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Effect of heterogeneous aqueous reactions on the secondary formation of inorganic aerosols during haze events

Jiannong Quan [a, b, *], Quan Liu [a, b, **], Xia Li [a], Yang Gao [a], Xingcan Jia [a], Jiujiang Sheng [a, b], Yangang Liu [c]

[a] Beijing Key Laboratory of Cloud, Precipitation and Atmospheric Water Resources, Beijing, China
[b] Institute of Urban Meteorology, Chinese Meteorological Administration, Beijing, China
[c] Brookhaven National Laboratory, Upton, NY 11973, USA

HIGHLIGHTS

- Heterogeneous aqueous reactions during haze events was investigated.
- The conversion of gas-phase of S and N to particle-phase was analyzed.
- Relationships were given between conversion ratio of S, N with RH and O_3.
- Evolution of aerosol composition and particle size were analyzed.

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ABSTRACT

The effect of heterogeneous aqueous reactions on the secondary formation of inorganic aerosols during haze events was investigated by analysis of comprehensive measurements of aerosol composition and concentrations [e.g., particular matters ($PM_{2.5}$), nitrate (NO_3), sulfate (SO_4), ammonium (NH_4)], gas-phase precursors [e.g., nitrogen oxides (NOx), sulfur dioxide (SO_2), and ozone (O_3)], and relevant meteorological parameters [e.g., visibility and relative humidity (RH)]. The measurements were conducted in Beijing, China from Sep. 07, 2012 to Jan. 16, 2013. The results show that the conversion ratios of N from NOx to nitrate (N_{ratio}) and S from SO_2 to sulfate (S_{ratio}) both significantly increased in haze events, suggesting enhanced conversions from NOx and SO_2 to their corresponding particle phases in the late haze period. Further analysis shows that N_{ratio} and S_{ratio} increased with increasing RH, with N_{ratio} and S_{ratio} being only 0.04 and 0.03, respectively, when RH < 40%, and increasing up to 0.16 and 0.12 when RH reached 60–80%, respectively. The enhanced conversion ratios of N and S in the late haze period is likely due to heterogeneous aqueous reactions, because solar radiation and thus the photochemical capacity are reduced by the increases in aerosols and RH. This point was further affirmed by the relationships of N_{ratio} and S_{ratio} to O_3: the conversion ratios increase with decreasing O_3 concentration when O_3 concentration is lower than <15 ppb but increased with increasing O_3 when O_3 concentration is higher than 15 ppb. The results suggest that heterogeneous aqueous reactions likely changed aerosols and their precursors during the haze events: in the beginning of haze events, the precursor gases accumulated quickly due to high emission and low reaction rate; the occurrence of heterogeneous aqueous reactions in the late haze period, together with the accumulated high concentrations of precursor gases such as SO_2 and NOx, accelerated the formation of secondary inorganic aerosols, and led to rapid increase of the $PM_{2.5}$ concentration.

1. Introduction

Beijing has been experiencing frequent occurrence of haze events in the past two decades (Che et al., 2007; Quan et al., 2011). This severe environment problem has dire impacts on human

* Corresponding author. Beijing Key Laboratory of Cloud, Precipitation and Atmospheric Water Resources, Beijing, China.
** Corresponding author. Beijing Key Laboratory of Cloud, Precipitation and Atmospheric Water Resources, Beijing, China.
E-mail addresses: quanjn1975@gmail.com (J. Quan), liuquan@bjmb.gov.cn (Q. Liu).

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health, traffic, weather and climate, and other important aspects and receives growing concern in the scientific community (Charlson et al., 1987; Ramanathan and Vogelmann, 1997; Tegen et al., 2000; Yu et al., 2002; Tie et al., 2009a,b). In efforts to understand the mechanism of heavy haze formation and evolution in Beijing, many haze-related aspects have been investigated, including aerosol composition (Sun et al., 2013a,b; 2014; Huang et al., 2014), particulate matter (PM) formation mechanisms (Guo et al., 2014), regional transport of pollutants (Zhao et al., 2013a,b), hygroscopic property of particles (Pan et al., 2009; Liu et al., 2011), effects of meteorology (Zhang et al., 2015), and even the feedback between aerosols and meteorological variables (Quan et al., 2013; Gao et al., 2015). Large emission of primary aerosols and the gaseous precursors of secondary aerosols, and stagnant meteorological conditions have been usually thought as the dominant factors driving the formation and evolution of haze pollution in North China Plain (NCP, Wang et al., 2014; Guo et al., 2014; Zhang et al., 2015).

It has been reported that $PM_{2.5}$ (particulate matter of 2.5 μm or less in aerodynamic diameter) concentration could reach as high as 600 μg m^{-3} in heavy haze events (Quan et al., 2014; Sun et al., 2014; Wang et al., 2014), and could increase by an order of magnitude in a period of 2–4 days (Quan et al., 2014; Guo et al., 2014). Meteorological conditions often play an important role in haze formation. For example, the decreased height of planetary boundary layer (PBL) in haze events suppresses particles into a shallower layer, and the weak wind slow down the horizontal transport. In addition to the meteorology factors, secondary particle formation can make a significant contribution to heavy haze events as well (Huang et al., 2014; Guo et al., 2014). Quan et al. (2014) revealed that the conversion from NOx and SO_2 to nitrate (NO_3) and sulfate (SO_4) were likely accelerated in the late haze period. Because visibility and thus photochemical activity are low and relative humidity (RH) increases sharply in the heavy haze period, the accelerated conversion of NOx and SO_2 might be caused by heterogeneous aqueous reactions. However, up to now the effect of heterogeneous aqueous reactions on secondary particle formation, especially in haze events, remains poorly understood and quantified.

The primary objective of this work is to investigate the effect of heterogeneous aqueous reactions on the secondary formation of inorganic aerosols during haze events based on comprehensive measurements collected during a field campaign from Sep. 7, 2012 to Jan. 16, 2013. The rest of the paper is organized as follows. Section 2 describes the instruments and measurements used in this study. The results and analysis are given in Section 3. The analysis focuses on (1) the variation of key variables in haze events, including visibility, $PM_{2.5}$, NOx, SO_2, NO_3, SO_4, and the conversion ratios of N (N_{ratio}) and S (S_{ratio}); (2) the relationship of N_{ratio} and S_{ratio} with RH and O_3; (3) the evolution of mean particle diameter (D_{mean}) of submicron aerosols; and (4) contribution of heterogeneous aqueous reactions. Section 4 provides the concluding remarks.

2. Instruments and measurements

Comprehensive measurements were conducted in a field campaign at the Baolian (BL) meteorological station, China Meteorological Administration (CMA) (39°56′N, 116°17′E). The BL station located between the west 3rd and 4th highways in Beijing. The distance of the station from nearby major roads is about 400 m. The surrounding region of this site is mainly residential district, without large point sources of $PM_{2.5}$. A number of quantities, including atmospheric visibility, mass concentration of $PM_{2.5}$, chemical composition of non-refractory submicron particles (NR-PM_1), and gaseous pollutants (SO_2, NOx, CO, O_3) were measured simultaneously, together with key meteorological variables of temperature, RH, pressure, wind speed, and wind direction.

Detailed description of above instruments was given by Quan et al. (2013, 2014). Briefly, the mass concentration of $PM_{2.5}$ was measured with a R&P model 1400a Tapered Element Oscillating Microbalance (TEOM, Thermo Scientific Co., USA) instrument, with a 2.5 μ m cyclone inlet and an inlet humidity control system. The aerosol size distribution for particles of 13–736 nm was obtained with a Scanning Mobility Particle Sizer (SMPS, Model 3936, TSI, USA) with a time resolution of 5 min. The collocated gaseous species, including CO, SO_2, NOx and O_3, were measured with various gas analyzers (Thermo Scientific Co., USA).

The chemical composition of NR-PM1 was measured with an Aerodyne high-resolution Time-of-Flight Aerosol Mass Spectrometer (HRToF-AMS). The sampling time resolution was 5 min. The measured composition of particles included sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), chloride (Chl), organic aerosols (ORG). The instrument was calibrated for ionization efficiency (IE) and particle sizing at the beginning, middle and end of the campaign following the standard protocols (Jimenez et al., 2003). The detection limits (DLs) of each NR-PM1 species were determined as 3 times the standard deviations (3σ) of the corresponding signals in particle-free ambient air through a HEPA filter. As a result, the 5 min DLs of organics, sulfate, nitrate, ammonium, and chloride were 0.058, 0.006, 0.008, 0.06 and 0.016 μg m^{-3}, respectively. The AMS data were analyzed for the mass concentrations and composition with the standard ToF-AMS data analysis software package (SQUIRREL version 1.50 and PIKA version 1.09) (Jimenez et al., 2003; DeCarlo et al., 2006). A collection efficiency (CE) factor of 0.5 was introduced to account for the particle loss, mostly due to particle bounce at the vaporizer (Canagaratna et al., 2007; Aiken et al., 2009; Huang et al., 2010). The values of relative ionization efficiency (RIE) used in this study were 1.2 for sulfate, 1.1 for nitrate, 1.3 for chloride and 1.4 for organics (Jimenez et al., 2003; Canagaratna et al., 2007). The RIE value of 4.0 was used for ammonium based on the analysis of pure NH_4NO_3 particles. Atmospheric visibility was measured with a PWD20 (Vaisala Co., Finland), and meteorology variables were observed by WXT-510 (Vaisala Co., Finland).

3. Results and discussion

3.1. General characteristics of haze events

The field campaign was carried out from Sep. 07, 2012 to Jan. 16, 2013, covering typical fall (Sep. 07 to Oct. 31) and winter (Nov. 01 to Jan. 16) conditions in Beijing. According to the definition by CMA that a haze event satisfies when the conditions of visibility ≤10 km and RH < 90%, there were a total of 28 haze events, with an averaged length of 4.7 days per haze event, during the experiment period (from Sep. 07, 2012 to Jan. 16, 2013). The visibility exhibits a clear periodic cycle of 4–7 days, being higher than 10 km (clean) in the beginning of each cycle, and reached around 2 km (polluted) within 2–4 days (Fig. 1a). The measured $PM_{2.5}$ mass concentration (Fig. 1b) exhibited a similar cycle, increasing from <50 μg m^{-3} in the beginning of haze events to several hundred micrograms per cubic meter at the late stage of haze events. The NOx (Fig. 1e) and SO_2 (Fig. 1f), as the precursors of NO_3 and SO_4, showed a cycle similar to that of $PM_{2.5}$ concentration, with the concentrations increasing from <10 ppb in the beginning of haze events to 50–100 ppb at the late stage of haze events.

Previous studies indicated that the decreased atmospheric dispersion capacity in haze events, characterized by lowered PBL heights and weakened wind speed (Quan et al., 2013, 2014; Zhang et al., 2015), could enhance $PM_{2.5}$ and gas pollutants concentrations. Besides that, the conversion of gas phases of N and S to