Simulated Seasonal Variations in Wet Acid Depositions over East Asia

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ABSTRACT
The air quality modeling system Regional Atmospheric Modeling System–Community Multi-scale Air Quality (RAMS-CMAQ) was applied to analyze temporospatial variations in wet acid deposition over East Asia in 2005, and model results obtained on a monthly basis were evaluated against extensive observations, including precipitation amounts at 704 stations and SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ concentrations in the atmosphere and rainwater at 18 EANET (the Acid Deposition Monitoring Network in East Asia) stations. The comparison shows that the modeling system can reasonably reproduce seasonal precipitation patterns, especially the extensive area of dry conditions in northeast China and north China and the major precipitation zones. For ambient concentrations and wet depositions, the simulated results are in reasonable agreement (within a factor of 2) with observations in most cases, and the major observed features are mostly well reproduced. The analysis of modeled wet deposition distributions indicates that East Asia experiences noticeable variations in its wet deposition patterns throughout the year. In winter, southern China and the coastal areas of the Japan Sea report higher SO$_4^{2-}$ and NO$_3^-$ wet depositions, whereas in autumn, higher SO$_4^{2-}$ and NO$_3^-$ wet depositions are found around Sichuan Province. Meanwhile, due to the high emission of SO$_2$, high wet depositions of SO$_4^{2-}$ are found throughout the entire year in the area surrounding Sichuan Province. There is a tendency toward decreasing NO$_3^-$ concentrations in rainwater from China through Korea to Japan, which is a consequence of the influence of the continental outflow from Eurasia. The same tendency is not found for SO$_4^{2-}$.

INTRODUCTION
Acid rain is a popular term for the atmospheric deposition of acidified rain, snow, sleet, hail, acidifying gases, and particles as well as acidified fog and cloud water. The primary precursors to acidity in the troposphere are SO$_2$ and NO$_x$ and organic compounds that are emitted and subsequently oxidized into more acidic forms through a complex series of interactions involving numerous chemical, meteorological, physical, and biological processes. Acid rain is a particularly important environmental issue in East Asia because this area has experienced extensive industrialization in the last three decades. Emissions of SO$_2$ and NO$_x$ have increased at significant rates due to the accelerated use of fossil fuels and automobiles. In addition, there have been large emission changes, in terms of both levels and types, in this area in recent years. For example, Asian NO$_x$ emissions have increased rapidly since the 1970s, when they contributed only a minor fraction of global emissions, and surpassed emissions from North America and Europe in the mid-1990s. Tonooka estimated that SO$_2$ and NO$_x$ emissions in China increased by 19% and 31% from 1988 to 1994, respectively. In Japan,

IMPLICATIONS
Seasonal variations of wet acidic depositions in East Asia were studied using the air quality modeling system RAMS-CMAQ. The simulated results provide information on transport, transformation, and wet deposition patterns of acidic substances over East Asia. This information can assist decision makers in designing emission regulations, especially for areas that have serious problems with acid deposits.
SO₂ emissions slightly decreased, but NOₓ emissions increased by 13% during the period from 1987 to 1995. Park estimated that anthropogenic emissions in Korea increased by 34% for SO₂ and by 122% for NOₓ during this same period.7

Many of the critical issues concerning acid deposition involve its impacts on natural and man-made systems. To assess these impacts, a great deal of effort has been devoted to determining the emissions magnitudes of acid deposition precursors and the distributions of these substances in East Asia through the use of field monitoring and numerical modeling.8,20

Although emissions patterns are essential in evaluating existing and potential acid deposition problems, acid rain pollution has not shown significant improvement despite the control measures implemented in recent years. Because acid deposition is basically a secondary pollutant and its precursors can travel long distances before being deposited, an identification of the transformation and transport processes is critical to understanding this phenomenon, particularly in delineating its extent and magnitude in Asia. Because there is still uncertainty in our understanding and modeling ability (e.g., simulated precipitations, related emissions variations, effects of long-range transport, and transformation and deposition mechanisms of S and N compounds in East Asia), these problems require further study. Besides, the relative precipitation contributions of SO₄²⁻ and NO₃⁻ have changed in accordance with the relative changes in SO₂ and NOₓ emissions. Further study is, therefore, warranted to gain insight into the seasonal distributions of wet depositions and the current precipitation levels of NO₃⁻/SO₄²⁻.

The purpose of this study was to apply a comprehensive air quality modeling system to study seasonal variations in wet acid deposition distributions. First, the model system and its inputs are briefly introduced. Then, the spatial and seasonal distribution patterns of wet deposition are analyzed based on the distribution of precipitation and the concentrations of major acidic species (SO₄²⁻, NO₃⁻, etc.), and a comparison is made to monitoring data obtained from Chinese meteorological stations and the Acid Deposition Monitoring Network in East Asia (EANET) stations. Finally, a summary and conclusions are given.

MODEL DESCRIPTION

In this paper, the air quality modeling system Regional Atmospheric Modeling System–Community Multi-scale Air Quality (RAMS-CMAQ)21 was employed to study the complex sequence of physical and chemical processes involved in acid deposition in East Asia. The RAMS-CMAQ modeling system contains two major components, the Community Multi-scale Air Quality (CMAQ)22 and the Regional Atmospheric Modeling System (RAMS). This modeling system can simulate concurrently the atmospheric and land processes affecting the transport, transformation, and deposition of air pollutants and their precursors on both regional and urban scales and has been widely applied to address issues regarding tropospheric ozone and anthropogenic aerosols, such as black and organic carbons, SO₄²⁻, NO₃⁻, NH₄⁺, and their precursors, in East Asia.23-25

CMAQ version 4.6 was employed in this study to account for chemistry in three phases: the gas phase, aerosols (solid or liquid), and the aqueous phase. CMAQ used meteorological fields simulated by RAMS version 6.0 and CMAQ was configured with the chemical mechanism CB05.26 The Cloud module in CMAQ performs several functions related to cloud physics and chemistry, and three types of clouds are modeled: subgrid convective precipitating clouds, subgrid nonprecipitating clouds, and grid-resolved clouds. The cloud module vertically redistributes pollutants for the subgrid clouds, calculates in-cloud and precipitation scavenging, performs aqueous chemistry, and accumulates wet deposition amounts. To depict aerosol evolution processes in the atmosphere, the Regional Particulate Model (RPM)27 module was included. In RPM, the particle size distribution is represented as the superposition of three lognormal subdistributions, and the processes of coagulation, particle growth by the addition of new mass, particle formation, dry deposition, scavenging, and aerosol chemistry are included. CMAQ uses a thermodynamic aerosol equilibrium model known as ISORROPIA to calculate the composition and phase state of the Na⁺-NH₄⁺-Cl⁻-SO₄²⁻–NO₃⁻-H₂O system in thermodynamic equilibrium with gas-phase precursors.

A general description of RAMS and its capabilities are given in Pielke et al.28 The current study used the Kain-Fritsch cumulus parameterization scheme29 (to represent the subgrid-scale convective cumulus) and the Kessler-type microphysics model.30 The microphysics module was used to simulate mesoscale clouds and precipitation phenomena. The level 2.5 turbulent closure model,31 the Land Ecosystem Atmosphere Feedback model,32 and the soil-vegetation model were also used for the simulation.

RAMS modeling was exercised in a four-dimensional data assimilation mode using analysis nudging with reinitialization every 4 days, leaving the first 24 hr as the initialization period. The three-dimensional meteorological fields for RAMS were obtained from the National Centers for Environmental Prediction (NCEP) final analyses data sets and were available every 6 hr with 1° × 1° resolution. Weekly mean sea surface temperatures (SSTs) and observed monthly snow cover information were used as the boundary conditions for RAMS calculations.

The model domain is 6656 × 5440 km² for CMAQ (shown in Figure 1) on a rotated polar stereographic map projection centered at 35°N and 110°E with a 64-km-grid cell. RAMS and CMAQ have the same model height. For RAMS, there are 25 vertical layers in the σₑ coordinates system unequally spaced from the ground to approximately 23 km, with approximately 9 layers concentrated in the lowest 2 km of the atmosphere to resolve the planetary boundary layer. For CMAQ, there are 15 levels, and the lowest 7 layers are the same as those in RAMS; the lowest layer is approximately 100 m.

The anthropogenic emissions and open biomass burning emissions of SO₂, NOₓ, NH₃, hydrocarbons, and particles were obtained from the monthly-based emissions inventory, which has a spatial resolution of 0.5° × 0.5°.35 NOₓ and ammonia from soil and natural hydrocarbon emissions were extracted from the Global Emissions Inventory Activity (GEIA) 1° × 1° monthly inventory.34 Aircraft-exhausted and lightning-produced NOₓ were derived from the Emission Database for Global Atmospheric Research (EDGAR) 1° × 1° monthly inventory.35 Volcanic SO₂ emissions were based on...
the estimates of Streets et al., and the Miyakejima (2005) estimates provided by the Frontier Research Center for Global Change of Japan.

The boundary conditions and initial conditions for CMAQ were adopted from the outputs of MOZART-4 (Model for Ozone and Related chemical Tracers, version 4).

RESULTS AND DISCUSSION
To analyze the horizontal distribution patterns of acid deposition, RAMS-CMAQ was executed continuously from December 26, 2004, to December 31, 2005. The modeling results were evaluated against actual precipitation amounts observed at 704 rain gauge stations and concentrations of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ in the atmosphere and in rainwater observed at 18 EANET stations. The locations of these sites are shown in Figure 1, and some basic information about EANET stations is given in Table 1.

The predominant weather pattern in East Asia is the monsoon system. In the winter (December, January, and February), winds flow clockwise out of the Siberian High, blowing cold, dry air south-southwestward toward the Himalayas and southeastern Asia, north-northeastward to northern Asia, and southeastward to China, Korea, and Japan. In the summer (June, July, and August), moisture-laden winds blow from the Pacific Ocean northwestward into China, Japan, and northern Asia. The period from October to May comprises the winter circulation pattern, typified by January. The period from June to September comprises the summer pattern, typified by July. Spring (March, April, and May) and autumn (September, October, and November) in East Asia correspond to the periods of transition between the winter and summer monsoons. Acid deposition patterns considered on a seasonal mean basis are discussed below.

Table 1. The locations and characteristics of EANET stations.

<table>
<thead>
<tr>
<th>Station</th>
<th>Country</th>
<th>Category</th>
<th>Latitude (°N)</th>
<th>Longitude (°E)</th>
<th>Height (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jinyunshan</td>
<td>China</td>
<td>Rural</td>
<td>29.82</td>
<td>106.37</td>
<td>800</td>
</tr>
<tr>
<td>Jiwozi</td>
<td>China</td>
<td>Remote</td>
<td>33.83</td>
<td>108.80</td>
<td>2100</td>
</tr>
<tr>
<td>Xiaoping</td>
<td>China</td>
<td>Remote</td>
<td>24.85</td>
<td>118.03</td>
<td>686</td>
</tr>
<tr>
<td>Zhuxian</td>
<td>China</td>
<td>Urban</td>
<td>22.20</td>
<td>113.52</td>
<td>45</td>
</tr>
<tr>
<td>Kanghwa</td>
<td>Korea</td>
<td>Rural</td>
<td>37.70</td>
<td>126.28</td>
<td>150</td>
</tr>
<tr>
<td>Cheju</td>
<td>Korea</td>
<td>Remote</td>
<td>33.30</td>
<td>126.17</td>
<td>72</td>
</tr>
<tr>
<td>Imhil</td>
<td>Korea</td>
<td>Rural</td>
<td>35.60</td>
<td>127.18</td>
<td>0</td>
</tr>
<tr>
<td>Rishiri</td>
<td>Japan</td>
<td>Remote</td>
<td>45.12</td>
<td>141.23</td>
<td>40</td>
</tr>
<tr>
<td>Ochishi</td>
<td>Japan</td>
<td>Remote</td>
<td>43.15</td>
<td>145.50</td>
<td>49</td>
</tr>
<tr>
<td>Tappi</td>
<td>Japan</td>
<td>Remote</td>
<td>41.25</td>
<td>141.35</td>
<td>105</td>
</tr>
<tr>
<td>Ogasawara</td>
<td>Japan</td>
<td>Remote</td>
<td>27.06</td>
<td>142.22</td>
<td>230</td>
</tr>
<tr>
<td>Sado</td>
<td>Japan</td>
<td>Remote</td>
<td>38.25</td>
<td>138.40</td>
<td>110</td>
</tr>
<tr>
<td>Hasso</td>
<td>Japan</td>
<td>Remote</td>
<td>36.68</td>
<td>137.80</td>
<td>1850</td>
</tr>
<tr>
<td>Oki</td>
<td>Japan</td>
<td>Remote</td>
<td>36.28</td>
<td>133.18</td>
<td>90</td>
</tr>
<tr>
<td>Yusuhara</td>
<td>Japan</td>
<td>Remote</td>
<td>32.73</td>
<td>132.98</td>
<td>225</td>
</tr>
<tr>
<td>Hedo</td>
<td>Japan</td>
<td>Remote</td>
<td>26.78</td>
<td>128.23</td>
<td>50</td>
</tr>
<tr>
<td>Ijira</td>
<td>Japan</td>
<td>Remote</td>
<td>35.57</td>
<td>136.70</td>
<td>140</td>
</tr>
<tr>
<td>Banryu</td>
<td>Japan</td>
<td>Urban</td>
<td>34.67</td>
<td>131.70</td>
<td>60</td>
</tr>
</tbody>
</table>

Seasonal Precipitation Patterns
Precipitation is important for determining the amount of wet deposition. Deposition of SO$_4^{2-}$ and NO$_3^-$ can be coupled to large-scale precipitation-producing weather systems, which deposit these acidic substances farther from emission sources than the same chemicals produced via gaseous-phase (dry) processes. For evaluating the model, simulated seasonal mean precipitation amounts were compared with observations at 704 rain gauge stations, including 681 Chinese meteorological stations and 23 EANET stations. Figure 2 shows both observed and modeled seasonal mean precipitation distributions in the winter, spring,
summer, and autumn of 2005. Statistical comparisons of the results are summarized in Table 2. The observed values in Figure 2 were averaged without interpolation for stations located in the same grid. The differences between simulated and observed seasonal mean precipitation amounts for the four seasons are shown in Figure 3.

As shown in Figure 2, the general features of climatological precipitation patterns in all four seasons in China, characterized by a gradual decrease of precipitation from southeast to northwest, were well reproduced. In all four seasons, the western part of north China held the lowest precipitation value in East Asia, which corresponds to semi-arid or grassland climate zones. Only in summer did this area receive any amount of rainfall, which was still less than 10 mm in most areas, as shown in Figure 2c. The extensive areas of dry conditions in northeast China and north China and the major precipitation zones were also well simulated for all four seasons. Seasonal precipitation variations were particularly high in East Asia, with maximum magnitudes occurring in summer, autumn, and spring; whereas the lowest magnitudes were observed in winter; these features were reproduced reasonably well by the modeling system. Predictive accuracies were relatively high in northwest China, most of North China, the Big Bend of the Yellow River, Xinjiang, and some regions between the low reaches of the Yellow and Yangtze rivers (Figure 3). However, major discrepancies between the modeled results and observations were found for the southern part of China. In winter, the modeling system underestimated the precipitation over the southern part of China, and precipitation levels in the three other seasons were overestimated by varying degrees. Such overestimated precipitation values were also reported by Ding Yi hui, who found that although the regional climate model RegCM_NCC was capable of predicting the major seasonal rain belts, precipitation amounts were significantly overestimated, especially in the southern part of China (where error percentages were 80–200%). Similar overestimations of precipitation levels were also reported by Kato et al. and Lee and Suh for East Asia and by Small et al. for central Asia. As suggested by Leung et al., this deficiency is likely to be predominantly associated with the cloud-radiation transfer parameterization.

The accuracy of the model varies from season to season, with the highest accuracy in April (NMB of −1.88% and R of 0.71) and the lowest in February (NMB of −48.56% and R of 0.58). In winter, East Asia is under the influence of the winter monsoon due to strong pressure gradients between the Siberian high-pressure systems over the East Asian continent and the low-pressure systems over the North Pacific. With the exception of southern China, precipitation levels were very low for China but were substantial for the coastal areas of the Japan Sea (Figure 2a and e). Rainfall levels in southern China and the coastal areas of the Japan Sea were well reproduced by the model. Values larger than 100 mm were observed over the northwest coastal areas of Japan, a feature that was modeled with comparable magnitude. However, the model underestimated precipitation levels in the southern region of the Yangtze River valley (Figures 2 and 3), and as a result, the modeled precipitation levels in winter (December, January, and February) were less than those observed (cf. Table 2).

Spring is the period of transition between the winter and summer monsoons in East Asia and exhibits elevated precipitation levels in southeastern China and northeastern China (Figure 2b). The simulated results (Figure 2f) in most areas of China were consistent with observations with regard to both patterns and magnitudes (e.g., in the north of China and along the Yellow River), whereas the model overpredicted the amount of precipitation in southern China. Table 2 shows that the modeling system can effectively reproduce spring rainfall patterns and levels. The total average monthly precipitation levels obtained by the model are in good agreement with those observed at 704 stations in March, April, and May. Moreover, the correlation coefficients between observed and modeled precipitation data are all larger than 0.70.

The summer monsoon brought wet and warm marine air to the continent from the India Ocean and the West Pacific, causing significant precipitation, particularly near the coast, where marine air and continental air interface. As shown by Figure 2c and g, the model effectively reproduces the sufficient summer precipitation levels in the low-latitude region. In the continental area, the highest summer precipitation levels occurred in northeastern China, the Huaihe River valley, along the Yangtze River, the coastal regions of Southeast China, Korea, and southern Japan, with maximum precipitation levels reaching 300 mm or more. Figure 2c and g also show that the summer was characterized by a large amount of precipitation in the Huaihe Basin (located in the middle of eastern China, about midway between the Yellow River and the Yangtze River) and relative dry conditions in the southern region of the Yangtze River valley. The model generally captured these major features but overestimated precipitation levels in the Guangdong, Guangxi, and Jiangxi provinces. In addition, the model underpredicted the precipitation over southwestern China in the eastern and southern foothills.

### Table 2. Statistics for observed and modeled monthly averaged precipitation amounts (mm) at 704 stations in 2005.

<table>
<thead>
<tr>
<th>Month</th>
<th>$C_{obs}$</th>
<th>$C_{model}$</th>
<th>$\sigma_{obs}$</th>
<th>$\sigma_{model}$</th>
<th>NMB (%)</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.11</td>
<td>11.41</td>
<td>27.84</td>
<td>16.19</td>
<td>−29.24</td>
<td>0.48</td>
</tr>
<tr>
<td>2</td>
<td>34.64</td>
<td>17.85</td>
<td>55.62</td>
<td>18.80</td>
<td>−48.56</td>
<td>0.58</td>
</tr>
<tr>
<td>3</td>
<td>37.32</td>
<td>25.63</td>
<td>51.70</td>
<td>33.57</td>
<td>−31.38</td>
<td>0.73</td>
</tr>
<tr>
<td>4</td>
<td>47.37</td>
<td>46.48</td>
<td>45.71</td>
<td>64.82</td>
<td>−1.88</td>
<td>0.71</td>
</tr>
<tr>
<td>5</td>
<td>110.35</td>
<td>134.27</td>
<td>118.36</td>
<td>226.04</td>
<td>21.71</td>
<td>0.76</td>
</tr>
<tr>
<td>6</td>
<td>137.30</td>
<td>197.15</td>
<td>149.78</td>
<td>378.23</td>
<td>43.65</td>
<td>0.75</td>
</tr>
<tr>
<td>7</td>
<td>135.43</td>
<td>174.40</td>
<td>106.66</td>
<td>194.64</td>
<td>28.62</td>
<td>0.41</td>
</tr>
<tr>
<td>8</td>
<td>141.86</td>
<td>174.05</td>
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<td>228.76</td>
<td>22.73</td>
<td>0.47</td>
</tr>
<tr>
<td>9</td>
<td>85.11</td>
<td>84.40</td>
<td>92.75</td>
<td>136.11</td>
<td>−0.83</td>
<td>0.52</td>
</tr>
<tr>
<td>10</td>
<td>41.81</td>
<td>25.45</td>
<td>49.93</td>
<td>44.11</td>
<td>−39.18</td>
<td>0.54</td>
</tr>
<tr>
<td>11</td>
<td>24.82</td>
<td>17.20</td>
<td>41.32</td>
<td>28.39</td>
<td>−30.74</td>
<td>0.63</td>
</tr>
<tr>
<td>12</td>
<td>12.85</td>
<td>9.92</td>
<td>22.92</td>
<td>17.03</td>
<td>−22.88</td>
<td>0.74</td>
</tr>
<tr>
<td>Yearly</td>
<td>68.75</td>
<td>76.52</td>
<td>95.46</td>
<td>175.67</td>
<td>11.30</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Notes: $C_{obs} =$ total mean of observed monthly precipitations; $C_{model} =$ total mean of modeled monthly precipitations; $\sigma_{obs} =$ standard deviation of observed monthly precipitations; $\sigma_{model} =$ standard deviation of modeled monthly precipitations; NMB = normalized mean bias; $R$ = correlation coefficient between observed and modeled precipitations.

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Figure 2. Observed seasonal mean precipitation amounts (mm/month) for (a) winter (December–February), (b) spring (March–May), (c) summer (June–August), and (d) autumn (September–November) of 2005; and simulated seasonal mean precipitation amounts (mm/month) for (e) winter (December–February), (f) spring (March–May), (g) summer (June–August), and (h) autumn (September–November) of 2005.
of the substantial Tibetan Plateau, where the existence of complex terrain features may cause unrealistic results. Autumn is a dry season in East Asia, and it is a transition period just like spring. Nonetheless, autumn still exhibited substantial rainfall over low-latitude areas in which the rain zone withdrew toward the equator. Both the observations and the simulations obtained for the continental area of East Asia, in general, displayed a downward precipitation trend in October compared to April, especially over the northeast edge of China and the coastal regions of Southeast China. The exceptions were Yunnan Province and the upper Yangtze River valley, in which October precipitation levels were above 100 mm, much higher than those observed in April for the same regions. The simulated pattern generally corresponds well with the observed one, but the model underpredicted October precipitation levels in the central area between the Yellow River and the Yangtze River.

Seasonal Ambient Concentration Distributions of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$

Winter emission distributions of $\text{SO}_2$ and $\text{NO}_x$ and the difference emission distributions between summer and winter for $\text{SO}_2$ and $\text{NO}_x$ are shown in Figure 4. Large spatial variations (in the emission rates) were found for both $\text{SO}_2$ and $\text{NO}_x$ in East Asia. Large $\text{SO}_2$ emissions can be seen in the Sichuan Basin, industrialized eastern China, and the volcano eruption over the Miyakejima area (located south of Tokyo, Japan). Higher $\text{NO}_x$ emissions are found in northern China, the region between the Yangtze River and the Yellow River, and the coastal region of southern China. The relatively strong $\text{NO}_x$ signature that results from transportation sources in Japan is also depicted in Figure 4. East Asia, especially China, has an apparent seasonality of emissions for both $\text{SO}_2$ and $\text{NO}_x$, with maximum emissions occurring in wintertime (the heating period). Because residential heating increases in winter, higher $\text{SO}_2$ emissions can be seen over central eastern China and the Sichuan Basin. Emission levels of $\text{NO}_x$ in northern China are also larger in winter compared to summer.

Figure 5 shows the observed and simulated monthly averaged ambient concentrations of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, and $\text{NH}_4^+$ obtained from 10 EANET stations located in Japan (see Figure 1 and Table 1 for station locations and categories). The ambient concentrations of $\text{SO}_4^{2-}$ were between 0.08 and 11.32 $\mu$g m$^{-3}$, whereas both $\text{NO}_3^-$ and $\text{NH}_4^+$...
concentrations were comparatively lower (between 0.01 and 2.82 mg/m³ for NO₃⁻ and between 0.01 and 3.25 mg/m³ for NH₄⁺). The simulated magnitudes for all three ions were consistent with observations.

Figure 5 shows that the concentrations of all three ambient ions exhibit strong spatial variations, with the highest maximums occurring at Banryu and Ijira and the smaller maximums occurring at Ogasawara. Ogasawara is located on isolated islands in the western Pacific (cf. Figure 1) that are slightly affected by local and domestic emissions from distant mega-city source regions. The levels of SO₄²⁻, NO₃⁻, and NH₄⁺ in Ogasawara are the lowest of all 10 stations studied. Oki, Yusuhara, and Hedo are all remote sites, but they are often under the influence of continental anthropogenic emissions and volcano exhausts. Thus, their SO₄²⁻, NO₃⁻, and NH₄⁺ levels do not differ significantly from those observed at Banryu and Ijira, which are urban and rural sites. Like Ogasawara, Hedo is a remote oceanic site that is influenced by continental outflow; thus, the species levels are lower for Hedo compared to Oki and Yusuhara, though they are still much higher in Hedo than in Ogasawara. Lower concentrations of these species are observed on Rishiri Island because it is located near the northern tip of Japan, which is dominated by background conditions; except for the outbreaks of Eurasian continental air pollution that occur in spring, SO₄²⁻ and NO₃⁻ concentrations over Rishiri Island are usually very low and, in fact, are comparable to those observed over the remote ocean.⁴³

Figure 5 shows that, in general, the model reasonably reproduced the monthly variations and spatial variations recorded at most stations. In this regard, at all 10 stations, the three species showed strong seasonal cycles with elevated values in the spring that are associated with the Asian winter monsoon season and the transport of pollutants from the Eurasian continent. Both observed and simulated SO₄²⁻ concentrations also peak in summertime, as reported by Carmichael at Cheju Island in Korea.⁴⁴ Observed and simulated NO₃⁻ levels both display minimums in summer, but the model overpredicted the levels observed during spring and winter. The seasonal cycles of SO₄²⁻ and NO₃⁻ are analyzed and discussed below. Observed NH₄⁺ levels show a maximum in summer, a pattern reflected in the simulated results; however, the model overpredicted the actual NH₄⁺ concentrations. During the 5-year period from 1982 to 1986, Yamamoto found a distinct seasonal trend in which NH₃ concentrations peaked in summer at an urban site in Yokohama, Japan,⁴⁵ and reported a good correlation between diurnal NH₃ concentrations and average air temperatures during the 5-year period. Carmichael also reported that NH₄⁺ concentrations tended toward a maximum in late spring-early summer at Cheju Island, Korea; his study suggests that high NH₄⁺ values in summer may reflect the strong temperature dependency of NH₃ emissions.⁴⁴

Figures 6 and 7 show simulated the seasonal mean SO₄²⁻ and NO₃⁻ concentration distributions in the boundary layer (from the surface to ~1000 m) for winter, spring,
summer, and autumn in 2005. Seasonal mean wind vectors at an altitude of approximately 500 m are also shown in Figure 6. Throughout the entire year, the maximum SO$_4^{2-}$ concentrations are found in the area surrounding Sichuan Province (Figure 6). This feature is attributed to both emissions and meteorological conditions. SO$_4^{2-}$ is primarily produced from the oxidation of SO$_2$, and the conversion of SO$_2$ to SO$_4^{2-}$ occurs via multiple pathways, including gas-phase oxidation to H$_2$SO$_4$ followed by condensation into the particulate phase, aqueous-phase oxidation in cloud or fog droplets, and various reactions on the surfaces or inside aerosol particles. Sichuan has higher SO$_2$ emissions (Figure 4), and the Sichuan Basin is enclosed on four sides by mountains and the Yunnan-Guizhou Plateau. Due to the seasonally variant, high frequency of calm winds and their temperature inversion strength, air pollutants have difficulties diluting in the Sichuan Basin. As a result, a large number of pollutants accumulate in the Sichuan Basin.

Figure 6a shows that elevated SO$_4^{2-}$ concentrations ($\geq 30$ $\mu$g m$^{-3}$) in winter are mainly found over central China. Because they are controlled by the Siberian High, the surface winds are initially northeastwards in northern China, Japan, and Korea, then they flow clockwise out to sea and move southwards along the coast into the South China Sea. This wind pattern brings large amounts of surface pollutants that originate in the boundary layers of Eurasia to the West Pacific Ocean, the South China Sea, and the Indian Ocean. Because temperature and water contents along this transport path are relatively high, SO$_2$ transported from the Asian continent can be quickly oxidized in the gas phase and the aqueous phase, producing a wide area in which SO$_4^{2-}$ concentrations larger than 10 $\mu$g m$^{-3}$ spread south and even expand to $10^3$ N.

Spring in East Asia is the period of transition between the winter and summer monsoons. As shown in Figure 6b, in eastern China the southwesterly winds south of $35^\circ$N sweep the pollution northeastward. Thus, high SO$_4^{2-}$ concentrations ($\geq 30$ $\mu$g m$^{-3}$) are found along the transport path from Hunan Province through Hubei Province to the convergence zone between 30$^\circ$N and 40$^\circ$N, where air
masses from the north encounter oceanic air from the south. This pollution is continually transported to the Yellow Sea, Korean peninsula, and Japan. It can be seen that the convergence zone over central and eastern China plays an important role in the springtime export of pollution from the Asian continent, as reported by Zhang et al.\textsuperscript{23}

In summer, the prevailing wind is from the south and southeast (onshore wind). The southern part of China in the boundary layer is affected by the summer monsoon; thus, \( \text{SO}_4^{2-} \) concentrations smaller than 10 \( \mu \text{g m}^{-3} \) are observed in most areas of southern China due to the deep boundary layer, deep convection, and mixing with low-latitude marine air. The \( \text{SO}_4^{2-} \) values around the area of Sichuan Province are higher than 40 \( \mu \text{g m}^{-3} \) throughout the year. In northern China, the areas of \( \text{SO}_4^{2-} \) in summer are higher than 40 \( \mu \text{g m}^{-3} \), which is larger than that observed during other seasons, due to both the higher production of \( \text{SO}_4^{2-} \) from \( \text{SO}_2 \) and meteorological conditions in summer. In summer, the water vapor content is elevated, and the wet marine monsoon produces higher [OH], resulting in a higher formation rate of \( \text{SO}_4^{2-} \) from \( \text{SO}_2 \). The southerly winds push pollution northwards and then northeasterwards, resulting in a \( \text{SO}_4^{2-} \) maximum in the Beijing-Tianjin-Hebei region, the Bay of the Bohai Sea, and Korea. Influenced by transportation from China, in summer the concentrations of \( \text{SO}_4^{2-} \) in most areas of Japan are higher than 10 \( \mu \text{g m}^{-3} \), as seen in Figure 4. Compared to other seasons, Japan is most strongly influenced in summer by pollution originating over the Asian continent.

The general flow field in autumn is shown in Figure 6d. Westerly and southwesterly winds prevail north of 40°N, and there are anticyclone circulations over central and eastern China. Following this wind flow, much of the pollution originating in central and eastern China flows clockwise along the coastal area of China and then returns to the south of China. As a result, in autumn, much of the pollutants were trapped in China, with higher \( \text{SO}_4^{2-} \) concentrations (\( \geq 30 \mu \text{g m}^{-3} \)) over southern China, and a smaller amount of \( \text{SO}_4^{2-} \) was transported to the western Pacific compared to spring.

Figure 7 shows that, throughout the year, the higher \( \text{NO}_3^- \) concentrations were generally found between the Yangtze River and the Yellow River because this area is characterized by high emissions of \( \text{NO}_x \) and \( \text{NH}_3 \).\textsuperscript{34,36}
Following the monsoon transition process, the location of the maximum NO$_3^-$ moved north from spring to summer and moved south in autumn, similar to the pattern observed for SO$_4^{2-}$. There is an obvious difference between the distribution patterns of NO$_3^-$ with SO$_4^{2-}$, in that the higher SO$_4^{2-}$ concentrations are all approximately 30 µg m$^{-3}$ for all four seasons, whereas maximal NO$_3^-$ concentrations have noticeable differences that depend on seasonal changes. Generally, the NO$_3^-$ concentrations are higher in winter and autumn, lower in spring, and lowest in summer. The highest NO$_3^-$ concentrations vary seasonally by a factor of approximately 4 with a maximum in winter ($\geq 40$ µg m$^{-3}$) and a minimum in summer ($\geq 10$ µg m$^{-3}$). In the model, NO$_3^-$ is produced from NO$_x$, and NO$_3^-$ aerosols and is normally present as particulate NH$_4$NO$_3$, formed from the reversible reaction of gas-phase NH$_3$ and HNO$_3$. Because HNO$_3$ is easily absorbed by rainwater and cloud-water, the concentration of NO$_3^-$ is heavily influenced by both temperature and precipitation.

Figure 7a shows that, in winter, the transport of NO$_3^-$ had a smaller impact over downwind marine areas than SO$_4^{2-}$ because when NO$_3^-$ is transported to the oceanic area, its concentration decreases very quickly. Significant gradients exist from eastern China through the coastal area to the West Pacific, with the 30 µg m$^{-3}$ starting concentration of NO$_3^-$ decreasing to less than 0.1 µg m$^{-3}$. From Figure 7b, we can see that the NO$_3^-$ concentrations decrease sharply from winter to spring and that high NO$_3^-$ concentrations are found around the Huaihe valley with a maximum lower than 30 µg m$^{-3}$. The highest concentration decreased in summer to below 10 µg m$^{-3}$. Figure 6d also shows that the higher NO$_3^-$ concentration found in autumn corresponds to the area over the Huaihe valley, with a highest concentration larger than 30 µg m$^{-3}$.

Figures 6 and 7 also show that most regions of Asia have higher concentrations of SO$_4^{2-}$ than NO$_3^-$, although NO$_3^-$ concentrations are a little higher than SO$_4^{2-}$ concentrations in some regions (e.g., in eastern China and northeastern China in the winter time), suggesting a greater importance of NO$_x$ emission in these regions. Since 1996, SO$_2$ emissions in China have slowly declined$^{46}$ because of measures such as restrictions on the use of coal-fired household stoves, the termination or relocation of heavily polluting industries in urban areas to the countryside, and the installation of scrubbers on coal-fired boilers. Many researchers agree that the rapid growth of the
transportation sector in Asia has caused NOx emissions to climb steeply. For example, the number of motor vehicles in China has increased dramatically in recent years from 6.2 million in 1990 to 36.0 million in 2003. The corresponding changes in SO2 and NOx emissions are significant in that they may considerably alter the relative levels of NO3\(^-\) and SO4\(^{2-}\) in precipitation in East Asia. The typical type of sulfuric acid in Asia is changing, and these changes have aroused serious concerns in public and government sectors.

**Seasonal Wet Deposition Distributions of SO4\(^{2-}\) and NO3\(^-\)**

Figure 8 compares modeled and observed monthly mean concentrations of SO4\(^{2-}\), NO3\(^-\), and NH4\(^+\) in precipitation observed at the 18 EANET stations. Most of the scatters fall within the reference lines within a factor of 2, whereas some discrepancies occur for some sites. In addition to the uncertainties in related meteorology for aerosol formation, such as the uncertainty of simulated precipitation fields, there are several explanations for the discrepancy. For example, some uncertainties exist in the model treatments that govern the processes for nitrate formation, including thermodynamic equilibrium and gas-to-particle partitioning between gaseous HNO3 and aerosol nitrate.\(^{47,48}\) Asian emissions of NH3 (2006), which play a key role in gas/aerosol partitioning,\(^{36}\) carry a significant uncertainty linked to the use of European-based emission factors (especially livestock).

Figure 8. Scatter plots of observed versus modeled monthly averaged contents (µmole L\(^{-1}\)) of (a) SO4\(^{2-}\), (b) NO3\(^-\), and (c) NH4\(^+\) in precipitation at 18 EANET stations.
and there are three stations in Japan in which the SO$_4^{2-}$ concentrations in precipitation are higher than 50 µmole/L (Tappi, 51.4 µmole/L; Oki, 55.9 µmole/L; Hedo, 59.3 µmole/L).

Figures 9 and 10 present the spatial distributions of simulated wet deposition in East Asia in winter, spring, summer, and autumn. They clearly show that East Asia experiences noticeable variations of wet deposition during different seasons.

The wet-deposition distribution patterns for both SO$_4^{2-}$ and NO$_3^-$ appear to be more dependent on meteorological conditions, particularly with regard to rain belt and wind flow patterns. From winter to summer, as the rain belt moved northward (Figures 2 and 3) and the pollution was swept northeastward (Figures 5 and 6), the highest SO$_4^{2-}$- and NO$_3^-$-wet depositions responded and moved northeastward, as seen in Figures 9 and 10. In winter, southern China and the coastal areas of the Japan Sea held the higher SO$_4^{2-}$ and NO$_3^-$ wet deposition concentrations. In the western coastal areas of the Japan Sea, wet deposition levels of NO$_3^-$(>12 millimole m$^{-2}$ month$^{-1}$) were higher than those of SO$_4^{2-}$. In spring, elevated SO$_4^{2-}$- and NO$_3^-$-wet deposition levels were found in northeastern China, southern China, and around the Yangtze River. In summer, a remarkable rise of precipitation in northeastern China, the valleys of the Huaihe and Yangtze rivers, Korea, and Japan lead to a noticeable increase in SO$_4^{2-}$ and NO$_3^-$ wet deposition concentrations. In autumn, the higher SO$_4^{2-}$- and NO$_3^-$-wet deposition levels were found around Sichuan Province. Meanwhile, due to the high emissions of SO$_2$, high wet deposition levels of SO$_4^{2-}$ were found in the area surrounding Sichuan Province throughout the entire year.

The values of NO$_3^-$/SO$_4^{2-}$ in precipitation are useful for evaluating the relative contributions of SO$_4^{2-}$ and NO$_3^-$ to the acidity of precipitation. Figures 9 and 10 show that the acid rain occurring over most of Asia is a typical sulfate-kind characterized by a higher wet deposition of SO$_4^{2-}$ and a lower wet deposition of NO$_3^-$. Although in some regions the wet deposition of NO$_3^-$ is somewhat higher than that of SO$_4^{2-}$. A ratio of 1.0 was found around the Taiwan Strait and the Tokyo district throughout the entire year, and a ratio of 2 was determined in winter, indicating that these areas are substantially affected by large NO emissions. There are also other areas in which NO$_3^-$ has significantly contributed to acid rain. In spring and autumn, a ratio of 1.0 mainly occurred in the areas around or downwind of big cities or industrial regions, such as some parts of north China, the Pearl River Delta, the Taiwan Strait, the Tokyo district, Korea, and a large area around the Japan Sea. In winter, a ratio of 1.0 is found for most of southeastern China. Takahashi and Fujita studied the results of six sites in western Japan from 1987 to 1996 and found a higher rate of NO$_3^-$ emissions than SO$_2$ emissions that may considerably alter the relative strengths of nitrate and sulfate in precipitation in this area.

**SUMMARY AND CONCLUSION**

Seasonal variations of wet acidic depositions in East Asia were studied by the air quality modeling system RAMS-CMAQ. Results for the year of 2005 were simulated, and the seasonal distribution patterns of wet deposition were
analyzed based on the distribution of precipitation and the major acidic species (SO$_4^{2-}$ and NO$_3^-$). In addition, the simulated results were compared to extensive observations, including monthly precipitation amounts from 704 stations, monthly averaged ambient aerosol concentrations of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ at 10 EANET stations and ion concentrations of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ in rainwater at 18 EANET stations.

Comparisons of the simulated and observed fields for winter, spring, summer, and autumn show that the modeling system was capable of effectively simulating the major seasonal rain belts and dry areas and showed magnitudes comparable to the observations. Spring was the best-predicted season, as indicated by its high correlation coefficient (>0.70), whereas other months depicted discrepancies in simulated precipitation for southern China. Comparison of model results with observations in terms of the concentrations of the relevant acidic species (SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$) and major ionic species in rainfall showed that, in general, the simulation could reproduce the major features observed for wet deposition and yield reasonable results (within a factor of 2) compared to observations in most cases.

The monthly averaged SO$_4^{2-}$ and NO$_3^-$ distributions in the boundary layer(s) for winter, spring, summer, and autumn in 2005 were also analyzed. Throughout the year, the maximum concentrations of SO$_4^{2-}$ were found in the area of Sichuan Province due to the high-S-content coal utilized and the special geographical conditions found there. In winter, a wide area with SO$_4^{2-}$ concentrations larger than 10 $\mu$g m$^{-3}$ spread south and even expanded to 10$^\circ$N, in accordance with changes in temperature and water contents along the transport path. In spring, higher SO$_4^{2-}$ concentrations were found along the transport path from Hunan Province through Hubei Province to the convergence zone between 30$^\circ$N and 40$^\circ$N, and then the pollution was continually transported to the Yellow Sea, the Korean peninsula, and Japan. In summer, the SO$_4^{2-}$ maximum was found in the Beijing-Tianjin-Hebei region, the Bay of the Bohai Sea, and Korea. Influenced by transportation from China, the concentration of SO$_4^{2-}$ is highest in summer in most areas of Japan throughout the year (>10 $\mu$g m$^{-3}$). Under the effect of anticyclone circulations over central and eastern China, much of the pollutants in autumn were trapped in China, with a larger area of high SO$_4^{2-}$ concentrations (>30 $\mu$g m$^{-3}$) existing over southern

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**Figure 9.** Modeled wet deposition fluxes (m mole m$^{-2}$ month$^{-1}$) of SO$_4^{2-}$ in (a) winter (December–February), (b) spring (March–May), (c) summer (June–August), and (d) autumn (September–November) of 2005.
China and a small amount of SO$_4^{2-}$ being transported to the West Pacific. The higher NO$_3^-$ concentrations were mainly found between the Yangtze River and the Yellow River throughout nearly the entire year because this area is characterized by high emissions of NO$_x$ and NH$_3$. Because the concentration of NO$_3^-$ is heavily influenced by temperature and precipitation, the NO$_3^-$ concentrations have noticeable seasonal differences. The highest NO$_3^-$ concentrations vary seasonally by a factor of approximately 4, with a maximum in winter $\geq$40 $\mu$g m$^{-3}$ and a maximum in summer $\geq$10 $\mu$g m$^{-3}$. Most regions of Asia have higher concentrations of SO$_4^{2-}$ than NO$_3^-$, whereas the magnitudes of NO$_3^-$ concentrations in some regions are slightly higher than concentrations of SO$_4^{2-}$ (e.g., in eastern China and northeastern China in winter), suggesting an increased importance of NO$_x$ emissions in these regions.

The spatial distributions of simulated wet deposition in East Asia in winter, spring, summer, and autumn clearly show that East Asia experiences noticeable wet deposition patterns during different seasons. In winter, southern China and the coastal areas of the Japan Sea demonstrate higher SO$_4^{2-}$ and NO$_3^-$ wet deposition levels. In spring, elevated SO$_4^{2-}$ and NO$_3^-$ wet deposition levels are found in northeastern China, southern China, and around the Yangtze River. In summer, a remarkable rise in precipitation in northeastern China, the valleys of the Huaihe and Yangtze rivers, Korea, and Japan leads to noticeable increases in SO$_4^{2-}$ and NO$_3^-$ wet deposition levels. In autumn, the higher SO$_4^{2-}$ and NO$_3^-$ wet deposition levels are found around Sichuan Province. Throughout the whole year, due to high emissions of SO$_2$, high SO$_4^{2-}$ wet deposition levels are found in the area surrounding Sichuan Province.

Both observed and simulated results display a tendency toward decreasing values of NO$_3^-$ and NH$_4^+$ mixing ratios in rainwater from China through Korea to Japan, indicating the influence of continental outflow from Eurasia. For all stations, except those in Banryu, the NO$_3^-$ and NH$_4^+$ rainwater mixing ratios displayed much lower values in Japan than in Korea. This tendency was not observed for SO$_4^{2-}$.

Acid rain precipitated in most of Asia is still a typical sulfate-kind characterized by a higher wet deposition of SO$_4^{2-}$ and a lower wet deposition of NO$_3^-$, although some areas are found to have higher levels of NO$_3^-$ than SO$_4^{2-}$, especially in the areas around the Taiwan Strait and the Tokyo district in winter.

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**Figure 10.** Modeled wet deposition fluxes (m mole m$^{-2}$ month$^{-1}$) of NO$_3^-$ in (a) winter (December–February), (b) spring (March–May), (c) summer (June–August), and (d) autumn (September–November) of 2005.
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