Dust Heterogeneous Reactions during Long-Range Transport of a Severe Dust Storm in May 2017 over East Asia

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Abstract: Dust aerosol has important climate and environmental effects, which could be changed by internally mixing with anthropogenic aerosol as a result of heterogeneous reactions; however, the importance of these reactions is not fully understood yet. In this study, synergetic observations and an air quality model were used to analyze the transport of a severe dust storm and its impacts on nitrate and sulfate levels over East Asia between 3 and 11 May 2017. The model successfully reproduced the occurrence and transport of the dust storm compared to dust RGB imageries of the Himawari-8 satellite and dust extinction coefficients observed by LIDAR. The model also reasonably simulated the variations of observed nitrate and sulfate concentrations, and the results indicated that the dust heterogeneous reactions were dominant pathways for nitrate formation, but they had limited contribution for sulfate in both fine and coarse mode in Fukuoka, Japan. Dust nitrate formed rapidly after leaving China, and the highest period-averaged concentration of dust nitrate (>5 µg m−3) was shown over the Yellow Sea. Based on model results; we found that the mass ratio of dust nitrate to dust aerosol could reach 10% over the Pacific Ocean. Our results confirmed the importance of heterogeneous reactions on compositions of dust particles.

Keywords: mineral dust; heterogeneous reaction; acid uptake; Himawari-8; LIDAR; NAQPMS

1. Introduction

Mineral dust is an important aerosol component due to its impacts on climate, ecosystems, and human health [1–4]. The dust particles could internally mix with the water-soluble aerosols with high hygroscopicity (e.g., Ca(NO3)2), through heterogeneous reactions with acid gases (e.g., HNO3), and become coated dust particles. As a result, the size and morphology of dust particles will be changed, and, consequently, the optical properties and direct climate effects will be different [5,6]. The hygroscopicity of coated dust particles is higher than pure dust particles and can become more efficient cloud condensation nuclei (CCN) compared to pure dust particles, altering the indirect climate effects of dust aerosols [7]. The formation of nitrate on dust could change the deposition of nitrate to ecosystems, especially over ocean area, where the nitrate from atmospheric deposition is important [8]. These processes may be more important over East Asia, where both the emissions of dust and anthropogenic
pollutants are very high, and the dust will pass through the highly polluted area during long-range transport [9].

The numerical models based on atmospheric physics and chemistry theory are useful tools to understand the importance of dust heterogeneous reactions, since it is difficult to know the contributions of different chemical pathways on the production of water-soluble aerosols based on observations. As early as in 1990s, box-model studies suggested that 0.9–2.1 µg m$^{-3}$ of nitrate and 0.3–10 µg m$^{-3}$ of sulfate could be formed on dust particles [10,11]. Earlier global model studies showed the importance of heterogeneous reactions in the atmosphere, but a rigorous evaluation is difficult due to a lack of measurements [12]. In recent years, global and regional chemical transport models (e.g., GEOS-Chem) were widely used to study dust heterogeneous reactions and suggested that they were neglectable in the troposphere [13–15].

Although there have already been some studies about dust heterogeneous reactions, as mentioned above, they are not fully understood yet. The reasons include large uncertainty in reactive uptake coefficient values [12,13] and a difficulty of accurate nitrate observation [14]. Recently, based on synergetic observations and air-quality model, it was found that the dust heterogeneous reactions had significant impacts on the composition and morphology of dust particles in Beijing, China [9,16,17]. Therefore, more studies are necessary to improve our understanding about the importance of the dust heterogeneous reactions over East Asia during the long-range transport of severe dust storms.

During 3 and 11 May 2017, a severe dust storm occurred and affected most of East Asia. In this study, we analyzed the impacts of dust heterogeneous reactions on fine (particle diameter (Dp) ≤ 2.5 µm) and coarse (2.5 µm < Dp ≤ 10 µm) mode nitrate ions (NO$_3^-$) and sulfate ions (SO$_4^{2-}$) during the long-range transport of this dust storm, based on synergetic observations and an air-quality model that included heterogeneous processes.

2. Data and Methods

2.1. Satellite Data

To trace the transport of dust plume, we used dust RGB imageries based on the observation data of Himawari-8, which is a third-generation Japanese geostationary meteorological satellite. Dust RGB imageries were created from Bands 11 (8.6 µm), 13 (10.4 µm), and 15 (12.4 µm) of the Advanced Himawari Imagers, which are based on different characteristics of absorption and scattering in the infrared wavelengths between dust, cloud, and land surfaces. Dust RGB imageries are available during both day and night, with horizontal and temporal resolutions of 0.02° (about 2 km) and 10 min, respectively. Dust RGB imageries were previously used to analyze the occurrence and transport of large-scale dust storms in the Gobi Desert [18] and Taklimakan Desert [19].

2.2. On-Site Observation Data

A continuous dichotomous aerosol chemical speciation analyzer (ACSA, version 12, Kimoto Electric Co., Ltd 3-1 Funahashi-cho Tennoji-ku Osaka 543-0024 JAPAN) was used to measure the hourly mass concentrations of particulate matter (PM), sulfate, and nitrate in both the fine and coarse mode on the rooftop (6th floor) of the Chikushi Campus of Fukuoka University (longitude: 130.5° E, latitude: 33.5° N), Fukuoka, Japan [20]. The location of Fukuoka can be found in Figure 1. ACSA also measured the fine and coarse mode aerosol acidity ($\Delta H^+$), which refers to the difference in the solution after the extraction of aerosol-soluble components relative to the pure extracting solution and is determined using a pH indicator absorption photometric method. The $\Delta H^+$ is calculated based on the following equation:

$$
pH_{tas} = -\log [\Delta H^+ \times 10^{-6} + 10^{-4.6}],
$$

(1)

where $pH_{tas}$ is the pH value of the solution after the extraction of aerosol-soluble components, and the pure extracting liquid had a pH of 4.6. The $\Delta H^+$ is a good qualitative indicator of dust aerosol due to
its alkalinity [21]. In addition, $\Delta H^+$ is also very important for dust heterogeneous reactions since dust will stop if the dust alkalinity is titrated when $\Delta H^+$ becomes positive.

![Figure 1](image_url)

**Figure 1.** Model domain and land use categories by Moderate Resolution Imaging Spectrometer (MODIS) data. B, S, and F indicate Beijing, Seoul, and Fukuoka. The blue line with triangle markers (every 6 hours) is the 72-h backward trajectory from Fukuoka at 20:00, on 6 May 2017 (JST).

To validate the air-quality-model results, we also used the hourly PM$_{2.5}$ (PM with Dp $\leq$ 2.5 $\mu$m) and PM$_{10}$ (PM with Dp $\leq$ 10 $\mu$m) mass concentrations in Beijing, China, and Seoul, Korea, measured by the Ministry of Ecology and Environment of the People’s Republic of China and Korean Ministry of Environment, respectively. As shown in Figure 1, Beijing and Seoul were on the path of backward trajectory, starting from Fukuoka, on May 6, 2017, at 20:00 (JST, Japan Standard Time), when the dust concentration reached a maximum. The backward trajectory was calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model [22].

To evaluate the model-simulated dust transport, we also used the dust extinction coefficients based on LIDAR measurements in Beijing, Seoul, and Fukuoka, which were operated by Asian Dust and aerosol LIDAR observation Networks (AD-Net) [23]. The LIDARs measured the vertical profiles of aerosol backscattering at 532 and 1064 nm, as well as the depolarization ratio at 532 nm, with high spatial and temporal resolution. The contributions of dust and anthropogenic aerosols to the total retrieved extinction coefficient were estimated based on the depolarization ratio (DR), supposing dust (DR = 0.35) and anthropogenic (DR = 0.02) aerosols were externally mixed [24].

Dust weather reported by the surface synoptic observations (SYNOP) over East Asia were also used to reveal the transport of dust by comparison with the Himawari-8 dust RGB imagery and the model-simulated dust concentration distributions.
2.3. Chemical Transport Model

We used the Nested Air Quality Prediction Modeling System (NAQPMS) [25,26] to simulate the transport of dust and its interaction with anthropogenic pollutants over the eastern part of Asia, as shown in Figure 1, with a horizontal resolution of 45 km, and 20 vertical layers in a sigma coordinate. The Weather Research and Forecasting model (WRF version 3.9.1.1) was used to simulate the meteorological fields which were necessary for NAQPMS. The anthropogenic emissions (e.g., SO2, NOx, NH3, CO, BC, OC, and VOCs) were taken from MEIC inventory [27] for China, with the base year of 2017, and the MIX inventory [28], with the base year of 2010 for other areas. The emissions of dust were calculated online as follows [26]:

\[ F = C_1 \frac{\rho_a}{g} E \cdot u^3 \left( 1 + \frac{u_0^2}{u^2} \right) \left( 1 - \frac{u_0^2}{u^2} \right) \left( 1 - \frac{\text{RH}}{\text{RH}_0} \right) \]

where \( F \) is the dust flux (kg m\(^{-2}\) s\(^{-1}\)), \( C_1 \) is a constant and set to \( 1.0 \times 10^{-5} \), and \( \rho_a \) (kg m\(^{-3}\)) and \( g \) (m\(^2\) s\(^{-2}\)) are the air density and acceleration due to gravity, respectively. \( E \) is the dust source function which reflects the impact of land-use categories (Figure 1), and \( u \) and \( u_0 \) are the friction and threshold friction velocities, respectively. RH and RH\(_0\) represent relative humidity and its threshold value, respectively. Sea salt emissions were also calculated online based on the work of Athanasopoulou et al [29]. Both dust and sea salt were separated into four bins that were, 0.1–1, 1–2.5, 2.5–5, and 5–10 \( \mu \)m. The emissions of the four dust bins accounted for 3.5%, 7.0%, 31.5%, and 58.0% of total dust flux, respectively.

NAQPMS used the Carbon-Bond Mechanism Z (CBM-Z) [30] as the gas-phase chemistry module, the ISORROPIA version 1.7 [31] as the aerosol thermodynamic module, the RADM mechanism [32] as the aqueous chemistry and wet deposition module, the Wesley scheme [33] as the dry deposition module, and a heterogeneous chemistry module with 28 heterogeneous reactions [26].

In addition to the long-range transport of the East Asia dust episode, this study mainly focused on the impacts of dust on the nitrate formation through the heterogeneous reaction between dust alkalinity (typically as CaCO\(_3\)) and HNO\(_3\), as follows:

\[ \text{CaCO}_3 + 2\text{HNO}_3 \rightarrow \text{Ca(NO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2 \]  

(3)

The nitrate produced by the above reaction was limited by dust alkalinity and is denoted as D-NO\(_3^-\) hereafter. The nitrate ions can also be produced by heterogeneous reaction between NaCl and HNO\(_3\) on sea-salt particles, denoted as S-NO\(_3^-\). The nitrate formed through thermal equilibrium between HNO\(_3\) and NH\(_3\) was denoted as A-NO\(_3^-\):

\[ \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 \]  

(4)

Similar to NO\(_3^-\), dust heterogeneous reactions can also produce SO\(_4^{2-}\) by the uptake of SO\(_2\), and the produced SO\(_4^{2-}\) was denoted as D-SO\(_4^{2-}\). While A-SO\(_4^{2-}\) represented SO\(_4^{2-}\) produced through gas-phase chemistry, aqueous-phase chemistry, and thermal-equilibrium processes, and S-SO\(_4^{2-}\) included both primary sea-salt SO\(_4^{2-}\) and sea-salt, heterogenous reactions produced SO\(_4^{2-}\).

A first-order reactive uptake parameterization with rate constant, \( k_i \), is used to calculate the heterogeneous reactions of acidic gas species \( s \) (e.g., SO\(_2\) and HNO\(_3\)) on different aerosol particles, \( i \), (e.g., dust and sea salt):

\[ k_i = A_i \times \left( \frac{r_i}{D_g} + \frac{4}{\nu \gamma_{i-s}} \right)^{-1}, \]

(5)

where \( A_i \) and \( r_i \) are the surface area density and the radius of aerosol particles, respectively, \( D_g \) is the molecular diffusion coefficient, \( \nu \) is the mean molecular speed of the gas, and \( \gamma_{i-s} \) is the reactive uptake coefficient of acidic gas species \( s \) (e.g., SO\(_2\) and HNO\(_3\)) on aerosol species, \( i \). The values of \( \gamma_{i-s} \) for dust are based on the previous study [13] and significantly increase with the increase of relative
humidity. The NAQPMS was successfully used for dust and anthropogenic-pollution analysis over East Asia [34–38].

3. Results

3.1. Dust Transport over East Asia

Figure 2 shows dust RGB imageries and SYNOP sites at which dust weather episodes were occurring for each day during 3–8 May 2017. The pink-shaded areas represent the range of the dust plume. The dust storm began over South Mongolia and West Inner Mongolia of China, on 3 May, and moved to North China on 4 May. Then, the dust plume slowly moved eastward and stayed over North China until 5 May. After that, the dust was continuously moving eastward, covered Korea Peninsula, and reached Japan on 6 May. The dust RGB imagery clearly showed the long-range transport of dust, which was consistent with SYNOP observations during 3 May and 6 May, as well as the backward trajectory from Fukuoka, at 20:00, on 6 May. After 6 May, the dust RGB imageries had difficulty showing the dust plume due to the dilution of dust, while the SYNOP observations indicated that the dust plume stayed over Korea and Japan on 7 May and 8 May.

The simulated daily horizontal distribution of dust concentration between 3 and 10 May 2017 at the first vertical level (z = 50 m) of the model is shown in Figure 3. A dust storm began to occur over South Mongolia and West Inner Mongolia of China, under strong wind (>10 m s\(^{-1}\)) condition, on 3 May, and arrived in North China on 4 May, with the maximum dust concentration larger than 1000 µg m\(^{-3}\). The dust plume slowly moved eastward under a sustained northeast wind and stayed over North China until 5 May; meanwhile, the dust concentration decreased significantly to less than 750 µg m\(^{-3}\) due to strong diffusion and deposition. The dust was transported to East China, Korea Peninsula, and Japan on May 6 and stayed there until 9 May; meanwhile, the dust concentration gradually decreased to less than 200 µg m\(^{-3}\). The movement of the dust plume was consistent with the backward trajectory from Fukuoka, on May 6, at 20:00, as shown in Figure 3b–d. On 10 May, the dust only existed over East China, with concentrations of 50–100 µg m\(^{-3}\). The model-simulated occurrence and transport of the dust storm showed good consistency with the dust process revealed by Himawari-8 and SYNOP observations in Figure 2.
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Figure 2. Dust RGB imageries with the surface synoptic observations (SYNOP) sites where dust weather occurred (red triangle for dust storm and circle for drifting and blowing dust) on each day (a–f) between 3 May and 8 May 2017 (JST). The green lines with triangle markers (every 6 h) in (c) and (d) show the 48-h backward trajectory from Fukuoka at 20:00, on 6 May 2017 (JST).
gradually decreased to less than 200 μg m\(^{-3}\). The movement of the dust plume was consistent with the backward trajectory from Fukuoka, on May 6, at 20:00, as shown in Figure 3b–d. On 10 May, the dust only existed over East China, with concentrations of 50–100 μg m\(^{-3}\). The model-simulated occurrence and transport of the dust storm showed good consistency with the dust process revealed by Himawari-8 and SYNOP observations in Figure 2.

Figure 3. Simulated daily horizontal distributions of dust concentrations (shades) and wind vectors (blue vectors) at the first vertical level (z = 50 m) of the model on each day (a–h) between 3 May and 10 May 2017 (JST). The red lines with triangle markers (every 6 h) in (c) and (d) show the 48 h backward trajectory from Fukuoka, at 20:00, on 6 May 2017 (JST).
3.2. Time Series of PM Concentration and Dust Extinction

Figure 4 shows the time series of the observed and simulated PM$_{10}$ and PM$_{2.5}$ concentrations in Beijing, Seoul, and Fukuoka, while Table 1 shows the model performance statistics. The dark yellow and magenta shades represent simulated dust and non-dust PM, respectively. Dust PM is defined as primary mineral dust particles, as well as nitrate and sulfate formed on the surface of dust particles through heterogeneous reactions. Non-dust PM includes BC, OA, secondary inorganic aerosol, and sea salt. The fractions of dust and non-dust PM are also shown as pie charts in Figure 4. The simulated PM$_{10}$ and PM$_{2.5}$ showed reasonably agreement with observations in all the three cities, since the mean fractional bias (MFB) and mean fractional error (MFE) both satisfied the model performance criteria (MFB $\leq \pm$60% and MFE $\leq$ +75%) proposed by [39]. The model reproduced the high concentrations of PM in Beijing during 4 May and 5 May well and showed peak PM$_{2.5}$ concentration of 554 $\mu$g m$^{-3}$, which was similar to the observed value (577 $\mu$g m$^{-3}$). The observed PM$_{10}$ failed to capture the peak value, since the instrument can only measure concentrations less than 1000 $\mu$g m$^{-3}$, but we were still able to see that the model successfully simulated the high PM$_{10}$ episode, with the peak concentration of 1711 $\mu$g m$^{-3}$.

![Figure 4](image-url). Time series of observed and simulated PM$_{2.5}$ (particulate matter (PM) with diameter $\leq$ 2.5 $\mu$m) (a,c,e) and PM$_{10}$ (PM with diameter $\leq$ 10 $\mu$m) (b,d,f) in Beijing (a,b), Seoul (c,d), and Fukuoka (e,f) between 3 May and 11 May 2017 (JST). The black dots are observed PM. The dark yellow and magenta shades represent simulated dust and non-dust PM concentrations, respectively, and the pie charts show the fraction of dust and non-dust PM.
Table 1. Statistics for the observed and simulated PM$_{10}$ and PM$_{2.5}$ in the three cities.

<table>
<thead>
<tr>
<th>Species</th>
<th>Site</th>
<th>N</th>
<th>MO (µg m$^{-3}$)</th>
<th>MM (µg m$^{-3}$)</th>
<th>MB (µg m$^{-3}$)</th>
<th>NMB (%)</th>
<th>RMSE (µg m$^{-3}$)</th>
<th>MFB (%)</th>
<th>MFE (%)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{10}$</td>
<td>Beijing</td>
<td>153</td>
<td>250.6</td>
<td>227.5</td>
<td>−23.1</td>
<td>−9.2</td>
<td>287.1</td>
<td>−39.0</td>
<td>74.6</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>Seoul</td>
<td>191</td>
<td>86.2</td>
<td>76.6</td>
<td>−9.7</td>
<td>−11.2</td>
<td>38.7</td>
<td>−28.8</td>
<td>52.2</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>Fukuoka</td>
<td>192</td>
<td>57.1</td>
<td>50.9</td>
<td>−6.2</td>
<td>−10.9</td>
<td>27.1</td>
<td>−12.8</td>
<td>45.3</td>
<td>0.87</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>Beijing</td>
<td>182</td>
<td>104.6</td>
<td>89.6</td>
<td>−14.9</td>
<td>−14.3</td>
<td>99.6</td>
<td>−24.6</td>
<td>65.8</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>Seoul</td>
<td>191</td>
<td>24.0</td>
<td>33.5</td>
<td>9.6</td>
<td>39.9</td>
<td>25.5</td>
<td>15.7</td>
<td>63.8</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Fukuoka</td>
<td>191</td>
<td>22.8</td>
<td>20.7</td>
<td>−2.1</td>
<td>−9.4</td>
<td>12.9</td>
<td>−11.9</td>
<td>46.0</td>
<td>0.70</td>
</tr>
</tbody>
</table>

N: number of data pairs; MO: mean observed concentration; MM: mean modeled concentration; MB: mean bias; NMB: normalized mean bias; MFB: mean fractional bias; MFE: mean fractional error; R: correlation coefficient.

The simulated PM$_{10}$ in Seoul was in good agreement with our observations during the dust period, especially for the PM$_{10}$ variations during 6 May and 9 May. However, the observed PM$_{2.5}$ concentration was too low to be accurate between 6 May to 7 May, since it was unreasonably low (only 21 µg m$^{-3}$) when the observed PM$_{10}$ reached a maximum of 267 µg m$^{-3}$. The large difference (NMB = 39.9%) and low correlation (R = 0.09) between simulated and observed PM$_{2.5}$ probably resulted from the inaccurate PM$_{2.5}$ observation during this period.

A high concentration of PM reached Fukuoka on the afternoon of 6 May and persisted for more than three days. The model generally reproduced the level and variation of this high PM pollution episode well. The only exception was on the evening of 8 May, when the observed PM$_{2.5}$ and PM$_{10}$ suddenly increased for only five hours, and the model failed to capture this short-term event. The rapid increase and decrease in the PM concentration was possibly due to some local emission sources that were not included and resolved in the model [21].

As shown in the pie charts in Figure 4, it can also be seen that the dust was a dominant component in all three cities, not only for PM$_{10}$ but also for PM$_{2.5}$. The dust fractions in PM were highest in Beijing, with 82% for PM$_{10}$ and 66% for PM$_{2.5}$. The fractions of dust in both PM$_{2.5}$ and PM$_{10}$ were lower in Seoul (51% and 70%) than in Fukuoka (58% and 75%), although the distance from Seoul to the dust-source area was shorter than for Fukuoka, indicating the importance of local anthropogenic pollutants over the Seoul area.

Figure 5 shows ACSA observed ΔH$^+$ of fine (fΔH$^+$) and coarse (cΔH$^+$) aerosol. When the PM$_{2.5}$ and PM$_{10}$ were dominated by non-dust aerosol before 6 May 2017, at 18:00, both fΔH$^+$ and cΔH$^+$ were positive. After that, both became negative, since dust came to Fukuoka, according to the model results, as shown in Figure 4, which indicated that the dust aerosol had a high alkalinity and was a major component of both PM$_{2.5}$ and PM$_{10}$.

Figure 5. Aerosol chemical speciation analyzer (ACSA)-observed ΔH$^+$ of (a) fine and (b) coarse aerosol.

Figure 6 shows LIDAR-observed and model-simulated vertical distributions of dust extinction coefficients in Beijing, Seoul, and Fukuoka. The model successfully captured the major dust episodes in
all three cities. Both the LIDAR observation and model result showed high dust extinction coefficients (>1 km\(^{-1}\)) in Beijing, from the early morning of 4 May until noon on 5 May. The model successfully simulated the dust episode over Seoul, especially the deep and strong dust plume that came to Seoul at 00:00, on 6 May (JST). However, LIDAR measurements indicated daily noontime boundary layer high dust-extinction coefficients that were not observed in Beijing and Fukuoka. This may be an indication of a local emission source near the observation site. This local emission source may explain the discrepancy between the simulated dust extinction coefficients and the LIDAR measurements. The model reproduced the variation and magnitude of dust extinction coefficients in Fukuoka compared with LIDAR data well. The dust arrived at Fukuoka on the afternoon of 6 May and stayed until 9 May, with dust-extinction coefficients of about 0.1 km\(^{-1}\). The NAQPMS model reproduced the observed vertical distributions of dust in Seoul and Fukuoka well and indicated that the dust-plume heights were generally less than 2 km. The dust-plume height was not observed by LIDAR in Beijing because the dust extinction coefficient was too large, and, therefore, the laser could not pass through the thick dust layer.

![LIDAR dust extinction](image)

**Figure 6.** LIDAR-observed (a,c,e) and model-simulated (b,d,f) vertical distributions of dust-extinction coefficients in Beijing (a,b), Seoul (c,d), and Fukuoka (e,f). Black represents cloud, and gray represents no data in the LIDAR observation figures.

### 3.3. Nitrate and Sulfate in Fukuoka

Observed and simulated time variations of NO\(_3^-\) and SO\(_4^{2-}\) in fine and coarse mode over Fukuoka are shown in Figure 7. The statistics for model performance are shown in Table 2. The NAQPMS results all satisfied the performance criteria (MFB ≤ ±60% and MFE ≤ ±75%) of air-quality models [39],

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The reactive uptake rate of HNO$_3$ in coarse mode. The dark yellow, blue, and magenta shades represent the simulated D-, S-, and A-NO$_3^-$ and SO$_4^{2-}$, respectively. The pie charts show the fraction from each chemical pathway of NO$_3^-$ formation.

Table 2. Statistics for the observed versus modeled fine and coarse nitrate and sulfate in Fukuoka.

<table>
<thead>
<tr>
<th>Species</th>
<th>N</th>
<th>MO (µg m$^{-3}$)</th>
<th>MM (µg m$^{-3}$)</th>
<th>MB (µg m$^{-3}$)</th>
<th>NMB (%)</th>
<th>RMSE (µg m$^{-3}$)</th>
<th>MFB (%)</th>
<th>MFE (%)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>fNO$_3^-$</td>
<td>135</td>
<td>1.2</td>
<td>2.3</td>
<td>1.1</td>
<td>90.1</td>
<td>1.6</td>
<td>50.8</td>
<td>69.2</td>
<td>0.63</td>
</tr>
<tr>
<td>cNO$_3^-$</td>
<td>135</td>
<td>2.0</td>
<td>1.5</td>
<td>−0.5</td>
<td>25.9</td>
<td>1.3</td>
<td>−5.9</td>
<td>57.0</td>
<td>0.82</td>
</tr>
<tr>
<td>fSO$_4^{2-}$</td>
<td>135</td>
<td>2.7</td>
<td>4.3</td>
<td>1.5</td>
<td>56.5</td>
<td>3.1</td>
<td>42.8</td>
<td>72.0</td>
<td>0.19</td>
</tr>
<tr>
<td>cSO$_4^{2-}$</td>
<td>128</td>
<td>0.4</td>
<td>0.7</td>
<td>0.3</td>
<td>63.7</td>
<td>0.5</td>
<td>58.4</td>
<td>70.9</td>
<td>0.18</td>
</tr>
</tbody>
</table>

N: number of data pairs; MO: mean observed concentration; MM: mean modeled concentration; MB: mean bias; NMB: normalized mean bias; MFB: mean fractional bias; MFE: mean fractional error; R: correlation coefficient.

Both simulated fine and coarse nitrate showed good correlation with observations (R = 0.63 for fNO$_3^-$ and 0.82 for cNO$_3^-$) and significantly increased during the dust period, which was consistent with the observations. The observed mean cNO$_3^-$ concentration (2.0 µg m$^{-3}$) was 68% higher than fNO$_3^-$ (1.2 µg m$^{-3}$), indicating the importance of coarse nitrate, which has not received enough attention.

The contributions of different chemical pathways on NO$_3^-$ and SO$_4^{2-}$ formation were also shown as pie charts in Figure 7. The results indicated that the heterogeneous reaction on dust particles is the major mechanism for NO$_3^-$ production in both fine and coarse mode, since the fraction of D-NO$_3^-$ to total nitrate was 60% and 72% in fine and coarse mode, respectively. The contribution of A-NO$_3^-$ (34%) was more important than S-NO$_3^-$ (6%) in fine mode, while it (10%) was smaller than S-NO$_3^-$ (17%) in coarse mode.

Although the model reproduced the increase of NO$_3^-$ during dust period, it overestimated the fNO$_3^-$ by a mean bias of 1.1 µg m$^{-3}$ and underestimated the cNO$_3^-$ by a mean bias of −0.5 µg m$^{-3}$. The model overestimated the D-NO$_3^-$ because only the simulated D-NO$_3^-$ was already higher (NMB = 15.3%) than the observations. The dust heterogeneous reactions were not limited by dust alkalinity, since the ΔH$^+$ was negative during the whole dust period (Figure 5); therefore, a reasonable explanation is that the reactive uptake rate of HNO$_3$ of fine dust particles was overestimated. A possible reason for the cNO$_3^-$ underestimation by the model may be that there was an underestimation of the reactive uptake rate of HNO$_3$ of coarse dust particles. This means that the reactive uptake rate of HNO$_3$ of fine dust particles may be smaller than that of coarse dust particles. The reason why fine
and coarse dust had different reactive uptake rates was not clear, and a potential reason is that large dust particles are more irregular and have a larger surface area. More studies are necessary in order to understand this problem.

Simulated $\text{SO}_4^{2-}$ concentrations had similar magnitudes to observed results, but the detailed time variation was not well reproduced, implying the difficulty of sulfate simulation, which was also shown in other models (e.g., CMAQ [34]). The coarse $\text{SO}_4^{2-}$ concentration observation (0.4 $\mu$g m$^{-3}$) was only 15% of fine $\text{SO}_4^{2-}$ (2.7 $\mu$g m$^{-3}$), which was different from NO$_3^-$, and the model also showed a similar ratio (16%), which indicated D-$\text{SO}_4^{2-}$ may not be very important for total $\text{SO}_4^{2-}$. This was further confirmed by the model results, since the simulated period-averaged D-$\text{SO}_4^{2-}$ was only 0.1 $\mu$g m$^{-3}$ in both fine and coarse mode. The A-$\text{SO}_4^{2-}$ was most important for fine and coarse $\text{SO}_4^{2-}$, with contributions of 94% and 53%, while contributions of S-$\text{SO}_4^{2-}$ were 4% and 33% of SO$_4^{2-}$, and D-$\text{SO}_4^{2-}$ only contributed for 2% and 15%.

4. Discussion

4.1. Formation of Dust–Nitrate along the Air-Mass Trajectory

Figure 8 shows the variations of dust concentration, RH, D-NO$_3^-$, A-NO$_3^-$, and HNO$_3$, as well as the ratio of D-NO$_3^-$ to dust concentration along the 36 h backward trajectory from Fukuoka, at 20:00, on 6 May 2017 (JST), as shown in Figure 3. We can see that the air mass containing dust located over North China (NC), on the morning of 5 May, was transported through the Bohai Sea (BS) and Liaoning Peninsula (LP) in the afternoon, the Yellow Sea (YS) in the evening, and then reached North Korea at 22:00. From the early morning of 6 May, the air mass passed through the Yellow Sea (YS) again, as well as South Korea (SK), and it reached the Tsushima Strait (TS) at 9:00. After slowly moving for 10 h over the TS, the air mass reached Fukuoka, Japan (JP).

Figure 8. Variations of (a) dust concentration and RH; (b) D-NO$_3^-$, A-NO$_3^-$, and HNO$_3$; (c) the ratio of D-NO$_3^-$ to dust concentration, the surface type (land and water), and terrain height along the 36-hour backward trajectory from Fukuoka, on May 6 2017, at 20:00 (JST), as shown if Figure 1. NC: North China, LP: Liaoning Peninsula, NK: North Korea, SK: South Korea, BS: the Bohai Sea, YS: Yellow Sea, TS: Tsushima Strait.
The dust concentration decreased rapidly over NC, along the trajectory, due to strong diffusion and deposition. The D-NO$_3^-$ concentration was less than 3 $\mu$g m$^{-3}$, and the D-NO$_3^-$/dust ratio was less than 0.5%, due to low RH (<30%) during this period. When the air mass reached the Bohai Sea, where RH was greater than 50%, the D-NO$_3^-$ quickly increased from 5 to 19 $\mu$g m$^{-3}$, faster than the increase of A-NO$_3^-$: Meanwhile, the ratio of D-NO$_3^-$ to dust also increased from 0.5% to 3%. After that, all the dust, D-NO$_3^-$ and D-NO$_3^-$/dust ratio decreased due to the impacts of the Liaoning Peninsula, including low RH and strong deposition. After the air mass was transported to the Yellow Sea, the dust and D-NO$_3^-$ continuously decreased, while the A-NO$_3^-$ and the D-NO$_3^-$/dust ratio increased significantly due to the high RH of nearly 100%. When the air mass reached North Korea, all the dust, D-NO$_3^-$, A-NO$_3^-$ concentration, and the D-NO$_3^-$/dust ratio decreased, probably due to the stronger dilution of A-NO$_3^-$ and coated dust over land area. From South Korea to Japan, the dust and A-NO$_3^-$ concentration decreased, while D-NO$_3^-$ and the D-NO$_3^-$/dust ratio gradually increased under higher HNO$_3$ concentration. After reaching Japan, the A-NO$_3^-$ decreased rapidly due to strong diffusion and deposition, and D-NO$_3^-$ became dominant in nitrate. These results indicated that the sea area with high RH plays a key role in the rapid formation of dust nitrate.

4.2. Horizontal Distribution of D-NO$_3^-$ and Its Influencing Factors

Figure 9 shows the horizontal distribution of average fine (Figure 9a,c) and coarse-mode (Figure 9b,d) D-NO$_3^-$ concentrations and the ratio of D-NO$_3^-$ to dust concentrations by shades, and dust concentrations by lines, as well as the RH and HNO$_3$ concentration during 3–11 May 2017.

![Figure 9. Horizontal distribution of average fine- (a,c) and coarse-mode (b,d) D-NO$_3^-$ concentrations and the ratio of D-NO$_3^-$/dust concentrations by shades and dust concentrations by lines, as well as the RH and HNO$_3$ concentrations during 3–11 May 2017.](image-url)
The region with the highest fine D-NO$_3^-$ concentration (>2 µg m$^{-3}$) was located over the Yellow Sea and East China, while the region with the highest coarse D-NO$_3^-$ concentration (>3 µg m$^{-3}$) was located in a very similar area with fine D-NO$_3^-$, but with a concentration level that was about 50% higher than that of the fine D-NO$_3^-$. The fine D-NO$_3^-$ was higher than the coarse D-NO$_3^-$ over downwind regions, e.g., North Japan and its surrounding area, due to a smaller dry deposition velocity of fine dust. As a result, the area affected by the fine D-NO$_3^-$ was wider than by the coarse D-NO$_3^-$. Figure 9c,d shows that the ratios of D-NO$_3^-$/dust was less than 1% in both fine and coarse mode over most areas of North China where fine dust was less than 50 µg m$^{-3}$ and coarse dust was less than 100 µg m$^{-3}$, due to low RH (<40%), as shown in Figure 9e, and the consequent low uptake rate of HNO$_3$ on dust; it rapidly grew larger than 8% and 6% in fine and coarse mode over the Yellow Sea region due to high RH (>80%), which is favorable for dust to uptake the HNO$_3$. The ratios of D-NO$_3^-$/dust also showed high value over South China due to relative high RH of about 60% and high HNO$_3$ concentration, with a maximum of more than 10 ppb. The ratios of both fine and coarse D-NO$_3^-$/dust increased to about 10% over downwind areas with low dust concentrations. These results highlight the importance of D-NO$_3^-$ and its potential effects on ocean ecosystems.

5. Conclusions

Synergetic observations and the Nested Air Quality Prediction Modeling System (NAQPMS) were used to analyze the transport of a severe dust storm and its impacts on NO$_3^-$ and SO$_4^{2-}$ over East Asia, between 3 May and 11 May 2017.

The model successfully reproduced the occurrence and transport of the dust storm by comparison with dust RGB images of the Himawari-8 satellite, the SYNOP dust weather report, on-site particulate matter (PM) observations, and LIDAR-observed dust extinction coefficients.

The NAQPMS model also generally reproduced the concentration levels of observed nitrate and sulfate over Fukuoka, Japan. The model results indicated that the dust heterogeneous reaction was the dominant pathway for nitrate formation, since the fraction of D-NO$_3^-$ to total nitrate was 60% and 72% in fine and coarse mode, respectively. However, the dust heterogeneous reaction had a limited contribution to sulfate, since the simulated period-averaged D-SO$_4^{2-}$ was only 0.1 µg m$^{-3}$ in both fine and coarse mode.

Dust nitrate formed rapidly after leaving China, and the mass ratio of dust nitrate to dust aerosol increased to greater than 8% and 6% in fine and coarse mode, respectively, over the Yellow Sea region, due to high RH (>80%), which is favorable for dust to uptake the HNO$_3$. The highest period-averaged concentration of dust nitrate (>5 µg m$^{-3}$) was shown over the Yellow Sea and East China. The mass ratio of dust nitrate to dust aerosol finally reached 10% downwind over Pacific Ocean. Our results confirmed the importance of dust heterogeneous reactions and implied their important impacts on the ocean ecosystem. Our results also indicated that the NAQPMS model can be used to quantify the potential effects of nitrate transport and deposition in the ocean.

In addition, our analysis suggested that the $\gamma_{dust-HNO_3}$ of coarse dust particles may be greater than that of fine dust particles due to the underestimation of coarse nitrate and overestimation of fine nitrate by the model. The reason was not clear yet, and more studies are necessary.

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