Synergistic effect of water-soluble species and relative humidity on morphological changes of aerosol particles in Beijing mega-city during severe pollution episodes

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Abstract. Depolarization ratio (δ) of backscattered light from aerosol particle is an applicable parameter for real-time distinguishing spherical and non-spherical particles, which has been widely adopted by ground-based Lidar observation and satellite remote sensing. From November 2016 to February of 2017, it consecutively suffered from numbers of severe air pollution at Beijing with daily averaged mass concentration of PM$_{2.5}$ (aerodynamic diameter less than 2.5µm) larger than 150 µg/m$^3$. We preformed concurrent measurements of water-soluble chemical species and depolarization properties of aerosol particles on the basis of a continuous dichotomous Aerosol Chemical Speciation Analyzer (ACSA-14) and a bench-top optical particle counter with a polarization detection module (POPC). We found that δ value of ambient particles generally decrease as mass concentration of PM$_{2.5}$ increased at unfavorable meteorological condition. Ratio of mass concentration of nitrate (NO$_3^-$) to that of sulfate (SO$_4^{2-}$) in PM$_{2.5}$ was 1.5 ± 0.6, indicating of great importance of NO$_3^-$ in the formation of heavy pollution. Mass concentration of NO$_3^-$ in PM$_{2.5}$ (NO3) was generally an order of magnitude higher than that in coarse mode.
In (cNO3) with a mean fNO3/cNO3 ratio of 14 ±10. Relatively high allocation (fNO3/cNO3 = 5) of NO3⁻ in coarse mode could be partially attributed to hygroscopic growth/coagulation of nitrate-rich fine mode particles under higher relative humidity condition. As a result, δ values of particles with Dp = 2 μm (δDp=2) and 5 μm (δDp=5) decreased evidently as the mass fraction of water-soluble species (NO3⁻ and SO4²⁻) increase in both PM_{2.5} and PM_{2.5-10} respectively. In particular, due to synergistic effect of RH, δDp=5 value could decrease by 50% as mass fraction of NO3⁻ in PM_{2.5-10} increased from 8% to 23%. It suggested that alteration of non-sphericity of mineral dust particles was evident owing to coating with pollutants and heterogeneous reactions on the surface of the particle during heavy pollution period. This study brings the attention to great variability of morphological changes of aerosol particles along the transport, which have great complex effects in evaluating their climate and health effect.

1 Introduction

Tropospheric aerosols, in particular the particles with aerodynamic diameter less than 2.5 μm (PM_{2.5}), have detrimental impact on human health. It degrades the air quality by increasing atmospheric turbidity, and affects regional/global climate by disturbing the solar radiation transfer in the Earth system via scattering/absorbing light directly and altering amount and lifespan of cloud (Ramanathan et al., 2001; Kaufman et al., 2002). In the past decades, intensive anthropogenic/industrial activities in East Asia emit huge amount of primary pollutants such as SO2, NOx, NH3, VOCs etc., which resulted in severe air pollution. PM_{2.5} was mainly composed of light-scattering species (sulfate, nitrate, ammonium, organics etc.) and light-absorbing matter (BC, BrC etc.). Under high relative humidity condition, most of aerosol particles absorb water vapor and undergo apparently hygroscopic growth, which lead to dramatic changes in its mass concentration, size distribution, optical properties (single scattering albedo etc.), as well as its corresponding morphologies. For example, freshly emitted rBC particles were normally in a chain-like aggregates with visible carbon monomers, and they are sometimes fully coated or partially coated by organics/inorganic matters. Due to atmospheric aging processes in polluted areas at high relative humidity rBC core tend to shrink to a compact one with apparent non-refractory coatings, and its light-absorbing capacity for thickly coated rBC also increased by a factor of 2.

Mineral aerosol is also one of the key compounds in East Asia, it was frequently reported to be coated by anthropogenic pollutants along its transport owing to heterogeneous reactions with reactive acidic gas and coagulation of soluble particles. In polluted area, photo-chemically formatted nitric acid (HNO₃) could easily react with CaCO₃ to form Ca(NO₃)₂ on the surface of dust particles. The consecutive water-absorbing process will also lead to apparent morphological changes of dust particles, which also impact on dust-cloud interaction (Tian et al., 2018) and new particle formation etc. Till now, online investigation on the morphological changes of aerosol particle in the ambient environment is still limit. The widely-adopted method to study the morphology and mixing state of particles is filter-based single particle sampling with electron-microscopy inspection in laboratory. For example, scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDX) could provide information about surface topography, composition of the sample surface by scanning it with a high-energy beam of electrons. Li et al., (2009) using Transmission electron microscopy (TEM) found that approximate
90% of sampled mineral particles were covered by visible nitrate coatings during pollution episode in Central East China. As a matter of fact, such hygroscopic coating on some individual dust particles was observed not only in polluted area but also at clean marine area. The observation on R/V during ACE-Asia found that dust particles mixed with chloride was sometimes dominant over sulphate and nitrate due to disassociation of acidified sea salt particles (Sullivan et al., 2007). Tobo et al., (2010) found that Asian dust particles could also be deliquescent to aqueous droplet as a result of formation of CaCl₂. Dust particle could also acquire sulphate coatings via either heterogeneous uptake of gaseous SO₂ and subsequent oxidation or coagulation within cloud or fog droplets (Kojima et al., 2006), as well as volatile carbonaceous species due to condensation processes (Kim and Park, 2012). Although diversity in chemical composition and structure of single particles with different degree of aging were investigated in the past studies (literatures), these analyses had to be inspected objectives one by ones, and such labor intensive operation cause difficult in broadening the results due to poor statistics (Li et al., 2009).

To obtain better understanding the real-time morphological variation of atmospheric processing particles, polarization property of backscattering light from the illuminated particle has been used as an applicable surrogate. For spherical particle, oscillation direction of magnetic wave of scattering light was identical to the incident light. Therefore, depolarization ratio (DR, here defined as the ratio of s-polarized to p-polarized backward component) was zero theoretically. However, for uncoated dust particles, the direction deviates significantly with a large DR value. Such characteristic is widely used to distinguish dust and spherical particles by both ground-based Lidar observation (Asian Dust and Aerosol Lidar Observation Network, AD-Net) (Müller et al., 2007; Thorsen et al., 2016; Hofer et al., 2017) and satellite on-board remote sensing (Cloud-Aerosol Lidar with Orthogonal Polarization on-board the CALIPSO) (Winker et al., 2010; Yu et al., 2015; Geng et al., 2011) presuming that spherical particles and dust were externally mixed. On the basis of this technique, studies on spatial-resolved distribution (Hara et al., 2008; Uno et al., 2008), transport pattern (Uno et al., 2009) of pollution and dust, and data processing algorithm (Nishizawa et al., 2007; Winker et al., 2009; Nishizawa et al., 2011) have been widely performed. For instance, Shimizu et al. (2004) summarized the contributions of different aerosol types on the total backscattering coefficient at multiple sites in East Asia using three-channel Mie scattering Lidar data. Huang et al. (2015) identified anthropogenic dust particles due to human activities and its contribution to global dust loading on the basis of CALIPSO observation. Recently, a multi-wavelength Mie-Raman Lidar (MMRL) and a new algorithm were developed to estimate extinction coefficients for black carbon, dust, sea salt, and air-pollution aerosols (a mixture of sulfate, nitrate and organic carbon substances) (Hara et al., 2017; Nishizawa et al., 2017).

It was worth noting that atmospheric particles were normally internally mixed. Once the dust particles were coated by other water-soluble pollutants, its polarization degree may decrease. Therefore, it is a challenge to accurately classifying in coated/uncoated dust particles due to its morphological diversity. In particular, Lidar adopted a volume depolarization ratio to discriminate different aerosol types; it was easily biased due to presence of small spherical particles in the volume of targeted air volume. To overcome this shortcoming, recently a bench-top optical particle counter equipped with a depolarization module (Polarization Optical Particle Counter) was developed to detect the size-resolved polarization of individual particles.
POPC is capable of investigating the temporal variation of mixing state of single dust particles. The observation at an urban site in Japan showed that DR of super-micron particles decreased evidently due to an increase of mass fraction of nitrate concentration during a long stagnant dust event (Pan et al., 2015). In Beijing, due to synergistic effect of water soluble substance at the surface of dust and relative humidity, the non-sphericity of dust particles even tent to be sphericalized (Pan et al., 2017; Wang et al., 2017). The long-term observation on such effect was still lacking.

From November 15, 2016 to February 18, 2017, Beijing was consecutively suffered from several severe air pollutions with hourly averaged mass concentration of PM$_{2.5}$ and PM$_{2.5-10}$ larger than 300 µg/m$^3$ and 100 µg/m$^3$. It provided a good chance to investigate into the interaction between dust particles with pollutants. During this period, chemical composition, size distribution, polarization properties of aerosol particles were concurrently measured, as well as vertical profile of backscattering coefficient by Lidar at a downtown tower site of Beijing mega city. The objective of this study was to investigate depolarization properties of aerosol particles in the polluted urban site on the single-particle basis, and to study the impact of both water-soluble species and relative humidity (RH) on the morphological changes of dust particles. This study will provide useful information in better understanding the physical and optical properties of particles in East Asia, and improving numerical simulation on its environment/climate effect.

2 Observations

2.1 Observation overview

The field measurement was performed at a tower campus of Institute of Atmospheric Physics/Chinese Academy of Sciences in the downtown area of Beijing mega city. The observation site located between 3rd North Ring road and 4th North Ring road, where anthropogenic emissions are intensive in the daytime. Within the campus (150 m x 50 m), there is a 325 m tower for meteorological measurement and scientific research; therefore anthropogenic activity nearby is limited. During the observation period, a continuous dichotomous Aerosol Chemical Speciation Analyzer (ACSA-14) was placed on the roof of two-story building in the campus. Polarization Optical Particle Counter was placed in air-conditioned room on the roof to measure polarization properties of single particle less than 10 µm. To avoid loss of particles in coarse mode, the sampled air was drawn into the room by a supporting pump (flow rate: 10 lpm) through 2 m long 1/4-inch vertically assembled stainless steel tube. From November 15 to December 15 2016, a UK-China joint field campaign, entitle as “In-depth study of air pollution sources and processes within Beijing and its surrounding region (APHH-Beijing)” was also performed in the tower campus. Detailed information about the objectives and instruments are shown in webpage (https://www.atmos-chem-phys.net/special_issue932.html).

2.2 Instruments

In this study, mass concentrations of particulate matter and water-soluble chemical compounds in both PM$_{2.5}$ and PM$_{2.5-10}$ were measured by ACSA-14 (KIMOTO electric Co. Ltd, Osaka, Japan) with 1-hour intervals at the observation site. The mass concentration of particulate matter was determined using beta-ray absorption method. Mass concentration of SO$_4^{2-}$ was
determined on the basis of BaSO₄-based turbidimetric method with addition of BaCl₂ dissolved in polyvinylpyrrolidone solution. Mass concentrations of NO₂ and water-soluble organic carbon were determined using ultraviolet absorption-
photometric method. Because mass concentration of NO₂ was general high in Beijing, the instrument generally collected aerosol samples in the first 5–10 minute in each hour and analyzed the samples in the rest time to guarantee follow Beer-
Lambert Law. The acidity of particles [H⁺], in unit of nmol/m³, was semi-quantitatively determined using pH-indicator absorption-photometric method. The basic equation is pH_solution = −log [H⁺ × 10⁻⁶+ 10⁻⁴⁺], presuming that all the water-soluble matter was dissolved in the extract liquid with pH value of 4.6. A factor of 10⁻⁴ was used to convert unit of [H⁺] from nmol/m³ to mol/L. The comparison of [H⁺] in PM₃₅ between ACSA and off-line filter-pack measurement showed a good linear correlation ([H⁺]_{ACSA} = 3.33 + 0.81×[H⁺]_{FP}) with r² = 0.54 (Personal communication with Prof. Osada in Nagoya University).

The details of the ACSA instrument are described in literature (Kimoto et al., 2013).

Depolarization ratio of single particle was determined using a Polarization Optical Particle Counter (POPC). POPC adopted a 780 nm linearly polarized laser beam to illuminate the aerosol particles that passed through measuring chamber vertically. The direction of vibration of the electric field of the incident laser is parallel to the plane of the scattering angle. Detailed information about POPC was described in literatures (Kobayashi et al., 2014; Pan et al., 2016; Pan et al., 2017). Forward scattering signal at 60 degree respect to direction of incident light was measured by a photodiode with acceptance angle 45 degree to determine the size of particle. The backward scattering signal at 120 degree was split into P component (horizontal with respect to the plane of the scattering angle) and S component. The depolarization ratio (DR) of the particles was defined as the ratio of S component to P component (S/P). To avoid the coincidence error of the measurements, the inlet flow rate of POPC was set to 80 ccm and was diluted with zero air (920 ccm, RH = 38 ± 1%). Overall measurement uncertainty in size determination was less than 15%.

During observation period, the vertical structure of backscattering coefficient for aerosols was derived from Mie-scattering Lidar system that installed at the same place of ACSA-14. This Lidar system, developed by the research group in National Institute for Environmental Studies (NIES), employs a flash-lamp-pumped Q-switching Nd:YAG laser as the light source. It emits pulsed lights with wavelength of 1064 nm and 532 nm with at a frequency of 10 Hz, and collects the backscattered light from the atmosphere by a 20 cm Schmidt-Cassegrain telescope. The light at 532-nm wavelength is also further separated into S and P component (Sugimoto et al., 2002). The algorithm for classifying sphere and dust particles was described in literatures (Shimizu et al., 2004; Nishizawa et al., 2011; Shimizu et al., 2017). To be note that, direct comparison of depolarization ratio between POPC and Lidar system is difficult. Firstly, Lidar system receives backscattering light at almost 180 degree with a field of view of 1 mrad; whereas POPC employs 120-degree backscattering signal. Secondly, Lidar system measures the total volume depolarization from a volume of targeted air parcel; whereas depolarization properties from POPC is on a single particles basis.
2.3 Footprint analysis

We simulated footprint region of aerosol particles at the observation site using NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (v4.9; available at http://ready.arl.noaa.gov/HYSPLIT.php). This model has been widely applied into calculating long-range or meso-scales transport and footprint regions of air pollutants with fast computational speed and high spatial resolution. HYPLIT model is capable of forward/backward run in time to simulate the dispersion/potential source of tracers in a given location. Detailed description and validations of this model was seen in literature. In this study, input meteorological data of model is the product (GDAS dataset) of Global Forecast System (GFS) from National Centers for Environmental Prediction (NCEP) with a spatial resolution of 0.5 by 0.5 degree, and a time-resolution of 3 hours (0000, 0600, 1200 and 1800 UTC from data assimilation product; 0300, 0900, 1500 and 2100 UTC from forecast model). By offsetting the release point by a meteorological grid point in the horizontal and 0.01 sigma units in the vertical, ensemble simulation have 27 trajectories were calculated simultaneously in each hour, providing great advantage in evaluate the uncertainty and potential footprint region. In the present study, the grids at which height of backward endpoint of air parcel was less than the height of mixing layer was labeled as potential footprint region.

3 Results and discussions

3.1 Overview in particulate matters and chemical species

3.1.1 Comparison of mass concentration of particulate matters

Figure 2a shows the temporal variations of mass concentrations of ambient PM$_{2.5}$ that were measured by ACSA-14 at the observation site. For comparison, mass concentration of PM$_{2.5}$ observed at a state-controlled monitoring station (Olympic Centre, about 3 km northeast of the LAPC site) was plotted in the figure. In general, two results were in consistent well with $r^2 = 0.8$, indicating that the pollution events were generally in regional scale with minor interference from emission sources nearby. During observation period, number size distribution of ambient particles with optical diameter between 0.3 μm - 10 μm were measured with POPC, and the mass concentration of PM$_{2.5}$ was estimated assuming that all the particles were spherical with a density of 1.77 g/cm$^3$. Mass concentration of PM$_{2.5}$ estimated by POPC was compared well with ACSA-14 measurement before January 7, 2017, when ambient relative humidity (RH) was almost above 40%. Whereas estimated mass concentration of PM$_{2.5}$ was underestimated obviously. One possible explanation is that, both air temperature and ambient RH after January 7, 2017 decreased evidently. The interaction between water-soluble matters in PM$_{2.5}$ and moisture were unlikely occurs, and the hypothesis of spherical shape of particles due to hygroscopic may resulted in relatively larger uncertainty in estimating the optical size of particle on the basis of scattering light. Another possibility is that the chemical composition of particles are different (discussed in section 3.1.2). As shown in Figure 2d, the northerly wind become stronger, which resulted in larger proportion of mineral dust matters, the latter which have larger density (2.2 - 2.8 g/cm$^3$). Deploying the same density for both particle in fine mode and coarse mode will lead to underestimation of total mass. It was pronounced for the case in January 29, 2017 that observation site was subject to floating dust event with a hourly averaged mass concentration of PM$_{10}$.
reached 734 µg/m³. Daily averaged mass concentration of PM_{2.5} measured by ACSA-14 was 354.3 µg/m³, four times higher than the values (77.1 µg/cm³) estimated by POPC. Deployment of a larger particle’s density of 2.8 g/cm³ only explain 35% of the difference. Low detection limit of particle size of POPC was 0.5 µm, and miscounting of particles less than 0.5 µm was estimated to contribute another 10% of the difference. The most possible reason is that the irregularity of particles in fine mode resulted in significant underestimating in particle diameter on the basis of scattering signal. However, the estimation of spherical particles diameter by POPC bears smaller bias theoretically. For example, during a typical anthropogenic pollutant dominant case on January 1, 2017, mass concentrations of PM_{2.5} and PM_{10} was as high as 438.8 and 626.2 µg/m³, respectively. Hourly averaged mass concentration of PM_{2.5} estimated by POPC correlated well with ACSA-14 measurement with a ratio of 1.1 ± 0.1. It was noticeable that PM_{2.5} accounted for 80% of PM_{10}, and ambient relative humidity was 65%. It was implied that anthropogenic water-soluble compounds in PM_{2.5} underwent hygroscopic processes that may alter asphericity of the particles (detail discussion in section 3.5).

Regarding the particles in coarse mode, mass concentration estimated by POPC is much better than that in fine mode. It was because, firstly, the detection efficiency of POPC for the particles in coarse mode was better than that in fine mode, and miscounting of particles in coarse mode by POPC was less likely to occur; secondly, interference of asphericity of particles in coarse mode was insignificant in determining size of particle according to scattering signal. Besides, change in the refractive index of particles due to mixing of mineral dust particles with anthropogenic pollutants (such as black carbon) also have limited impact in size determination. In general, daily averaged mass fraction of PM_{2.5-10} in PM_{10} (PM_{2.5-10}/PM_{10}) was ranging 0.25 ~ 0.7 (Supplementary Figure). The minimum value occurred in severe pollution days when daily averaged mass concentration of PM_{2.5} was larger than 250 µg/cm³ (Air Quality Level: VI), whereas PM_{2.5-10}/PM_{10} ratio increased as mass concentration of PM_{2.5} decrease. It was because formation of secondary particulate matters (such as sulfate and nitrate) during pollution episode was so overwhelming that make the contribution of mineral dust decrease, although mass concentration of PM_{2.5} increased. Number of studies have addressed the importance of mineral dust in promoting new particle formation (Nie et al., 2012) and conversion of SO_2 to sulfate (He et al., 2012), both of which was related to formation of OH radical. However, this study was performed in winter, role of mineral dust in the formation of regional pollution is out of scope of this study.

3.1.2 Chemical compounds in fine and coarse mode

In winter, nitrate, sulfate and water-soluble organic carbon (WSOC) were found in both fine mode and coarse mode (Figure 3). Mass concentration of nitrate in the fine (fNO_3) was 28.3 ± 33.7 µg/m³ averagely with a maximum value of 190.9 µg/m³. Mass concentration of nitrate in the coarse mode (cNO_3) was 2.9 ± 4.8 µg/m³. The maximum value of cNO_3 (43.1 µg/m³) occurred at the different time from that for fNO_3, implying of complicated mass equilibrium of nitrate among different size range. Table 1 summarizes the fNO_3/cNO_3 ratio as a function of mass concentration of PM_{2.5} at RH > 40% and RH < 40%.

We found that, when ambient RH was less than 40%, fNO_3/cNO_3 ratio has a positive correlation with mass concentration of PM_{2.5}, which demonstrated that nitrate mass preferentially formed in fine mode and mass transfer of nitrate toward coarse
mode was unlikely happen due to weak hygroscopicity of particles; However, when ambient RH was larger than 40%, fNO3/cNO3 ratio did not increase with PM$_{2.5}$ concentration with a mean of 12.4 ± 6.5. The possible explanations were, first, once the aerosol phase nitrate formed in the fine mode, it absorbed water vapor simultaneously and grew larger; second, ambient nitric acid may directly stick on the surface of particles in coarse mode through heterogeneous processes; Although high concentration of PM$_{2.5}$ in Beijing was regard as synergistic contributions from both local formation and long-range transport, it did not influence the fNO3/cNO3 ratio, at least in the present study.

Mass concentration of sulfate in the fine mode (fSO4) and in the coarse mode (cSO4) were 18.9 ± 24.8 µg/m$^3$ and 2.2 ± 2.5 µg/m$^3$ with maximum values of 143.1 µg/m$^3$ and 25.2 µg/m$^3$, respectively. As shown in Figure 3b, the variabilities of fSO4 and cSO4 concentrations have the same trend. fSO4/cSO4 ratio increased with mass concentration of PM$_{2.5}$, irrespective of ambient RH, because sulfate in the fine mode mainly formed via homogeneous reaction between sulfuric acid with ammonia.

The positive correlation between fSO4/cSO4 ratio and RH indicated that water vapor also took effect in the formation of sulfate. It was worthy to note that, fNO3/fSO4 ratio varied among cases due to different air mass origin and meteorology condition. For instance, on Dec 21, 2016 (blue shaded strip in Figure 3), mass concentration of fNO3 and fSO4 were 122.4 µg/m$^3$ and 74.1 µg/m$^3$, with a fNO3/fSO4 ratio of 1.6; however, on Jan 1, 2017 (red shaded strip in Figure 3), mass concentration of fSO4 increased to 125.2 µg/m$^3$ and fNO3 decrease to 99.2 µg/m$^3$ with a fNO3/fSO4 ratio of 0.79. Backward trajectory analysis for the case on Jan 1, 2017 showed that the air mass was mainly transport from North China Plain along Taihang Mountain, coal burning in NCP in winter may contribute to the sharp increase of fSO4; however, for the case on Dec 21, 2016, the air mass was mostly stagnant near Beijing area, and the intensive emission of NOx resulted in the large difference between fNO3 and fSO4. The variability of WSOC in both fine mode (fWSOC) and coarse mode (cWSOC) were consistent with fSO4 with maximum values of 167.6 µg/m$^3$ and 8.7 µg/m$^3$ (Figure 3c).

Mass fraction of total water soluble matters (WSM) in PM$_{2.5}$ and acidity of the particle are shown in Figure 3d. Here, WSM includes only SO$_4^{2-}$, NO$_3^-$, WSOC, and NH$_4^+$, the latter of which was estimated on the basis of equation ([NH$_4^+$] = 18×([SO$_4^{2-}$]/96×2 + [NO$_3^-$]/62×2 – [H$^+$]/1000). In general, mass fraction of WSM in PM$_{2.5}$ during pollution period was higher than that during clean period. On average, WSM/PM$_{2.5}$ was 0.5 ± 0.16. We found that, WSM/PM$_{2.5}$ was more likely related to origin and residence time of air mass that the ambient loading of PM$_{2.5}$ concentration. For example, daily averaged mass concentration of PM$_{2.5}$ reached the maximum (447.5 µg/m$^3$) on Jan 1, 2017; whereas maximum value of WSM/PM$_{2.5}$ (0.80) occurred on Jan 7, 2017 when the pollution period almost ended. On Jan 1, 2017 observation site was prevailing southwesterly wind which introduced pollutants from NCP where industrial emission was intensive; However, air mass was mostly from east region on Jan 7, 2017, and high concentration of cNO3 (Figure 3a) and high RH (Figure 2d) indicated that heterogeneous processes played a key role. Molte concentration of [H$^+$] in fine mode (H$^+$) correlate well with mass concentration of fSO4 (Figure 3d), implying of possibility of presence of surplus of sulfuric acid that converted from SO$_2$ that emitted from coal burning during heating period.
Table 1 The relationship between fNO3/cNO3, fSO4/cSO4 and mass concentration of PM2.5 at different RH condition.

<table>
<thead>
<tr>
<th>RH Classification</th>
<th>PM2.5 Classification</th>
<th>PM2.5 (µg/m³)</th>
<th>fNO3/cNO3</th>
<th>fSO4/cSO4</th>
<th>RH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;25</td>
<td>Avg.</td>
<td>16.3</td>
<td>6.3</td>
<td>12.5</td>
<td>6.8</td>
</tr>
<tr>
<td>25-50</td>
<td>Avg.</td>
<td>37.5</td>
<td>7.2</td>
<td>15.1</td>
<td>7.2</td>
</tr>
<tr>
<td>50-75</td>
<td>Avg.</td>
<td>59.9</td>
<td>7.8</td>
<td>17.5</td>
<td>8.5</td>
</tr>
<tr>
<td>&gt;75</td>
<td>Avg.</td>
<td>98.2</td>
<td>23.4</td>
<td>26.2</td>
<td>12.1</td>
</tr>
</tbody>
</table>

3.2 Volume size distribution and depolarization ratio (δ)

Volume size distribution of aerosols and averaged depolarization ratio (δ) during observation period are shown in Figure 4. In general, evolution of all the pollution cases were well captured by POPC. Volume size distribution of aerosols showed a pronounced peak at 1 µm, at which secondary anthropogenic pollutants were dominant. Correspondingly, δ value of particles were normally less than 0.1, consistent with the previous study in East Asia (Pan et al., 2016). On Nov 19, 2016, two peaks were observed at size range of 1 µm and 2–3 µm. δ value of particles at two size were as low as 0.1. Such pattern of volume size distribution has been described in previous study (Pan et al., 2015, 2016), which classified such phenomena as a mixing pollution type that both anthropogenic pollutants and mineral dust particles interacted. Five-day trajectory analysis indicated that air mass mainly originated from Mongolia Plateau and they were stagnant over East China for days (supplementary figure). Volume peak at size of 4–5 µm was not observed probably due to fast gravity settling of large particles in coarse mode during their stagnancy. On Nov 26, 2016, the observation site was influenced by floating dust, and volume size distribution had a pronounced peak at 4–5 µm, as expected. δ value of submicron particles also increased to 0.3, implying of the substantial presence of irregular mineral particles in the fine mode. From Dec 30, 2016 to Jan 8, 2017, it had a long-lasting pollution period in Beijing. Volume size distribution of aerosols varied due to impacts from both change in Planet Boundary Layer height and origin of aerosols. Multi-peak fitting analysis indicated that volume size distribution had two peaks with a dominant peak at size of 0.9 µm and another peak at size of 2 µm. Different from case on Nov 19, 2016, the δ values of particles were 0.2–0.4, though ambient RH was the same (> 60%). It implied that chemo-physical properties of the particles were different, probably due to impact by mineral dust. Detailed discussion was in section 3.3.2.

3.3 Variability of δ value for particles of different size

3.3.1 δ value for particles in fine mode

As pointed out in previous study, δ value generally depends on the size of particle (SF2). Histogram analysis on the particles at size of 1 µm showed that there was one peak mode at a δ_{Dp=1} value of 0.11; For the particles at size of 2 µm, a multi-
Gaussian fitting for frequency distribution of δDp=2 value showed there were one dominant peak at a value of 0.17 and a shoulder value of 0.23, the latter of which was mostly related to the impact of dust event. We found that variability of δDp=2 value of particles in fine mode was a synergistic effect of both water-soluble inorganic matter (WSI) and RH. For example, in Figure 5, δDp=2 value of particles decreased gradually from 0.3 to 0.1 as mass fraction of WSI in PM2.5 increase from 0.2 to 0.65, and RH increased from 38% to 85%. It notes that, δDp=2 value decreased only when RH > 60% and mass fraction of WSI > 0.6. Mass fractions of both fSO4 and fNO3 in PM2.5 showed a negative correlation with δDp=2 value with a slope of −0.3 and -0.1, respectively. We speculated that fNO3 might play a key role in decreasing of δDp=2 value of particles in the fine mode because fNO3 was accounting for ~50% of total WSI and deliquescent point of ammonium nitrate was ~60%, and the impact of ammonium sulfate was less important since it started to undergo hygroscopic growth only at higher RH (79%). Quantitatively distinguishing respective contribution of fNO3 and fSO4 on the decrease of δ value of particles was difficult in the present study.

3.3.2 δ value of mineral dust aerosols

For the particles at size of 5 μm, histogram analysis of δDp=5 value had a wide range 0.3 - 0.55. Laboratory experiments on typical spherical particles at a size of 5.124 μm (SS-053-P) showed that their δDp=5 value was 0.07 ± 0.01. The larger δDp=5 value (> 0.3) of mineral dust particle in the ambient air indicated that they were aspherical in shape. Figure 6 showed time variation of vertical profile of extinction coefficient of dust particles derived from ground-based Lidar observation. We can see that there was a typical dust event on Dec 26, 2016 with a PM2.5/PM10 ratio of 68%, and extinction coefficient of dust particles at site was larger than 0.3 Km⁻¹. δDp=5 value of dust particle was varying around 0.5, and no decrease of δ value of dust particles was observed due to low cNO3 concentration and low RH (Figure 6). Another dust impact case was from Jan 1, 2017 to Jan 7, 2017, we found that δDp=5 value of dust particles were apparently low with a mean value of 0.35. In particular, during the period that mass concentration of cNO3 increased up to 10 μg/m³ and ambient RH was ranging above 60%, hourly averaged δDp=5 value of dust particles decreased to 0.2, implying that cNO3 on the surface of dust particle may form as Ca(NO3)₂ owing to heterogeneous processes, and consecutive hygroscopic growth resulted in the decrease of its δDp=5 value. Compared with the case on Dec 26, 2016, impact of this dust event was relative weak with a PM2.5/PM10 ratio of 27%. It was worth noting that all the mineral dust impacting cases were captured by both Lidar and POPC observations, nevertheless, the mixing state of mineral dust particles could be illustrated better with POPC measurement according to their δDp=5 variations.

Once the morphology of mineral dust particles was modified due to cNO3 coating at high RH condition, Lidar observation may underestimate the impact of dust due to decrease of δDp=5 value of particles. Such phenomena maybe more likely to happen at the downstream of polluted area. For instance, dust particles were found to be spherical due to interaction with HCl and HNO3 at marine area (Tobo et al., 2012). Observations using POPC at Kyushu area of Japan also indicated that there was a large amount of larger particles with a δDp=5 value between 0.05 ~ 0.15 when air mass came from NCP of China, implying that the morphology of dust particles were altering with transport (Pan et al., 2015, 2016).
3.4 Footprint analysis of mineral dust particles

As discussed above, the decrease of δDp=5 value of mineral dust particles were influenced by both mass concentration of cNO3 and ambient RH. We choose two mineral dust-influencing episodes to demonstrate the impact (Figure 7). Here, footprint region of the air mass was calculated for the period that hourly averaged mass concentration of cNO3 was higher than 5 μg/m³. For the episode between Nov 24 and Dec 7 2016, the footprint region of air mass covered west of Inner Mongolia province and South of Hebei province. The particles in coarse mode seemed to mostly related with anthropogenic dust (defined as dust aerosols due to human activity, such as agriculture, industrial activity, transportation etc.) in NCP where NOx emission and atmospheric nitrate loading were also high. Averaged RH was relatively low with a mean value of 30% (Figure 7c). However, for the episode between Jan 1 and Jan 8, 2017, averaged RH within the footprint region around NCP was as high as 60% (Figure 7d), although mineral dust particle had similar origins. Adsorption of water vapour and consecutive heterogeneous reaction lead to obvious decrease of δDp=5 value of mineral dust particles. It indicated that a synergetic effect of both nitrate in coarse mode and high RH condition lead to morphological changes in dust shape. The variability of morphological changes was simulated on the basis of T-matrix methodology and randomly oriented elongated ellipsoid particles. We found that observed maximal δDp=5 value (0.5) of dust particle corresponded to an aspect ratio (defined as ratio of the longest dimension to its orthogonal width) of 1.7. When δ value of mineral dust particles decrease to 0.2, the aspect ratio was estimated to be 1.5, not being “spherical”. Therefore, we considered such dust particles as being ‘quasi-spherical’. Huang et al., (2015) pointed out that layer-integrated δ value of anthropogenic dust particles in the PBL of NCP was lower than that of Taklimakan dust on the basis of CALIPSO Lidar measurement, mostly due to mixed with other more spherical aerosol within the PBL. Because Lidar observation just provide a averaged δ value of all the particle in the detecting volume, external mixing of dust particle with substantial amount of secondary anthropogenic particles in spherical shape could also result in a low δ value. From view point of this study, irregularity of anthropogenic dust particles in NCP were possibly the same as the nature dust in the source region, however, their interaction in particular at high RH condition will obviously lead to decrease in δ value.

3.5 Impact of heterogeneous reaction on δ value of particles

As shown in Figure 8, δ value of particles decrease obviously with increase of mass fraction of water soluble Matters (WSM), in particular at high RH condition. For the particles at Dp = 2 μm, their δDp=2 value was normally 0.3 when mass fraction of WSM in PM2.5 was less than 0.2, whereas it decreased to 0.1 when the mass fraction of WSM increased to 0.6, and RH also increased to 80% (Figure 8a). The linear relation was because the growth of particles in fine mode was closely related to formation of secondary inorganic matters (sulfate, nitrate, etc.) and organic aerosols. Throughout the atmospheric chemistry processes, the positive feedback between aerosol and water vapor was ubiquitous. For example, hygroscopic processes of
anthropogenic secondary inorganic resulted in abundance of aerosol liquid water content, and the latter of which could provide an efficient media of multiphase reaction which promote new particle formation, and so on. Therefore, the particles in PM$_{2.5}$ generally approach to spherical in shape, resulted in a low $\delta_{Dp=2}$ value, and the high RH and the high possibility that spherical particles formed. The morphological changes of particles in PM$_{2.5}$ could be well simulated on the basis of T-matrix method (Pan et al., 2017).

For mineral dust particles, As discussed, the $\delta_{Dp=5}$ value (0.3~0.5) was clearly higher than that of particle in fine mode because of this high irregularity (Figure 8b). Since the mass concentration of cSO$_4$ and cNH$_4$ were insignificant in coarse mode, the $\delta_{Dp=5}$ value was plotted versus mass fraction of cNO$_3$ in PM$_{2.5:10}$. Decrease of $\delta$ value of dust particles as a function of mass fraction of cNO$_3$ in PM$_{2.5:10}$ was also obvious, especially when RH was higher than 60%. Numbers of studies have reported emission of anthropogenic dust in NCP was significant, and Calcium was the most abundant crustal element in NCP. We believed that that Ca(NO$_3$)$_2$ present on the surface of mineral dust particles, and the decrease of $\delta_{Dp=5}$ value of particle in coarse mode was mostly due to heterogeneous reactions and consecutive water-absorbing processes. Such kind of mineral dust particles coated with anthropogenic pollutants have been observed by numbers of previous electro-microscopic studies (literatures). Previous studies also demonstrated the presence of cSO$_4$ on the surface of dust particles, nevertheless, we think the effect of cSO$_4$ on the decrease of $\delta_{Dp=5}$ value was negligible because the mass fraction of cSO$_4$ was tiny (<0.02) and the CaSO$_4$ was hard to dissolve in limited amount of aerosol liquid water content. To note that, the chemical compounds (such as kaolinite, illite, humic matters, etc.) of particles in coarse mode was very complicated, $\delta_{Dp=5}$ value just indicate a synthetically effect of morphological changes as a result of all physical and chemical processes. To quantitatively characterize their optical and environmental effect, detailed studies on $\delta_{Dp=5}$ value variability of one-fold compound in the laboratory was still essentially need.

4 Conclusions and implications

Depolarization properties of aerosol particles is an important parameter classifying the aerosol types and describing the variability of morphology of particles, which was related to complicated mixing processes and heterogeneous reactions. It also has great impact on its transport and regional/global climate due to alteration of optical properties of particles. In 2017, a field joint campaign (In-depth study of air pollution sources and processes within Beijing and its surrounding region, APHH-Beijing) was performed at an urban site in Beijing mega city. One of key aims of the project is to assess the processes by which pollutants are transformed through atmospheric chemical reactions. Taking this opportunity, we performed an online observation on the depolarization ratio of single particles using a Polarization Optical Particle Counter. The chemical compositions (SO$_4^{2-}$, NO$_3^-$, WSOC) and acidity of particles in both fine mode (PM$_{2.5}$) and coarse mode (PM$_{2.5:10}$) was determined using a continuous dichotomous Aerosol Chemical Speciation Analyzer (ACSA-14). The main conclusions are as follows: (1) Depolarization ratio ($\delta$) of ambient particles generally increase with its size due to increase in irregularity of the particles, and the characteristic values of $\delta$ for the particles at Dp = 1 $\mu$m and 2 $\mu$m were 0.11, 017, respectively. Once the
observation site was influenced by dust event, both of δ values increased to above 0.3 due to presence of submicron mineral dust particle in irregular shape. The δ value of the particles at Dp = 2 µm was mainly determined by the mass fraction of water-soluble inorganic matter in PM$_{2.5}$, in which water vapor was fully involved in their atmospheric formation processes. (2) In NCP, anthropogenic dust was an important contributor to the atmospheric loading of particles, their δ values (0.2-0.3) were found to be smaller than that (0.5) of nature dust because of adsorption of acidic substance (such as HNO$_3$) and coagulation with water-soluble anthropogenic pollutants (nitrate, sulfate) and consecutive chemical reactions on the surface of dust. Ambient relative humidity plays a key role in altering the morphology of mineral dust as a result of hygroscopic processes of deliquescent substances such as Ca(NO$_3$)$_2$, in particular when RH > 80%. In this study, we found that δ values of mineral dust particle in NCP could be as smaller as 0.2, which could be termed as “quasi-spherical”. (3) We found that allocation of anthropogenic pollutants in fine and coarse mode was influenced by the RH along the trajectories of air mass, and increase of nitrate mass in coarse mode was highly associated with the dust event. It indicated that the mineral dust particles in NCP was mostly coated with anthropogenic pollution, upon which classification and quantitative determination of anthropogenic dust emission was possible, though a pioneering study have been done on the basis of satellite remote sensing and land type (Huang et al., 2015).

In this study, we provided solid evidences in morphological changes of mineral dust particles in NCP. Variability of δ value of particles is also a valuable parameter in distinguishing how mineral dust particle interacted with anthropogenic pollutants in formation of regional-scale haze pollutants. This result also spurs us to revisit decades of Lidar observation data in better describing the transport and vertical distribution of Asian dust and pollution, and its regional environmental effects under the scenarios of China thirty years’ rapid urbanizations. A reliable optical model capable of discriminating multiple aerosol types was necessary for detailed analysis of polarization-related remote sensing observations. This study suggested that an integrated observation network with single-particle-based depolarization measurement was necessary for synthetically understanding chemo-physical properties of Asian dust issue.

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**References**


Figures

Figure 1. Geographic location of observation site and NOx emission in East Asia (a), the transportation map of Beijing mega city and location of tower campus of IAP.
Figure 2. Temporal variation of mass concentration of PM$_{2.5}$ (a), PM$_{2.5-10}$ (b), PM$_{10}$ (c) measured by ACSA14 and derived from POPC measurement, wind speed and direction (d) and relative humidity (e) at observation site. The three scatter plots in the right indicate the linear relationship between ACSA14 and POPC, the correlations are $Y_{POPC} = -6.8 + 0.89X_{ACSA14}$ ($r^2 = 0.86$), $Y_{POPC} = -19.5 + 0.84X_{ACSA14}$ ($r^2 = 0.77$), $Y_{POPC} = -27.7 + 0.87X_{ACSA14}$ ($r^2 = 0.81$) for PM$_{2.5}$, PM$_{2.5-10}$ and PM$_{10}$ respectively.
Figure 3 Temporal variations of mass concentrations of nitrate (a), sulfate (b) and water-soluble organic matters (c) in fine mode and coarse mode, and acidity of particle ($\text{H}^+$) in the fine mode (d).
Figure 4 Volume concentrations of particles and corresponding depolarization ratio as a function of time during observation period. For better view the performance of the instrument, the observation results are shown in three-time slots.
Figure 5 Temporal variabilities of δ value for particles at size of 1 µm and 2 µm (a) and mass fraction of water-soluble inorganic matter (WSI, Blue: nitrate; Red: sulphate; Green: ammonium) in PM$_{2.5}$, ambient RH (b).
Figure 6 Vertical profile of extinction coefficient of dust particles derived from Lidar observation (a) and variability of $\delta$ value of mineral dust particles and NO$_3^-$ in coarse mode aerosols (b) as a function of time. Here we choose the particles at a size of 5 $\mu$m to indicate the mineral dust particles, marked as $\delta_{Dp=5}$ correspondingly.
Figure 7 Footprint regions of mineral dust particles for the periods when averaged mass concentration of cNO3 was higher than 5 µg/m³, while δDp values were higher than 0.4 (a) and lower than 0.2 (b), and corresponding mean RH (c) and (d) in each grid within the footprint area on the basis of ensemble Hysplit analysis. Footprint height was defined as a height that endpoint of backward trajectory was lower than the height of mixing layer in that grid.
The variation of $\delta_{Dp=2}$ as a function of mass fraction of WSM in PM$_{2.5}$ (a), and $\delta_{Dp=5}$ as a function of mass fraction of cNO$_3$ in PM$_{2.5-10}$. The color represents the hourly averaged relative humidity during measurement.