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Significant impacts of heterogeneous reactions on the chemico-physical properties of dust particles during severe dust events over East Asia in 2015

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Abstract

Heterogeneous processes play an important role in changing the chemical, physical, optical, and radiative characters of dust particles at regional and global scales, especially in East Asia, where both the emissions of mineral dust and anthropogenic pollutants are huge. To investigate the chemical and physical impacts of heterogeneous reactions on dust particles, three dust and/or air pollution episodes were observed and simulated in Beijing, China and Fukuoka, Japan during 27 March and 2 April, 2015. The results confirmed that heterogeneous reactions were the major mechanisms producing coarse mode nitrate and sulfate in the presence of dust particles, with the concentrations of coarse mode nitrate reaching $19 \mu\text{g}/\text{m}^3$ in Beijing and $4 \mu\text{g}/\text{m}^3$ in Fukuoka. We also found that heterogeneous processes and subsequent hygroscopic growth significantly changed the mixing state and size of dust particles. As a result of the internal mixing of nitrate, sulfate, and aerosol liquid water, the volume concentration of dust doubled when the relative humidity (RH) was relatively high ($> 80\%$), and the dust particles tended to be spherical when the volume fraction of dust coatings reached 20%.

Keywords : *Dust, heterogeneous reaction, hygroscopic growth, mixing state, particle size, depolarization, sphericity*

1. Introduction

A large amount of mineral dust particles are mobilized into the atmosphere by strong surface winds over arid terrain in Asia, and can be transported long distances (e.g., to the northern Pacific, North America, and even one full circuit around the globe)¹⁾. This enhances the heterogeneous chemistry of the atmosphere²⁾, and influences the climate by scattering and absorbing

incoming solar radiation³⁾. Compared with pure secondary anthropogenic sulfate and nitrate, sulfate and nitrate carried on dust can be transported over much longer distances. When aged by water soluble aerosol components during transportation, the size, shape, and hygroscopicity of mineral particles may be altered. As a result, the coated dust particles will change their optical properties, and become more efficient cloud condensation nuclei (CCN), which will consequently change both the direct and indirect climate effects of dust particles at regional and global scales.

Calcium (Ca) in Asian dust accounts for 39% of the total of seven crustal elements (Si, Al, Mg, Ca, Na, and K), in contrast with Saharan dust particles where Ca only comprises up to 17%⁴⁾. Calcium-rich Asian dust particles readily react with anthropogenic acidic species, such as sulfuric and nitric acid. Meanwhile, dust particles may also directly take up high levels of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2)⁵⁾, leading to the formation of water-soluble sulfate and nitrate in

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large quantities. Therefore, the mixing of Asian mineral dust with anthropogenic pollutants is a critical issue in understanding the problem of ‘polluted dust’.

Beijing, China is very close to the source region of dust particles (about 200 km away), and its surrounding area has a larger emission intensity of anthropogenic pollutants than other regions of China, or even the world. In general, during blowing dust events, a strong northwest wind usually carries dust particles through Beijing quickly and directly, and the concentration of anthropogenic pollutants in Beijing decreases significantly due to the high wind speed and dilution. Therefore, almost no sulfate is formed and nitrate is only formed in small quantities on the surface of dust particles during their transport from source areas to Beijing⁶⁾. Transmission electron microscopy (TEM) observations in Beijing have indicated that only 5% are covered by visible coatings in the dust sample⁷⁾. However, during 29 March to 1 April of 2015, high concentrations of suspended dust and anthropogenic pollutants were trapped in the Beijing area, which provided a good opportunity to observe and simulate the impacts of heterogeneous reactions on the chemico-physical properties of dust particles.

In this study, we used a polarization optical particle counter (POPC) to observe the mixing and sphericity of particles of different sizes in Beijing, China for the first time, and we also made POPC observations in Fukuoka, Japan. Filter samples of PM_{2.5} (particulate matter [PM] with an aerodynamic diameter less than or equal to 2.5 μm) and PM₁₀ (PM with an aerodynamic diameter less than or equal to 10 μm) were collected twice a day in Beijing and analyzed by ion chromatography (IC). In Fukuoka, a continuous dichotomous aerosol chemical speciation analyzer (ACSA) was used to observe the chemical composition of PM_{2.5} and PM₁₀. The Nested Air Quality Prediction Modeling System (NAQPMS) was also used to simulate the mixing of dust particles with anthropogenic pollutants. Based on the observations and model results, the impacts of heterogeneous chemical reactions on the chemico-physical properties (e.g., chemical composition, particle size, hygroscopicity, and sphericity) of dust particles during severe dust events over East Asia in 2015 was studied in detail.

2. Experimental

2.1 Observations

Online observation of the light-polarization property of single particles was performed using a POPC (YKG

Corp., Yamanashi, Japan) at the Institute of Atmospheric Physics (IAP: 116.4°E, 39.9°N), Beijing and Kyushu University (130.5°E, 33.5°N), Fukuoka, during the spring of 2015. Beijing is located in the downstream region of dust sources (about 200 km away), while Fukuoka is located more than 1,500 km away from the major dust source regions (Fig. 1). POPCs were previously used successfully for dust monitoring in Korea⁸⁾ and Japan⁹⁾, however, this is the first time it was used for dust monitoring in China. A POPC measures the intensity of the forward scattering signal and two depolarized components (s-polarized, p-polarized) of the backward scattering signal for each single particle illuminated by a linearly polarized laser at a wavelength of 780 nm¹⁰⁾. The intensity of forward scattering was used to determine the size of individual particles. The depolarization ratio (DR), denoted as the ratio of the intensity of the s-polarized component to the backward scattering signal $[S/(S+P)]$, was an indicator of the non-sphericity of the particle. Supermicron particles with a DR > 0.2 and submicron particles with a DR > 0.5 were regarded as being “non-spherical” (e.g., dust). Supermicron particles with a DR < 0.2 had a spherical structure (e.g., anthropogenic pollutants or sea salt)¹⁰⁾. POPCs have been used to investigate the time-resolved mixing state of mineral dust and anthropogenic aerosols^{8, 9)}.

PM_{2.5} and PM₁₀ were collected on Teflon filters at the IAP at 12 h intervals from March 27 to April 12, 2015. For the extraction of water-soluble components from the aerosol filter sample (diameter of 2 cm), 10 mL of ultra-pure water was added to the sample vial, and then ion-chromatography (ICS-1600 for anions and ICS-1100 for cations; Thermo Fisher Scientific, Waltham, MA, USA) was used to analyze the aerosol ion concentration.

The mass concentrations of anthropogenic aerosols in both PM_{2.5} and PM₁₀ were concurrently measured using a continuous dichotomous ACSA (ACSA-12, Kimoto Electric Co., Ltd., Osaka, Japan) at 1 h time intervals at Kyushu University, Fukuoka⁹⁾. The ACSA-12 determines PM, black carbon (BC), sulfate, and nitrate on the basis of β ray absorption, near-infrared light scattering, a BaSO₄-based turbid metric, and a UV spectrophotometric method, respectively, with an uncertainty of ~10%¹¹⁾.

A dual-wavelength (1,064 nm, 532 nm) depolarization Lidar developed by the National Institute for Environmental Studies (NIES)¹²⁾ was used to continuously observe aerosols below 6 km at 15 minute intervals at the IAP, Beijing¹³⁾. The Lidar employs a flash lamp-pumped Nd:YAG laser with a second

harmonics generator. The scattered light is received with a 20 cm Schmidt-Cassegrain telescope, and is then collimated and directed to a dichroic mirror to separate received light at 532 and 1,064 nm. The 1,064 nm signal is detected with an avalanche photodiode (APD). The 532 nm wavelength corresponds to depolarization and the light is directed to a polarizer. The polarization components are detected with two photomultiplier tubes (PMTs). The Fernald inversion method is applied to derive the extinction coefficient with S1 set to 50 sr in the inversion process.

2.2 Numerical Models

The NAQPMS¹⁴⁾ was used to simulate the dust and air pollution processes. The model has been used previously to simulate the heterogeneous reactions occurring on dust and BC^{15, 16)}. NAQPMS was configured with the same horizontal resolution and domain as the Weather Research and Forecasting (WRF) model (Fig. 1), and with 20 vertical layers in a sigma coordinate.

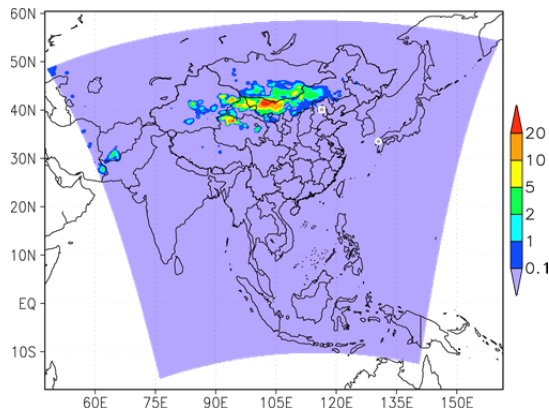


Fig.1 Model domain and spatial distributions of dust emissions (unit: ton/km²) during 27 March to 1 April, 2015. The white square and circle indicate the locations of Beijing and Fukuoka, respectively.

Dust emissions were computed online using a modified size-segregated dust deflation module^{16, 17)}. The mineral dust emission intensity (F), considering soil categories, vegetation fraction percentages, and snow/ice cover, was determined using the following equation:

$$F = C_1 \cdot \frac{\rho_a}{g} \cdot E \cdot u^{*3} \left(1 + \frac{u_0^*}{u^*}\right) \cdot \left(1 - \frac{u_0^{*2}}{u^{*2}}\right) \cdot \left(1 - \frac{RH}{RH_0}\right) \quad (1)$$

where F is the dust flux (kg m⁻² s⁻¹). The constant C_1 is set to 1.0×10^{-5} , and ρ_a (kg m⁻³) and g (m² s⁻²) are the air density and acceleration due to gravity, respectively.

The dust source factor (E) represents the uplifting capability of the land surface, and reflects the impact of land use categories, vegetation fractions, and snow/ice cover on dust fluxes. In the desert, without vegetation and snow cover, dust particles are easily uplifted to the boundary layer, and E is set to 1.0. In contrast, E is set to 0.0 in evergreen forest. u^* and u_0^* are the friction and threshold friction velocities. u_0^* is related to soil type, mineral particle size distribution, surface roughness, and soil moisture. RH and RH_0 represent relative humidity and its threshold value, respectively. In this study, u_0^* was set to 0.45, 0.35, 0.6, and 0.4 m s⁻¹ in the Gobi, China Loess, Hunshandak deserts, and other dust source regions, respectively, while RH_0 was set to 40 %, following Li *et al.*¹⁶⁾. The dust particle size was separated into four size bins covering the range of 0.43–10 μm (0.43–1 μm; 1–2.5 μm; 2.5–5 μm, and 5–10 μm) in diameter.

The anthropogenic emissions (e.g., SO₂, NO_x, NH₃, CO, BC, OC, and VOCs) were from the MIX (mosaic Asian anthropogenic emission inventory for Model Inter-Comparison Study [MICS]-Asia and Hemispheric Transport of Air Pollution [HTAP] projects, <http://meicmodel.org/dataset-mix.html>) with base year 2010 prepared by Li *et al.*¹⁸⁾.

To simulate the mixing of aerosols with pollutant gases, 28 heterogeneous reactions on sulfate, soot, dust and seasalt particles have been included by Li *et al.*¹⁶⁾. The first-order rate constant (k) of each reaction is calculated by uptake coefficient (γ) and surface area density of particles (A) using the following equation suggested by Jacob¹⁹⁾:

$$k = \left(\frac{r}{D_g} + \frac{4}{c\gamma}\right)^{-1} \times A \quad (2)$$

where r is the dust particle mean radius, D_g is the gas phase diffusion coefficient, c is the mean molecular speed of the gas, γ is the uptake coefficient, and A is the surface area density of the particles. Among the 28 heterogeneous reactions, the 12 reactions on dust particles and their uptake coefficients are listed in Table 1.

The WRF (version 3.7.1) model was used to investigate the detailed meteorological conditions over East Asia. The model was configured with a horizontal resolution of 45 km (Fig. 1) and 30 vertical layers. National Centers for Environmental Prediction (NCEP) operational global final analysis (FNL) data (1° × 1°, <http://dss.ucar.edu/datasets/ds083.2/>) were used as the initial and boundary conditions.

Table 1. Heterogeneous reactions on dust particles and reactive uptake coefficients

Heterogeneous Reactions	γ
$\text{O}_3 + \text{dust} \rightarrow \text{products}$	2.7×10^{-5}
$\text{HNO}_3 + \text{dust} \rightarrow \text{NO}_3^-$	$\frac{c \times \text{RH}}{(1 - \text{RH}) \times (1 - (1 - c) \times \text{RH})} \times 0.018$ ($c = 8$)
$\text{NO}_2 + \text{dust} \rightarrow 0.5\text{HONO} + 0.5\text{HNO}_3$	2.1×10^{-6}
$\text{NO}_3 + \text{dust} \rightarrow \text{HNO}_3$	1.0×10^{-3}
$\text{N}_2\text{O}_5 + \text{dust} \rightarrow 2\text{HNO}_3$	3.0×10^{-2}
$\text{OH} + \text{dust} \rightarrow \text{products}$	1.0×10^{-1}
$\text{HO}_2 + \text{dust} \rightarrow 0.5\text{H}_2\text{O}_2$	2.0×10^{-1}
$\text{H}_2\text{O}_2 + \text{dust} \rightarrow \text{products}$	$12 \times \text{RH}^2 - 5.95 \times \text{RH} + 4.08$
$\text{SO}_2 + \text{dust} \rightarrow \text{SO}_4^{2-}$	1.0×10^{-4}
$\text{CH}_3\text{COOH} + \text{dust} \rightarrow \text{products}$	1.0×10^{-3}
$\text{CH}_3\text{OH} + \text{dust} \rightarrow \text{products}$	1.0×10^{-5}
$\text{HCHO} + \text{dust} \rightarrow \text{products}$	1.0×10^{-5}

The back and forward trajectories of air masses are calculated by a Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT; version 4) model (<http://ready.arl.noaa.gov/HYSPLIT.php>) during the dust period based on NCEP GDAS global assimilation data (<ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas0p5>) with 0.5 degree resolution every 3 hours.

3. Results and Discussion

3.1 The Dust and Air Pollution Episodes and Model Evaluation in Beijing Region

Three high PM concentration episodes with meteorological parameters were well observed and simulated in Beijing during March 27 to April 1, 2015, as shown in Fig. 2. $\text{PM}_{2.5}$ was observed by tapered element oscillating microbalance (TEOM), while $\text{PM}_{2.5-5}$ (PM with diameter larger than 2.5 μm yet less than 5 μm) and PM_{5-10} (PM with diameter larger than 5 μm yet less than 10 μm) were constructed by POPC using a density of 1.8 g/cm^3 . Comparisons of the observed and simulated time series of meteorological parameters (wind vector, wind speed and RH) in Fig. 2 (a–c) also indicated that the model simulation showed a good consistency with observations.

The first high PM concentration episode is classified as an anthropogenic air pollution episode on March 27 (Episode A). During this episode, wind speed was less than 5 m/s, and wind direction was south (Fig. 2a and 2b), which is the typical meteorological condition for heavy air pollution processes in Beijing. Fine particles ($\text{PM}_{2.5}$) was dominate with a concentration larger than 100 $\mu\text{g}/\text{m}^3$ (Fig. 2d), while $\text{PM}_{2.5-5}$ and PM_{5-10} concentrations were both less than 50 $\mu\text{g}/\text{m}^3$ (Fig. 2e and

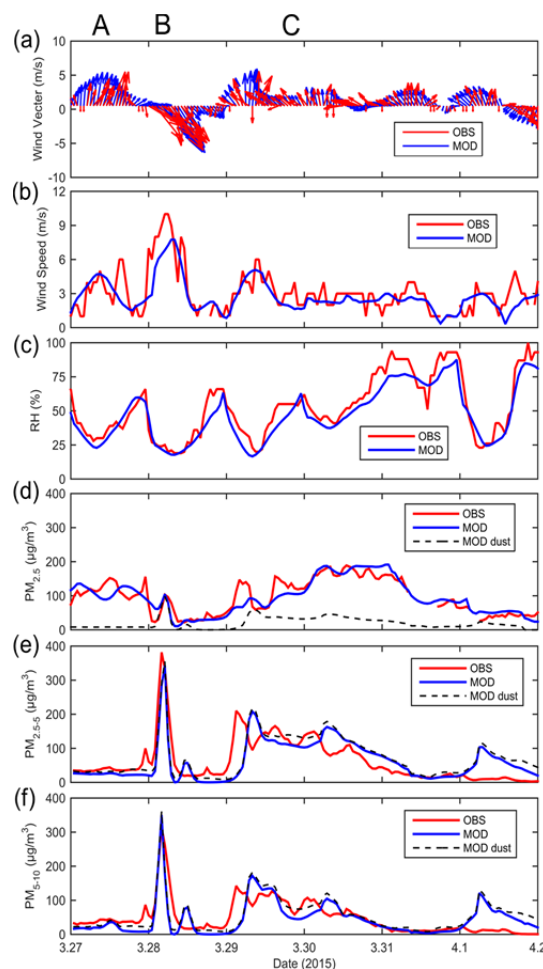


Fig.2 Time series of observed and simulated meteorological parameters (a, wind vector; b, wind speed; c, relative humidity) and particulate matter (PM) (d, $\text{PM}_{2.5}$; e, $\text{PM}_{2.5-5}$; f, PM_{5-10}) concentrations in Beijing. Black dashed lines in (d–f) indicate simulated dust PM, while blue lines indicate total PM (= anthropogenic + dust).

2f). From the simulated anthropogenic PM and dust concentration, it is clearly shown that $\text{PM}_{2.5}$ was mostly anthropogenic particles, while $\text{PM}_{2.5-5}$ and PM_{5-10} were mostly dust.

The second high PM concentration episode is a pure dust episode, on March 28 (Episode B). This pure dust episode is a blowing dust process with a strong northwest wind higher than 10 m/s, lasting for only about 5 hours. During this episode, the $\text{PM}_{2.5}$ concentration was less than 103 $\mu\text{g}/\text{m}^3$; however, $\text{PM}_{2.5-5}$ and PM_{5-10} concentrations increased significantly with maximum values of 382 $\mu\text{g}/\text{m}^3$ and 314 $\mu\text{g}/\text{m}^3$, respectively.

The third high PM concentration episode is a mineral dust mixing with anthropogenic air pollution episode

during March 29 to March 31 (Episode C). This mixing dust episode was a floating dust process with a weaker south wind less than 5 m/s, different from typical dust processes with a strong north wind. During this episode, the $\text{PM}_{2.5}$ concentration increased gradually to a maximum of about $200 \mu\text{g}/\text{m}^3$, while the $\text{PM}_{2.5-5}$ and PM_{5-10} concentration decreased gradually from a maximum of about $200 \mu\text{g}/\text{m}^3$ and $150 \mu\text{g}/\text{m}^3$, and dust particles were mixing with anthropogenic pollutants.

Figure 3a and 3b shows the dust transport pattern on March 28 03:00 UTC (Episode B) and March 29 12:00 UTC (Episode C), while Figs 3c and 3d are backward and forward trajectory from Beijing ending at the same

time with Fig. 3a and 3b, respectively. Dust particles were mainly emitted from Mongolia and Inner Mongolia province of China (Fig. 1), and arrived at Beijing rapidly (within half a day) following the strong northwest wind ($> 10 \text{ m/s}$) on March 28 (Fig. 3a and 3c), and stayed in Beijing for only about 5 hours (Episode B). Then, the dust was quickly transported to about 500 km southeast of Beijing (i.e., Hebei and Shandong province). However, the dust cloud once swept out from the Beijing region, and was transported back to Beijing again under the south wind over North China on March 29 (Fig. 3b and 3d); the high PM concentration in Beijing then continued for about 2 days (Episode C) (Fig. 2).

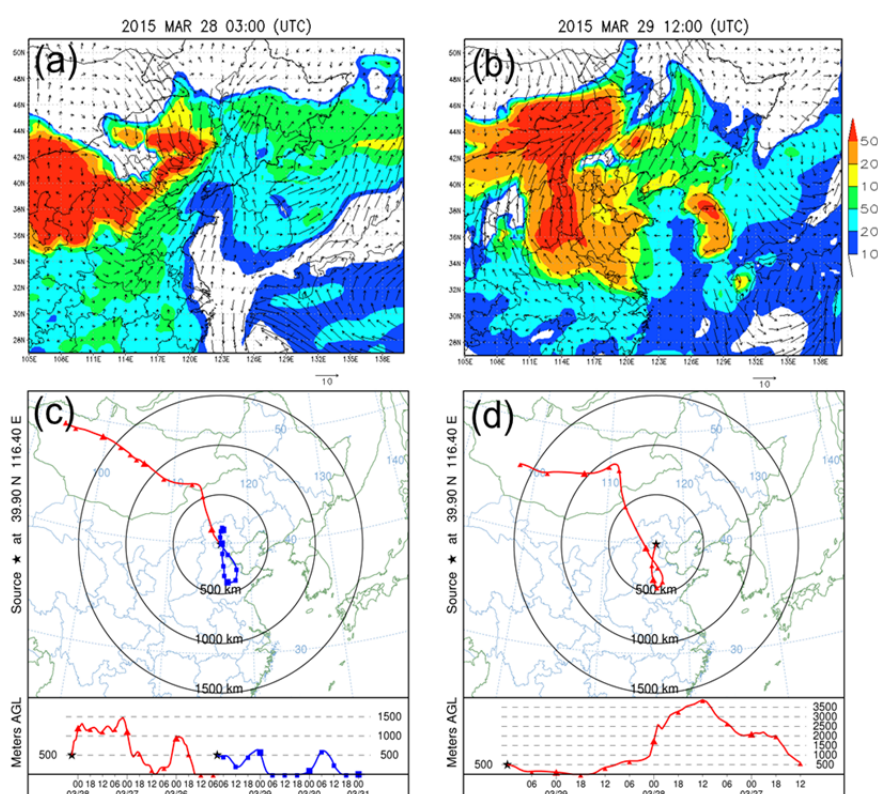


Fig.3 Horizontal distribution of dust concentration (unit: $\mu\text{g}/\text{m}^3$) and wind vector (unit: m/s) on March 28 03:00 UTC (a) and 29 12:00 UTC (b). (c) and (d) are backward (Red) and forward (blue) trajectory from Beijing at the same time with (a) and (b).

Figure 4a and 4c present time-height indications of the extinction coefficients of non-spherical aerosols (mostly mineral dust) and spherical aerosols (mostly anthropogenic particles) derived from Lidar measurements using a method based on the assumption of external mixing between two types of particles with different particle DRs¹²⁾. The NAQPMS model simulated results are also shown in Fig. 4b and 4d. The vertical distributions of aerosol during the three episodes were quite different. On March 27 (Episode A), the aerosol extinction coefficient was mainly caused by the

anthropogenic aerosol, and it reached heights less than 1,500 m. However, on March 28 (Episode B), the dust extinction coefficient was dominant, and it reached as high as 4 km, and lasted for about 5 hours. During March 29 to 31 (Episode C), both dust and anthropogenic aerosols reached about 2 km, less than the height during Episode B, indicating that only the dust in the lower layer went back. The model results were in close agreement with the Lidar retrieval for both the timing and vertical distribution of high concentration events.

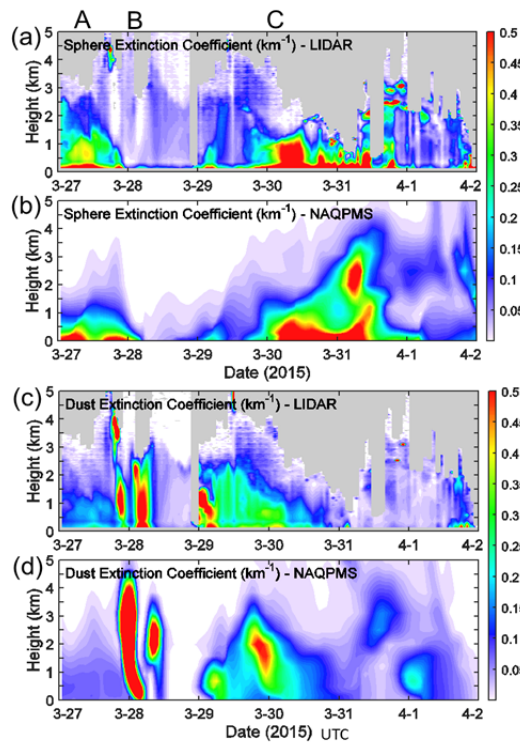


Fig.4 Lidar-observed (a, c) and model-simulated (b, d) time-height indications of anthropogenic (a, b) and dust (c, d) extinction coefficients.

Time series of PM_{10} concentration, volume size distributions and mode DRs of ambient particles observed by POPC at Beijing are shown in Fig. 5, and the PM_{10} concentration observed by TEOM is also shown in Fig. 5a. The constructed PM_{10} mass concentration by POPC is also consistent with the online measurement of PM_{10} by TEOM. From Fig. 5b, we can see that the volume concentrations of ambient particles generally had two significant peaks in the submicron and/or coarse mode size ranges, representing anthropogenic particles and mineral dust particles. During Episode A (March 27) submicron particles had a larger volume concentration; while coarse mode particles were dominate during Episode B (March 28); however, during Episode C (from March 29 to March 30), coarse mode particles decreased gradually and mixed with the increasing submicron particles. To reveal the sphericity of coarse and submicron particles, the DRs of particles at each size range as a function of time are shown in Fig. 5c. Because the DR value of any size range particles was always characterized by a skewness of the distribution, a mode DR (MDR) value was used to represent their typical depolarization property. As shown in Fig. 5c, particles with diameter larger than $2\ \mu m$ had larger DR values, indicating that they were more non-spherical, and DR values were higher during dust

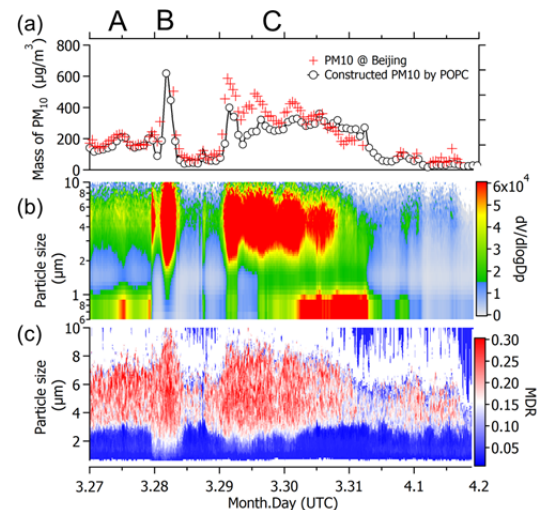


Fig.5 Time series of PM_{10} concentration (a), volume size distributions (b) and mode depolarization ratios (MDRs) (c) of ambient particles at Beijing.

periods (Episodes B and C) compared to non-dust periods.

3.2 Transport of Dust and Pollution to Fukuoka

Figure 6 compares the observed and simulated time series of PM concentrations with different bin size at Fukuoka. In general, PM concentrations were underestimated by the model during March 27 to 29; however, the model captured the peak of PM concentration on March 30 and showed a similar magnitude (about $40\ \mu g/m^3$ for $PM_{2.5}$ and $PM_{2.5-5}$, $60\ \mu g/m^3$ for PM_{5-10}). Similar to Beijing, $PM_{2.5}$ in Fukuoka was mostly anthropogenic particles, while almost all the $PM_{2.5-5}$ and PM_{5-10} were mineral dust.

Similar to Fig. 5, POPC observations at Fukuoka are shown in Fig. 6 (d-f). The constructed PM_{10} by POPC are also consistent with the PM_{10} observed by ACSA (Fig. 6d). The PM_{10} concentration of Fukuoka reached about $107\ \mu g/m^3$ in March 30, and consisted mostly of coarse particles with diameter larger than $2\ \mu m$ (Fig. 6e), but with more submicron particles compared to the pure dust Episode B of Beijing. As shown in Fig. 6f, on March 30, DR values of the particles with diameters larger than $2\ \mu m$ increased significantly, as they were affected by non-spherical dust particles, while DR values of submicron particles were still low. By comparison of the Fukuoka dust episode with Episode B of Beijing, it is indicated that the dust particles were mixed with anthropogenic aerosols gradually during the transportation from China to Japan.

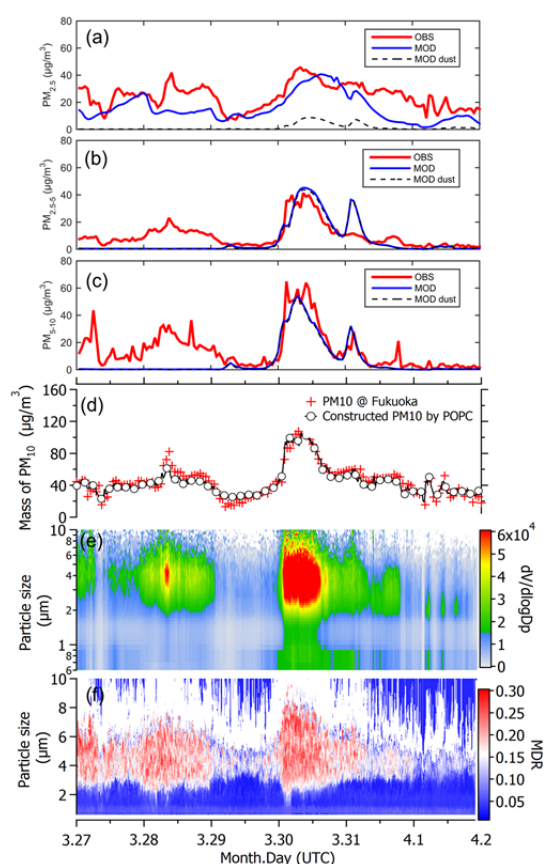


Fig.6 Time series of observed and simulated PM concentrations at Fukuoka: (a) $\text{PM}_{2.5}$; (b) $\text{PM}_{2.5-5.5}$; (c) PM_{5-10} ; and PM_{10} concentration (d), volume size distributions (e) and MDRs (f) of ambient particles measured by a polarization optical particle counter (POPC) at Fukuoka. Black dashed lines in (a–c) indicate simulated dust PM, while blue lines indicate total PM.

Figure 7 presents the backward trajectory from Fukuoka ending on March 30 at 12:00 UTC. From the trajectory plot, it is shown that the high-concentration dust on March 30 was transported from the northeast part of the Beijing-Tianjin-Hebei area from March 28, at the same time as with Episode B in Beijing, which indicates that the dust of Fukuoka on March 30, and of Episode B in Beijing, were the same dust plume. However, different to the trajectory in Fig. 3c and 3d, this trajectory went straight to Kyushu Island after it passed north Hebei without turning back, because the heights of air masses along the trajectories in Figs. 3 and 7 were different on March 28. The air mass on March 28 in Fig. 3 was in the atmospheric boundary layer ($< 1,500$ m), while the air mass on March 28 in Fig. 7 was in the middle troposphere (about 5,000 m).

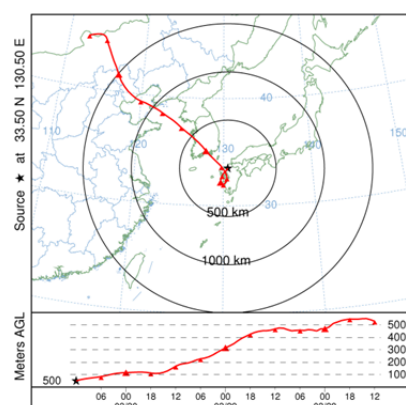


Fig.7 Backward trajectory from Fukuoka ending on March 30 at 12:00 UTC.

3.3 Impacts of Heterogeneous Reactions on Aerosol Mixing State and Chemical Composition

To identify the aerosol mixing state of the different episodes, volume concentrations as a function of particle size and DR for anthropogenic aerosols (Episode A), mineral dust (Episode B), and mixing particles (Episode C) in Beijing are shown in Fig. 8a, 8b and 8c, respectively; concentrations during the dust episode in Fukuoka are also shown. It can be seen that anthropogenic aerosols were mostly in the submicron range, with DR values < 0.2 (Fig. 8a). Mineral dust had a larger diameter ($D_p > 3 \mu\text{m}$) and a non-spherical morphology associated with larger DR values (0.2–0.4); the fraction of calcium ions mass concentration relative to the total mass concentration of sulfate, nitrate, ammonium and calcium reached 40% in both $\text{PM}_{2.5}$ and PM_{10} (Fig. 8b). During Episode C (Fig. 8c), both anthropogenic aerosols with small diameters and DR values and dust particles with large diameters and DR values shown to be present in a large volume, indicating they were mixing together during this period. The mass fraction of calcium ions was only 3% in $\text{PM}_{2.5}$ and 11% in PM_{10} , indicating that the mineral dust decreased significantly compared to Episode B, because of deposition and diffusion of dust particles and formation of secondary inorganic aerosols during the transportation. From Episode B to Episode C, the fine mode calcium fraction decreased, from 40% to 3%, more rapidly than for the coarse mode (from 40% to 11%), because of more anthropogenic secondary inorganic aerosols formation in fine mode than in coarse mode. As the dust of Fukuoka on March 30 was transported from Episode B of the Beijing region, by comparison of Fig. 8b and 8d, it is clearly seen that there were more fine mode

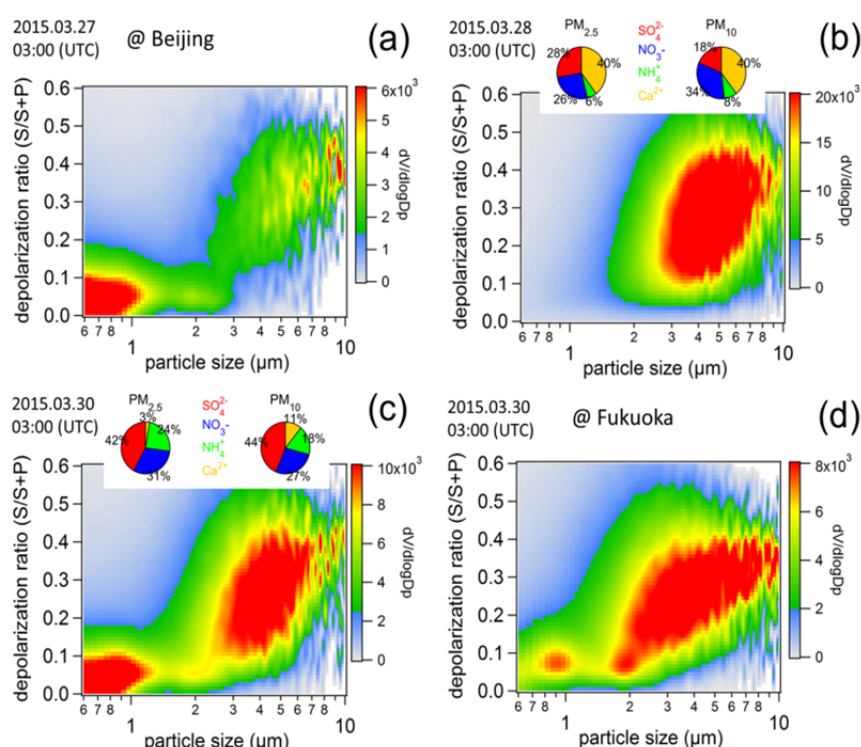


Fig.8 Volume concentrations as a function of particle size and DR during (a) anthropogenic pollution, (b) mineral dust, (c) mixed dust episode in Beijing, and (d) mixed dust episode in Fukuoka. The red, blue, green, and yellow colors in the pie charts indicate the mass fraction of sulfate, nitrate, ammonium and calcium ions in PM_{2.5} and PM₁₀.

particles, and DR became smaller in Fukuoka than in Beijing, which indicated that the dust particles were mixed with anthropogenic aerosols during the transportation.

Figure 9 shows the observed and simulated fine and coarse mode aerosol chemical composition in Beijing. The simulated fine mode concentrations of ammonium, nitrate and sulfate, with maximum values of 27 μg/m³, 61 μg/m³ and 44 μg/m³, respectively, were in good agreement with the observed fine mode concentrations. The simulated fine mode concentrations of ammonium, nitrate and sulfate were mainly due to anthropogenic pollutants, with no dust ammonium and less than 5 μg/m³ of dust nitrate and sulfate. The simulated coarse mode concentrations of calcium, nitrate and sulfate had maximum values of 9 μg/m³, 19 μg/m³ and 7 μg/m³, respectively, and were products of heterogeneous reactions on dust; this is also in good agreement with observed coarse mode concentrations. Furthermore, both observation and model results showed that the coarse mode concentrations of nitrate, sulfate and calcium ions were low during the air pollution episode, but high during the mixing dust episode; meanwhile, the coarse mode ammonium concentration was always low. These

results confirmed that heterogeneous reactions were major sources of coarse mode nitrate and sulfate in the presence of dust particles.

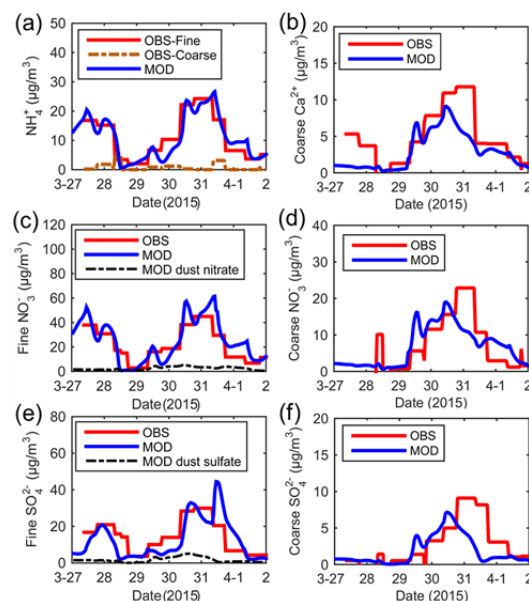


Fig.9 Observed and simulated fine and coarse mode chemical composition in Beijing.

Observed and simulated coarse mode nitrate levels in Fukuoka are also shown in Fig. 10. Observed coarse mode nitrate in Fukuoka was usually less than $1 \mu\text{g}/\text{m}^3$, but increased significantly and reached $4 \mu\text{g}/\text{m}^3$ during the dust period. The model generally captured this variation and showed a similar peak magnitude. The simulated coarse mode nitrate was nearly zero during the non-dust period, because NAQPMS supposed that all the anthropogenic nitrate was in the fine mode.

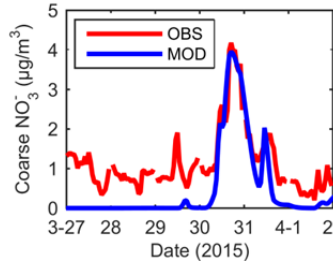


Fig.10 Observed and simulated coarse mode nitrate in Fukuoka.

3.4 Impacts of internal mixing on hygroscopic growth and sphericity of dust particles

Since the heterogeneous reactions had changed the chemical composition of dust particles, the secondary inorganic coatings and their hygroscopic growth significantly changed the mixing state, the size and the sphericity of dust particles. Figure 11 shows the time

series of the volume concentration (a) and volume fraction (b) of dust, secondary inorganic aerosol and aerosol water content, and also (c) the time series of DR. The maximum volume of nitrate and sulfate coatings reached about 10 ppbV and 20% of the dry coated dust particles; meanwhile, the aerosol liquid water reached 10 to 20 ppbV due to hygroscopic growth (Fig. 11a), and made the dust particles become larger by a factor of 2 on March 31 and April 1 (Fig. 11b) when the RH was relatively high ($> 80\%$, Fig. 2e). As a result of internal mixing of nitrate, sulfate and aerosol liquid water, the DR decreased significantly (Fig. 11c), and the dust particles became spherical (DR < 0.1) when the volume fraction of dust coatings reached to 20% (Fig. 11d).

The relationship between aerosol DR and volume percentage of coatings to coated dust particles can be expressed as (Fig. 11d):

$$\text{DR} = 0.12 \times e^{-2.25 \times \frac{V_c}{V_{cd}}} \quad (3)$$

where $V_c (= V_a + V_w)$ is the total volume of coatings, V_a is the volume of secondary aerosol coatings on the dust surface, and V_w is the volume of aerosol liquid water content due to the hygroscopic growth of V_a . $V_{cd} (= V_d + V_c)$ is the volume of coated dust particles. V_d is the volume of dust cores. The volume of aerosol liquid water content V_w was calculated based on Shamjad *et al.* ²⁰):

$$V_w = V_a \left(\frac{\text{RH}}{100 - \text{RH}} \kappa \right) \quad (4)$$

where $\kappa (= \sum V_i \kappa_i / \sum V_i)$ is the hygroscopicity of

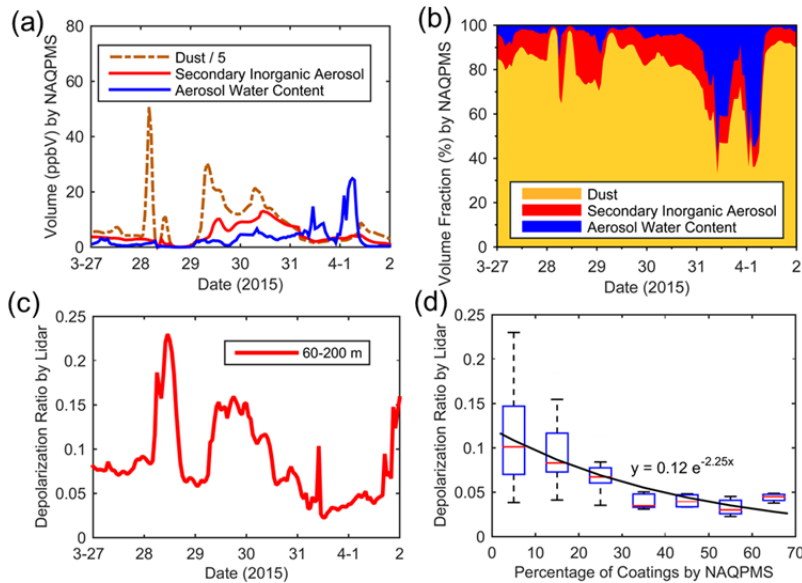


Fig.11 Time series of (a) volume concentration and (b) volume fraction of Nested Air Quality Prediction Modeling System (NAQPMS) simulated dust, secondary inorganic aerosol and aerosol water content; (c) time series of Lidar-observed DR averaged between 60 m and 200 m and (d) relationship of Lidar-observed DR and NAQPMS-simulated volume percentage of coatings.

coatings on the dust particles, and V_i and κ_i are the volume concentration and hygroscopicity of each individual species coating on the dust particle surface.

Based on formulas (3) and (4), the relationship between DR with RH and the volume concentration of the dust core and coatings can be expressed as:

$$DR = 0.12 \times \exp \left\{ -2.25 \times \left(1 - \frac{V_d}{V_a \left(1 + \frac{RH}{100 - RH} \kappa \right) + V_d} \right) \right\} \quad (5)$$

From formula (5), we can clearly see that, when V_a and/or RH become larger, the DR will become smaller. It is indicated that for specific dust particles, the more secondary inorganic coatings it has, the more spherical it will likely tend to be; meanwhile, the higher ambient air RH is, the more spherical dust particles tend to be. Good agreement shown in Fig. 11(d) confirms that the NAQPMS heterogeneous reaction and its hygroscopic growth processes well explain the Lidar observation results.

4. Summary

We investigated the impacts of heterogeneous reactions on the chemico-physical properties of dust particles during severe dust events over East Asia in 2015, based on observation and model results. We found the following: (1) heterogeneous reactions were major mechanism for coarse mode nitrate and sulfate in the presence of dust particles in East Asia, and the concentration of coarse mode nitrate was increased to about $20 \mu\text{g}/\text{m}^3$ in Beijing and $4 \mu\text{g}/\text{m}^3$ in Fukuoka. As a result of internal mixing of nitrate, sulfate and aerosol liquid water, (2) the volume of dust particles grew significantly, and even doubled when the RH was relatively high ($> 80\%$), and (3) the DR decreased with the increasing of coatings, and the dust particles became spherical when the volume fraction of dust coatings reached 20%.

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