

Letter

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Abstract

Particle phase state is key factor for determining gas-particle partitioning, particle reactive gas uptake, and multiphase chemical reactions, with associated links to secondary aerosol formation. In the present study, particle phase state was investigated by measuring particle rebound fraction f in the highly polluted atmosphere of Beijing, China. The particle phase state was sensitive to ambient relative humidity (RH). The particles changed from rebounding to adhering when RH increased above 60%, suggesting a transition from

semi-solid to liquid state. This transition RH was below the deliquescence RH of both (NH₄)₂SO₄ and NH₄NO₃. Sub-micrometer particles were in the liquid state during heavy haze episodes. This might be because the elevated RH and inorganic fraction in particles resulted in the enrichment of aerosol liquid water content. The transition to a liquid phase state, marking the beginning of the haze episode, might kick off a positive feedback loop. The liquid particles might readily uptake pollutants that then react to form inorganics, thereby further increasing water uptake. We propose that the liquid phase state facilitates the mass transfer and multiphase reactions of the particles, thereby accelerating secondary particle growth in haze over the North China Plain.

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1 Introduction

Aerosol particles are ubiquitous in the atmosphere and play a profound role in human health, air quality, atmospheric chemistry, and global climate¹⁻². They are suspended reaction vessels in which chemical and physical processes can occur. The chemical and physical processes, such as the gas-particle partitioning² and heterogeneous and liquid phase reactions³⁻⁴, are significantly influenced by the particle phase state. Phase state refers to liquid, semi-solid, or solid, and it can change with relative humidity (RH)⁵. The characteristic time of mass transport of gases and bulk phase diffusion in liquid, semisolid, and solid particles can vary from seconds to years³. Considering the lifetime of atmospheric aerosols, the interaction between gases and particles may be confined to the surface region for particles in the solid and semi-solid phase, yet may occur in the bulk for particles in the liquid phase⁶⁻⁷.

In boreal forests, biogenic secondary organic aerosol (SOA) particles can adopt a solid and semi-solid state⁸. Measurements conducted in the Amazon forest, by comparison, showed that sub-micrometer particles were primarily in the liquid state for prevailing RH conditions under background conditions⁹, yet anthropogenic influences could contribute to the presence of non-liquid particles in the atmospheric particle population¹⁰. Observations in the southeastern USA indicated that at typical ambient RH and temperature, organic particles were mostly liquid¹¹. In a modeling study, Shiraiwa et al.¹² predicted the global distribution of particle phase state for secondary organic aerosols and suggested that in the middle and upper troposphere SOA should be mostly in the glassy solid phase state. Other studies concerning the particle phase state depends strongly on chemical composition and RH¹³⁻¹⁶.

The North China Plain (NCP), especially Beijing with a high population density, experiences serious air pollution. Secondary aerosol production is considered as a main cause of particulate pollution during haze events¹⁷⁻¹⁸. Recent studies showed that heterogeneous reactions could play a profound role in heavy haze formation¹⁹⁻²¹. As mentioned, particle phase state is key factor determining the uptake of reactive gas molecules, gas to particle partitioning, and heterogeneous chemical reactions, all of which can depend on phase state by affecting water and reactant diffusivity in the surface and bulk regions of the aerosol particles^{3, 5-}

^{6, 22-24}. Measurements of the particle phase state of atmospheric particles over NCP, however, have not yet been made, impeding our understanding of the formation mechanisms of heavy haze.

In the study presented herein, a three-arm particle rebound impactor apparatus equipped with a RH adjustment system was employed to measure the rebound fraction f of size-resolved particles in the atmosphere of Beijing, China. The rebound fraction f was used to infer the particle phase state at ambient RH. The observations showed that the sub-micrometer particles were in the liquid state during heavy haze pollution periods, suggesting that liquid particles might play a significant mechanistic role in severe haze formation in China.

2 Methodology

Measurements were carried out at the Peking University Atmosphere Environment Monitoring Station (PKUERS) on the roof of a six-floor building on the campus of Peking University, located in the northwestern urban area of Beijing. The rebound fraction f of size-resolved particles was measured from 1 to 19 January 2017 using the three-arm impactor. It was a modified version of that described in Bateman et al²⁵, which was built from three single-stage impactors operated in parallel. One of the three impactors had no plate, while the other two had an uncoated plate and a grease-coated plate, respectively. The uncoated plate had a solid surface and allowed the particles to rebound, whereas the grease-coated plate had a sticky surface and could capture all particles that struck it. The particle populations exiting the three impactors were measured in sequence using a Condensational Particle Counter (CPC, TSI model 3772) by the control of a valve system, which contained three solenoids and two actuators (See Fig. S1). Thus, rebound fraction f was defined as:

$$f = \frac{N_2 - N_3}{N_1 - N_3} \tag{1}$$

where N_1 was the whole particle population, N_2 was the population of particles that did not strike plus those that struck but rebounded from the impaction plate, and N_3 was the population of particles that did not strike the impaction plate. The instrument was equipped with an RH adjustment system, which contained two RH probes and a Nafion RH conditioner. Probe 1 detected the ambient RH and probe 2 detected the instrument RH. During the measurement, probe 2 was adjusted to the measured ambient RH. The particles were first dried to 20% RH and then humidified to the ambient RH before passing into the impactors. The cut-point of the impactors was 95 nm (see Fig. S2). From the dried particle population, 300nm mono-disperse particles (mobility diameter) were selected by a Differential Mobility Analyzer (DMA, TSI model 3080).

The non-refractory chemical composition of the particles was measured using an Aerodyne HR-ToF- AMS^{26} . The aerosol liquid water content (ALWC) was calculated using the ISORROPIA-II model²⁷. Only inorganic components were considered in this calculation. The calculated ALWC might therefore be lower than the actual ALWC because the water associated with water-soluble organics was not included. The Supporting Information provides a detailed description of other measurements, including meteorological parameters, black carbon concentration, photolysis frequency (J(NO₂)) and particle number size distribution, and PM_{2.5} mass concentration.

3 Results and Discussion

Sub-micrometer particles were in the liquid state during heavy haze episodes. Figs. 1 (A) and (B) show the time series of particle number size distribution and PM₁ Particulate Matter chemical composition from 13 to 19 January 2017 during a typical air pollution cycle in Beijing. There was a transition from clean to polluted days during this time period. The time series of $J(NO_2)$ and O_3 concentration are plotted in Fig. 1 (C). On the morning of January 13, strong northerlies brought clean air associated with low PM₁ mass concentration (5 μ g/m³). At 10:30 AM (local time), a photochemically driven new particle formation (NPF) event (Fig. 1 (A)) took place, associated with an increased ozone concentration (Fig. 1 (C)). The newly formed particles subsequently grew to >100 nm within 24 hours. After January 13, the wind speed decreased to <3 m/s, indicating the occurrence of stagnant conditions. Correspondingly, the PM₁ mass concentration (Fig. 1 (B)) increased step-wise from ~5 μ g/m³ to several hundred micrograms per cubic meter. The average daily particle mass growth rate was 37.7 μ g/m³/day. The episode ended at midnight on January 18.



Figure 1. Time series of particle number size distribution (A), PM_1 chemical composition (B), $J(NO_2)$ and O_3 concentration (C), and rebound fraction *f* and ambient RH (D) from 11 to 17 January 2017.

The measured non-refractory PM₁ (NR-PM₁) chemical composition (Fig. 1 (B)) showed that the mass concentrations of sulfate, nitrate, and ammonium increased during the haze episode, indicating that large amounts of secondary inorganic aerosols were produced during haze episode. The inorganic PM accounted for around 60% of PM₁ during the air pollution cycle. The black carbon accounted for about 13% of PM₁ and did not show an evident enhancement. The remaining, as measured by the AMS, was organic material contributing 27% of NR-PM₁. The chemical composition demonstrated that secondary transformation could be a major reason for the haze formation. As shown in Fig. 1 (C), the low ozone concentration and low J(NO₂) values indicated weak photochemical reactions. The enhancement in secondary inorganic ions might be caused by heterogeneous and liquid reactions, rather than gas phase chemical processes.

As shown in Fig. 1 (D), the RH was below 30% until 8:00 PM on January 14, at which point the ambient RH increased markedly. Afterwards, the ambient RH was relatively high (around 60%) for a sustained period. The rebound fraction f was highly sensitive to ambient RH. It was around 0.8 for RH < 20% during the NPF event, suggesting that the particles were in a semi-solid state during this time period. The rebound fraction decreased from 0.8 to 0.2 when ambient RH increased from 10% to around 60% at midnight on January 14. The smaller rebound fraction indicates that the particles had transitioned into a liquid phase state. During the

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entire haze episode, the rebound faction was <0.2, indicating that the majority of sub-micrometer particles were liquid. At noon on January 17, the RH decreased to 40%, and the rebound fraction increased to 0.4. On January 18, the rebound fraction was \sim 0.7 when RH decreased to 30% after the haze episode.

The particle phase state was sensitive to ambient RH. Water in the particle-phase could play as a plasticizer⁵. In order to investigate the effects of condensed water on the particle phase state, the rebound fraction *f* measured during the entire sampling episode is plotted as a function of both ambient RH and aerosol liquid water content in Fig. 2 (A) and (B). As shown in Fig. 2 (A), the rebound fraction decreased with increasing ambient RH. At RH< 20%, the rebound fraction was ~0.8, indicating a semi-solid or solid phase of the particles. As RH increased from 20% to 60%, rebound fraction changed from 0.8 to 0.2, meaning that the particles were in a range of phase states. Deliquescence RH (DRH) decreases when pure materials are mixed together²⁸. Both laboratory experiments²⁹⁻³² and field measurements³³⁻³⁴ show that presence of organic material further decreases DRH. For these reasons, the phase transition of particles occurred at RH values (Fig. 2 (A)) that were much lower than the DRH of either (NH₄)₂SO₄ and NH₄NO₃ in pure form (i.e., the major constituents of atmospheric particulate matter in this study).

We compared our results with previous laboratory experiments as well as field studies, as shown in Fig.2 (A). Our results were similar to the observations reported for Alabama, US, which showed that the rebound fraction started to decrease at RH values approaching 40 to $60\%^{11}$. For RH > 60%, the rebound fraction was below 0.2, indicating that particles had transitioned into a liquid phase. By comparison, the rebound fraction measured in central Amazonia was greater than 0.1 until 80% RH⁹. Laboratory studies show that the RH threshold for semisolid-to-liquid phase transition were 40% RH for isoprene-derived SOA and 70% for toluene-derived and α -pinene-derived SOA¹⁴⁻¹⁵. The differences among these results could be explained by the significant fraction (on average 53%) of particle composition that was inorganic in the atmosphere of Beijing, whereas organic PM₁ dominates in central Amazonia⁹. As represented by the colored markers in Fig. 2 (A), the liquid phase particles in Beijing were dominated by sulfate, nitrate, and ammonium between 40% and 80%. This indicated that the hygroscopic inorganic-rich particles easily changed to a liquid phase by taking up water at relatively low ambient RH in the atmosphere of Beijing.

The abundant aerosol liquid water content (ALWC) softened the particles in a liquid phase during the polluted episodes. Fig. 2 (B) displays the rebound fraction f versus ALWC. The markers are colored by ambient RH, and the circle sizes are scaled by PM₁ mass concentration. As was the case for RH-dependency, the rebound fraction decreased for increasing ALWC. As indicated by the size of markers, the particles transitioned to a liquid state (f < 0.2) for increasing PM₁ mass concentration. The rebound fraction was <0.2 for PM₁ mass concentrations higher than 70 µg/m³, indicating that the particles were in the liquid phase during haze episodes. The colored markers in Fig. 1 (B) show that the PM₁ mass concentration increased for increasing RH. Overall, the elevated ambient RH and inorganic fraction during the haze episodes softened the particles, resulting in a liquid phase state.

Temperature and oxidation state of the organic component are also recognized as important factors affecting particle phase state^{3, 5}. The influence of ambient temperature (T) and the oxygen-to-carbon ratio (O:C) of the organic composition on particle rebound fraction f was investigated. There was no clear correlation, however (see Fig. S3 and Fig S4), again suggesting the dominance of the inorganic component on particle phase state during the study period.



Figure 2. Rebound fraction *f* as function of ambient RH (A) and aerosol liquid water content (B). In panel (A), the markers were colored by the mass fraction of inorganic matters (F_{inorg}) in NR-PM₁. In panel (B), the markers were colored by the oxygen-to-carbon (O: C) elemental ratio of organic materials of the PM. The

marker size was scaled by PM_1 mass concentration.

Liquid phase particles appear to facilitate secondary particle formation in haze over NCP. Fig. 3 shows the RH-dependencies of $PM_{2.5}$ mass concentration and of the total particle surface area concentration during wintertime (November-January, 2017) in the atmosphere of Beijing. The $PM_{2.5}$ mass concentration increases for increasing ambient RH. This was a typical phenomenon for the atmosphere of NCP: the haze episodes occurred during time periods associated with elevated RH and stagnant weather conditions. In addition, the inorganic fraction accounted for a considerable fraction of $PM_{2.5}$ (52%) during haze episodes in winter time in Beijing³⁵. The increased RH and abundant particulate inorganic components led to an increasing ALWC. As a result, particulate particles transformed into liquid phase during haze episodes. With increased $PM_{2.5}$ mass concentration, the particle surface area concentration increased as well (See Fig. 3). When the ambient RH was >60%, the $PM_{2.5}$ mass concentration and particle surface area concentration were respectively >100 µg/m³ and >1500 µm²/cm³. In addition, the particle number concentration was dominated by accumulation mode particles (See Fig. S5). This indicates that the liquid particles provided the abundant reaction sites for heterogeneous reactions during haze episodes.



Figure 3. RH dependency of PM_{2.5} mass concentration and particle total surface area concentration during wintertime in the atmosphere of Beijing.

The diffusion coefficients of small atmospheric gas molecules (N_2O_5 , O_3 , SO_2 , NO_x et al.) are several magnitudes larger in the liquid phase compared to the solid or semi-solid phases³. This suggests that the liquid phase can facilitate the uptake and mass transport of reactive trace gases into the particles during heavy haze episodes, thereby accelerating the secondary transformation of gaseous pollutants, such as SO_2 and N_2O_5 . An

implication could be that the particle phase impacts the volatilization of semi-volatility organic carbons (SVOCs) and NH₄NO₃ in aerosol particles, thereby possibly producing bias in aerosol physicochemical measurements³⁶. We also propose that the transition to the liquid phase marks the beginning of the haze episode and kick off a positive feedback loop. The liquid particles readily uptake pollutants that react to form inorganics, which then uptake even more water. In this light, the strict control strategies of sulfur emissions in China might lead to a decreased sulfate fraction and increased nitrate fraction in PM_{2.5}. For example, from 2013 to 2015 the SO₂ emissions decreased by 44.9% and the NO₂ emissions by 9.8% over the North China Plain (Source from mid-term report for evaluation on the effectiveness of "China's Action Plan for Air Pollution Prevention and Control"). As a result, due to the lower deliquescence RH of nitrate, the feedback loop proposed could start at an even lower RH at the present time and further in the future.

Associated Content

Supporting Information

Figure S1. Schematic diagram of the three-arm impactor. Figure S2. Transmission fraction curve of impactors. Figure S3. Rebound fraction f dependency of environmental temperature. Figure S4. Rebound fraction f dependency of particle organics oxidation (oxygen to carbon ratio O: C). Fig S5. RH dependency of PM_{2.5} number concentration during wintertime in the atmosphere of Beijing.

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Figure 1. Time series of particle number size distribution (A), PM1 chemical composition (B), J(NO2) and O3 concentration (C), and rebound fraction *f* and ambient RH (D) from 11 to 17 January 2017.

178x119mm (300 x 300 DPI)



Figure 2. Rebound fraction *f* as function of ambient RH (A) and aerosol liquid water content (B). In panel (A), the markers were colored by the mass fraction of inorganic matters (Finorg) in NR-PM1.

157x130mm (300 x 300 DPI)



Figure 2. Rebound fraction *f* as function of ambient RH (A) and aerosol liquid water content (B). In panel (B), the markers were colored by the oxygen-to-carbon (O: C) elemental ratio of organic materials of the PM. The marker size was scaled by PM1 mass concentration.

143x113mm (300 x 300 DPI)



Figure 3. RH dependency of PM2.5 mass concentration and particle total surface area concentration during wintertime in the atmosphere of Beijing.

148x112mm (300 x 300 DPI)





Figure S2. Transmission fraction curve of impactors

166x105mm (300 x 300 DPI)



Figure S3. Rebound fraction f dependency of environmental temperature.

140x124mm (300 x 300 DPI)



Figure S4. Rebound fraction *f* dependency of particle organics oxidation (oxygen to carbon ratio O:C).

101x81mm (300 x 300 DPI)



Fig. S5 RH dependency of PM2.5 number concentration during wintertime in the atmosphere of Beijing.

139x86mm (300 x 300 DPI)