatures and observed monthly snow cover information.

The anthropogenic emissions (0.25° × 0.25°) of precursors and primary aerosols including carbon monoxide, carbon dioxide, NO$_x$, sulfur dioxide, volatile organic...
compounds, black carbon, organic carbon, and fine and coarse particulate matter (PM$_{2.5}$ and PM$_{10}$), were based on the estimates by Zhang et al. (2009) and Li et al. (2014), which included the following categories: power, industry, residential, and transport. Agricultural NH$_3$ emissions were based on the estimates by Huang et al. (2012). In addition, the boundary conditions for CMAQ were obtained from the outputs of Model for Ozone and Related Chemical Tracers, version 4 (MOZART-4).

### 3. Results and discussion

#### 3.1. Comparison of observed and simulated results

RAMS–CMAQ was executed from 26 December 2009 to 31 December 2010. The observed monthly precipitation amounts at 839 rain gauge stations in China were used in the evaluation of precipitation. The locations of these stations are shown in Figure 1. The measured concentrations of non-sea-salt sulfate (nss-SO$_4^{2-}$), NO$_3^-$, and NH$_4^+$ at 24 EANET (Acid Deposition Monitoring Network in East Asia) stations were used to assess CMAQ. The locations of the EANET sites are also provided in Figure 1.

Table 1 shows the statistics for observed and modeled monthly precipitation amounts at 839 stations in 2010. Generally, the model simulated the observed precipitation pattern reasonably well, and the modeled annual mean precipitation, 63.00 mm, was nearly the same as that of the observation, 77.56 mm, with an annual normalized mean bias (NMB) of −18.77% and an annual mean correlation coefficient ($R$) of 0.79. These discrepancies were caused mainly by uncertainties in related cumulus convection parameterizations (Huang, Zhang, and Zhu 2009).

Generally, observed rainfall gradually decreased from southeast to northwest, which was well simulated by RAMS–CMAQ (Figure 2). Seasonal precipitation variations were sharp in East Asia, with the highest amount, 120 mm, occurring in summer in South China, and the lowest amount, 20 mm, occurring in winter in most of China. These temporal and spatial distribution characteristics were reasonably reproduced by the model.

In winter, modeled rainfall levels in most of China were less than 20 mm. However, substantial precipitation occurred in South China and in the coastal areas of the Japan Sea. In spring, a remarkable rise in modeled rainfall occurred across Southeast and Northeast China. During summer, high modeled rainfall mainly occurred in Northeast China, several regions between the middle reaches of the Yellow and Yangtze rivers and Southeast China, with maximum precipitation levels of more than 220 mm. Autumn is the period of transition from summer to winter monsoon. A downward precipitation trend compared with summer was revealed, although substantial precipitation still existed in the coastal regions of South China.

Table 1 shows the fit between simulated and observed monthly mean concentrations of NH$_4^+$, NO$_3^-$, and nss-SO$_4^{2-}$ for precipitation at the 24 EANET stations. The simulated results in Japan and Korea were in good agreement with these observations. However, obvious discrepancies between the model and observation were found in inland cities of China. Some Chinese sites are close to large cities, such as Chongqing and Xi’an, where emissions are intensive, but the regional model grid size is too large to resolve expansive emissions and terrain gradients (Li and Han 2012). The model overestimated the concentration of

### Table 1. Quantitative performance statistics for the monthly precipitation amount (mm) simulated by RAMS–CMAQ at 839 stations in China.

| Month | $C_{\text{obs}}$ | $C_{\text{model}}$ | $\sigma_{\text{obs}}$ | $\sigma_{\text{model}}$ | NMB ($) | $R$ |
|-------|-----------------|-------------------|---------------------|---------------------|----------|-----|
| 1     | 22.79           | 14.86             | 39.89               | 22.47               | −34.77   | 0.73|
| 2     | 29.18           | 22.52             | 45.67               | 27.15               | −22.82   | 0.77|
| 3     | 51.30           | 28.53             | 74.19               | 29.30               | −44.39   | 0.78|
| 4     | 86.51           | 50.69             | 101.51              | 55.81               | −41.41   | 0.77|
| 5     | 112.55          | 90.78             | 103.51              | 105.73              | −19.34   | 0.64|
| 6     | 133.19          | 121.87            | 147.77              | 173.61              | −8.50    | 0.74|
| 7     | 156.14          | 182.36            | 123.48              | 190.26              | 16.79    | 0.29|
| 8     | 132.46          | 102.48            | 106.78              | 97.38               | −22.63   | 0.40|
| 9     | 107.26          | 78.84             | 95.04               | 105.42              | −26.50   | 0.71|
| 10    | 55.58           | 31.48             | 113.10              | 72.54               | −43.36   | 0.88|
| 11    | 16.11           | 10.49             | 20.99               | 14.83               | −34.90   | 0.51|
| 12    | 27.67           | 21.12             | 40.23               | 23.99               | −23.67   | 0.60|
| Year  | 77.56           | 63.00             | 53.03               | 57.43               | −18.77   | 0.79|

$^a$Observed monthly precipitation (mm).

$^b$Modeled monthly precipitation (mm).

$^c$Observed standard deviation (mm).

$^d$Modeled standard deviation (mm).

$^e$Normalized mean bias (%).

$^f$Correlation coefficient between observed and modeled precipitation.
Figure 2. Observed seasonal mean precipitation amounts for (a) winter (December–February), (b) spring (March–May), (c) summer (June–August), and (d) autumn (September–November) of 2010 and simulated seasonal mean precipitation amounts for (e) winter, (f) spring, (g) summer, and (h) autumn.
value in dry seasons (winter and autumn) was larger than that in rainy seasons (summer and spring). This negative relationship between rainfall and nitrogen concentrations is consistent with the results of previous studies (Huang et al. 2010). However, values in Northeast and Northwest China, where lower emissions were found, were higher in summer than those in other seasons. This result implies that long-range transport, particularly the prevalent south-easterly wind in summer, may cause elevated concentrations in remote areas downwind of polluted regions under low-precipitation conditions (An et al. 2002).

The values of $\text{NH}_4^+$/$\text{NO}_3^-$ in precipitation were analyzed, and the results are discussed below. $\text{NO}_3^-$, the major precursor of $\text{NO}_3^-$ in precipitation, originates from fossil fuel combustion by power plants, automobiles, and biomass burning (Zhao et al. 2009). $\text{NH}_4^+$, the major precursor of $\text{NH}_4^+$ in precipitation, originates mainly from fertilizer and human and animal excrement. Therefore, the ratio of $\text{NH}_4^+$ to $\text{NO}_3^-$ can reflect the relative contribution of reactive nitrogen from industry and transportation, agriculture, and human sources.

3.2. Temporal and spatial distribution of $\text{NH}_4^+$ and nitrate concentrations in precipitation

Although the distributions of $\text{NH}_4^+$ and $\text{NO}_3^-$ concentrations in precipitation were similar, the concentration of the former was higher than that of the latter. A comparison of the concentration levels in the four seasons revealed that the value in dry seasons (winter and autumn) was larger than that in rainy seasons (summer and spring). This negative relationship between rainfall and nitrogen concentrations is consistent with the results of previous studies (Huang et al. 2010). However, values in Northeast and Northwest China, where lower emissions were found, were higher in summer than those in other seasons. This result implies that long-range transport, particularly the prevalent south-easterly wind in summer, may cause elevated concentrations in remote areas downwind of polluted regions under low-precipitation conditions (An et al. 2002).

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and animal husbandry to nitrogen deposition (Li et al. 2013). The values of \( \text{NH}_4^+ / \text{NO}_3^- \) are usually much smaller than 1 in the U.S. and in European countries, and usually over 1 in China, indicating a relatively larger effect of agriculture activities. During spring, the ratio of \( \text{NH}_4^+ / \text{NO}_3^- \) in South China was significantly higher than 2, greater than that in other parts of the country. As spring approaches, numerous farming activities begin in South China, causing increases in \( \text{NH}_3 \) emissions. In winter, very low ratios were noted in North China, mainly because residential heating causes an increase in \( \text{NO}_x \). The Beijing–Tianjin–Hebei region and the Yangtze and Pearl River deltas, important commercial regions in China, displayed relatively lower ratios throughout the year, at less than 2. In general, seasonal \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) concentrations in rainwater are mainly controlled by seasonal precipitation and long-range transport; whereas, the ratio of \( \text{NH}_4^+ \) to \( \text{NO}_3^- \) is largely affected by nitrogen management of local anthropogenic activity.

### 3.3. Temporal and spatial distribution of nitrogen wet deposition over East Asia

Nitrogen wet deposition (\( \text{NH}_4^+ + \text{NO}_3^- \)) in the summer and spring accounted for 71% of the annual total (3.9 Tg N yr\(^{-1} \),
concentrations are two important factors controlling the seasonal variation in wet deposition. This analysis showed that precipitation plays a larger dominant role in seasonal variation of wet deposition.

For the year, the model results were 1–18 kg N ha\(^{-1}\) yr\(^{-1}\), which is slightly greater than those reported in the U.S. High wet depositions greater than 12 kg N ha\(^{-1}\) occurred in Bohai Bay, the North China Plain, Shanxi and Sichuan provinces, the southern region of the Yangtze River, and the southern foothills of the Tibetan Plateau. Most researchers have reported critical loads of terrestrial ecosystems at approximately 10–20 kg N ha\(^{-1}\) yr\(^{-1}\) (Duan et al. 2001; Grigal 2012; Lu and Tian 2007). Considering only wet deposition in this study, we conclude that nitrogen deposition exceeds the critical loads in many areas of China. Liu et al. (2011) reported that critical loads in Northeast and Northwest China are commonly very low, at less than 15 kg N ha\(^{-1}\) yr\(^{-1}\). In contrast, the critical loads of nitrogen in the southeast region are relatively high (Duan et al. 2000). The highest wet depositions in Northeast China were larger than 16 kg N ha\(^{-1}\) yr\(^{-1}\), which indicates that the potential risk of nitrogen saturation is higher in Northeast China than that in other regions of the country.

4. Conclusion

The RAMS–CMAQ modeling system was employed to simulate seasonal variations in nitrogen wet deposition in East Asia recorded in 2010. Comparison of the simulated and observed precipitation for the various seasons showed that RAMS can reproduce major precipitation zones and dry areas. Comparison of modeled and observed major ionic species showed that the simulation generally reproduced the major features observed for wet deposition, with most of the scatter falling within the reference lines within a factor of 2.

The annual nitrogen wet deposition fluxes over China ranged from 1 to 18 kg N ha\(^{-1}\) yr\(^{-1}\) in 2010. It was also found that the annual total wet deposition of nitrogen in mainland China was 3.9 Tg N yr\(^{-1}\). The main nitrogen in wet deposition was NH\(_4\)\(^+\) accounting for 65.76% of the total amount, indicating a relative larger effect of agriculture activities. Nitrogen wet deposition in the summer accounted for 42.7% of the annual total. The present analysis shows that precipitation and aerosol concentrations are major factors controlling the seasonal variation in wet deposition.

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