Front. Environ. Sci. Eng. 2021, 15(2): 34
https://doi.org/10.1007/s11783-020-1326-x

REVIEW ARTICLE

Secondary aerosol formation in winter haze over the Beijing-Tianjin-Hebei Region, China

Dongjie Shang[1], Jianfei Peng[2], Song Guo[1], Zhijun Wu[1], Min Hu (✉)[1,3]

1 State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China
2 Department of Atmospheric Sciences, Texas A&M University, College Station, TX 77843, USA
3 Beijing Innovation Center for Engineering Sciences and Advanced Technology, Peking University, Beijing 100871, China

HIGHLIGHTS

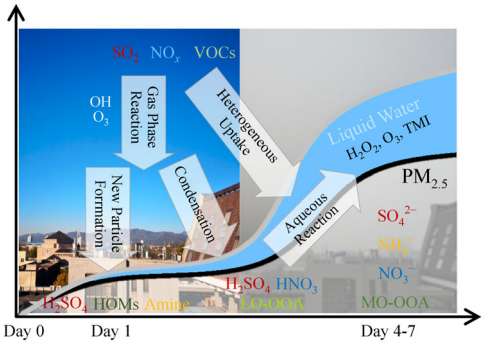
- Characteristics and interannual variation of aerosol pollution are illustrated.
- Mechanisms of secondary aerosol formation in winter haze of North China are reviewed.
- Directions in future studies of secondary aerosol formation are provided.

ARTICLE INFO

Article history:
Received 15 April 2020
Revised 14 August 2020
Accepted 17 August 2020
Available online 8 October 2020

Keywords:
Secondary aerosol formation
Regional haze
Photochemical reaction
Aqueous reaction
Chemical mechanism

GRAPHIC ABSTRACT



ABSTRACT

Severe haze pollution occurs frequently in the winter over the Beijing-Tianjin-Hebei (BTH) region (China), exerting profound impacts on air quality, visibility, and human health. The Chinese Government has taken strict mitigation actions since 2013 and has achieved a significant reduction in the annual mean $PM_{2.5}$ concentration over this region. However, the level of secondary aerosols during heavy haze episodes showed little decrease during this period. During heavy haze episodes, the concentrations of secondary aerosol components, including sulfate, nitrate and secondary organics, in aerosol particles increase sharply, acting as the main contributors to aerosol pollution. To achieve effective control of particle pollution in the BTH region, the precise and complete secondary aerosol formation mechanisms have been investigated, and advances have been made about the mechanisms of gas phase reaction, nucleation and heterogeneous reactions in forming secondary aerosols. This paper reviews the research progress in aerosol chemistry during haze pollution episodes in the BTH region, lays out the challenges in haze formation studies, and provides implications and directions for future research.

1 Introduction

Severe regional haze pollution, characterized by rapid increases of fine particulate matter ($PM_{2.5}$) in the atmosphere (Liu et al., 2013), occurred frequently in winter over the Beijing-Tianjin-Hebei (BTH) region (China) in recent years, leading to serious visibility degradation and exerting profound negative impacts on human health (Pöschl, 2005; Chen et al., 2013; Cao et al., 2014). Severe haze events usually occurred with extensive temporal and spatial coverage in the BTH region (Sun et al., 2016a). For example, in January 2013, a continuous and large scale haze event spread over more than 1 million km^2 in Northern China with extraordinarily high $PM_{2.5}$ concentrations (hourly concentration up to ~900 $\mu g/m^3$) (Zheng et al., 2015). Although annual average $PM_{2.5}$ concentrations decreased considerably over recent years over the BTH region due to effective emission controls (Zhang

✉ Corresponding author
E-mail: minhu@pku.edu.cn

et al., 2018), there were still more than 20 percent of winter days in 2018 with daily average $PM_{2.5}$ exceeding 75 μg/m^3, which is the daily average $PM_{2.5}$ standard of China.

The regional haze issue is closely associated with a unique combination of economic development, topography and climate features in the BTH region. With 111 million permanent residents residing in an area of 218000 km^2, the BTH region is one of the most densely populated regions in the world (National Statistical Yearbook 2018 of China). The rapid industrialization and urbanization over the last few decades have been accompanied by fast-growing energy consumption. In 2013 fossil fuel combustion in this region led to emissions of 1.1 teragram (Tg) primary particles, 2.3 Tg of SO_2, 2.7 Tg of NO_x, as well as 2.2 Tg of volatile organic compounds (VOCs) (Qi et al., 2017). With Yanshan Mountains to the north and Taihang Mountains to the west of the BTH region blocking air mass movement (Chen et al., 2019), pollutants emitted locally and transported from the southern part of North China Plain tended to accumulate in the BTH region, under low pressure weather conditions. Locating beside the eastern leeward slope of Tibet Plateau, the "harbor effect" (Xu et al., 2015) could result in temperature inversion in the middle and lower troposphere of eastern China, reducing the diffusion capacity of atmosphere in eastern China, which also facilitates the accumulation of pollutants leading to haze formation.

Quick actions and strong policies were taken to control pollution emissions and improve the air quality in the BTH region. For example, $277 billion financial allocations were used to support Action Plan on Prevention and Control of Air Pollution (2013–2017) aiming at reducing the $PM_{2.5}$ annual concentration by 25% from that in 2012 (China Daily, 2013). The primary $PM_{2.5}$ emission in China was 7.6 Tg in 2017, reduced 33% compared with that in 2013, as a result of China Coal Cap projects and other actions (Zheng et al., 2018). The policies and actions achieved major results through economic restructuring and technology upgrade (Liu et al., 2019a); according to the report on the State of the Ecology and Environmental in China, from 2013 to 2018, the annual average concentration of $PM_{2.5}$ and SO_2 over the BTH region decreased by 41% and 72%, respectively.

Despite the reductions in the annual mass concentrations of $PM_{2.5}$ and the frequency of heavy haze events between 2013 and 2018, the severity of haze showed little alleviation (Zhang et al., 2020). Furthermore, the chemical mechanisms of the explosive particle mass concentration growth during pollution episodes still remained unclear. In addition, during severe pollution periods $PM_{2.5}$ mainly consisted of secondary components, i.e. secondary inorganic constituents including sulfate, nitrate and ammonium (SNA), and secondary organic aerosols (SOA) formed from oxidation of VOCs (Guo et al., 2014). Thus, elucidating aerosol chemistry behind the rapid formation of secondary aerosols is one key to solve the haze problem.

There are various formation pathways of SNA and SOA in the atmosphere. The relationships between $PM_{2.5}$ concentrations and the emissions of its precursors are nonlinear (Zhao et al., 2017; Lu et al., 2018). Models with known chemical reactions about SO_2, NO_x and VOCs oxidation and secondary aerosol formation can not reproduce the rapid increases of particle mass during haze formation in the fall and winter over the BTH region (Han et al., 2014; Wang et al., 2014a; Wang et al., 2014c; Zheng et al., 2015; Chen et al., 2016; Cheng et al., 2016; Tang et al., 2016; Liu et al., 2020). The contributions from local emissions, secondary chemical formation and regional transport were not clearly quantified, hindering the joint efforts among different parts of the BTH region to control air pollutants' emissions (Zheng et al., 2015). A deeper understanding of the chemical formation mechanisms is needed for air pollution control under the air pollution complex characteristics in China (Kulmala, 2015).

Different from former reviews on mechanisms of secondary aerosol formation (Ma et al., 2012; Zhang et al., 2015a), this work summarizes the current state of knowledge on the chemistry of secondary aerosol formation in the fall and winter of the BTH region, discusses the limitations of our understandings, and makes recommendations on future studies. The knowledge and recommendations can serve as a reference for future studies and mitigation of regional particle pollution in areas in the world with rapid economic growth and large anthropogenic emissions.

2 Characteristics of haze formation

In the BTH region, haze was caused by atmospheric $PM_{2.5}$ pollution contributed by primary emission and secondary formation. The unique geography of the BTH region as well as meteorological conditions favored rapidly secondary formation in the winter.

2.1 Source identification of aerosol particles

The understanding and control recommendations on regional haze in the BTH region were first established based on source apportionment studies (Lv et al., 2016; Li et al., 2017b). These studies applied receptor models, e.g., Chemical Mass Balance (CMB) model and Positive Matrix Factor (PMF) model, and atmospheric transport models, e.g., Weather Research and Forecasting — Community Multiscale Air Quality (WRF-CMAQ) model and Comprehensive Air Quality Model with extensions (CAMs), to determine the contributions from various sources to $PM_{2.5}$. The sources of atmospheric $PM_{2.5}$ and its

precursors in the winter over the BTH region include residential and industrial coal combustion, biomass burning, traffic emission, and soil and construction dust (Wang et al., 2009; Cheng et al., 2013; Zhang et al., 2015b; Elser et al., 2016; Han et al., 2016b; Hu et al., 2016; Sun et al., 2016b; Tan et al., 2016; Yao et al., 2016; Hu et al., 2017; Cheng et al., 2018; Gao et al., 2018; Li et al., 2018; Li et al., 2019a; Liu et al., 2019d). Among the primary sources, coal combustion (~20%) and biomass burning (~20%) are the most important during haze events (Li et al., 2018; Li et al., 2019a), while traffic emissions become more important during clean period (Liu et al., 2019d). Compared with primary emissions, secondary formation contributes more to $PM_{2.5}$ concentration during polluted periods, indicating important roles of aerosol chemical formation in haze (Liu et al., 2019d).

2.2 Secondary components in $PM_{2.5}$

The explosive growth of secondary components in aerosols has a dominant effect on haze development over the BTH region during fall and winter (Guo et al., 2014; Yang et al., 2015; Yao et al., 2016; Cao et al., 2017; Ma et al., 2017; Li et al., 2019a; Xie, 2020); emissions of elemental carbon (EC), primary organic aerosols (POA), mineral elements and other components in particles also increase during haze accumulation period (Tan et al., 2016; Zhang et al., 2016; Li et al., 2019a).

Field measurements reveal that haze formation in Beijing always follows a two-stage cycle lasting for several days (Tan et al., 2018), i.e., a new particle formation process to generate large number concentration of nano-particles, followed by subsequent growth of these particles to over 100 nm diameter to concentrations as high as 150 μg/m^3 from efficient secondary formation of SNA and SOA (Guo et al., 2014; Zamora et al., 2019).

SNA and oxidized organic aerosols (OOA) derived by high resolution aerosol mass spectrometer (HR-AMS) contribute about 60%–80% to mass concentration of particles with diameter less than 1 μm (PM_1) in Beijing (Hu et al., 2017). The organic fraction in particles decreases during haze episodes (Sun et al., 2014; Zhang et al., 2014; Zheng et al., 2016; Wang et al., 2019), but it is still dominant in $PM_{2.5}$ increases during late fall and winter (41%). The OA fraction is followed by the nitrate fraction (20%) (Tan et al., 2018). SNA are efficiently formed by strong gas to particle conversion and oxidation reactions, as the sulfur and nitrogen oxidation ratios, calculated as $SO_4^{2-}/(SO_4^{2-}+SO_2)$ and $NO_3^-/(NO_3^-+NO_x)$, exhibit higher levels during haze events (Zheng et al., 2016).

Due to the implementation of coal combustion control policies, e.g., the replacement by natural gases and establishment of non-coal burning areas in the BTH region, nitrate (Yang et al., 2015; Tan et al., 2018; Xu et al., 2019a; Xu et al., 2019b) has replaced sulfate (Sun et al., 2014; Wang et al., 2014b; Wang et al., 2014c; Han et al., 2016a; Zheng et al., 2016) as the primary inorganic component in $PM_{2.5}$ during severe haze episodes. Figure 1 shows the chemical fractions of $PM_{2.5}$ in Beijing in winter. The daily average $PM_{2.5}$ concentrations on haze days of 2013 and 2018 were 150 μg/m^3 and 131 μg/m^3, respectively, indicating small decline in haze severity.

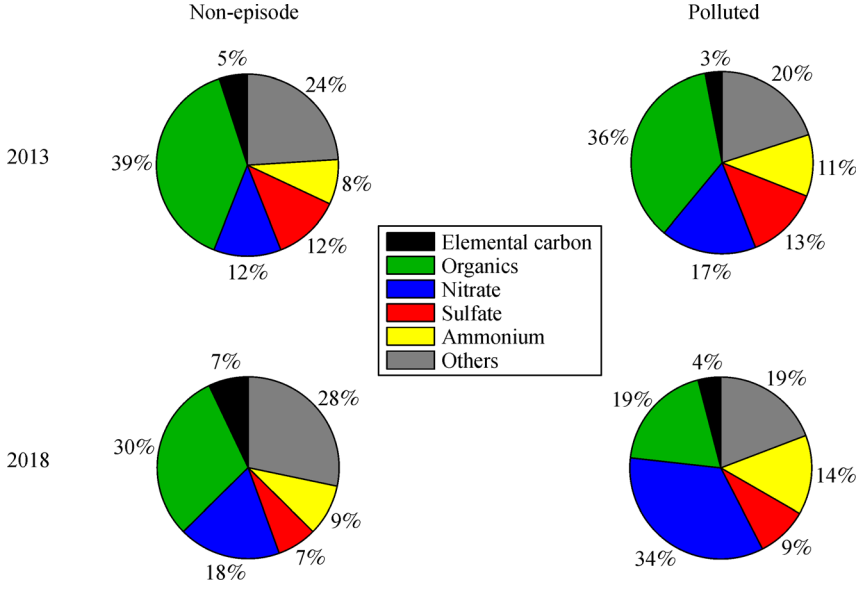


Fig. 1 Fractions of $PM_{2.5}$ in the winter of Beijing during non-episode (daily averaged $PM_{2.5} < 75$ μg/m^3) and polluted periods (daily averaged $PM_{2.5} > 75$ μg/m^3) in year of 2013 and 2018. (Data from the filter samples collected at the PKUERS site, the campus of Peking University. Elemental carbon and organic carbon (OC) are measured by the Sunset ECOC instrument, concentration organics are calculated as 1.6*OC; SNA are measured by ion chromatography).

Sulfate concentrations during pollution period decreased during 2013–2018, from 19.2 μg/m^3 to 12.1 μg/m^3. A comparison between non-episode and polluted periods shows the fraction of organics decreased from 30% in non-episode $PM_{2.5}$ to 19% in $PM_{2.5}$ during pollution episode in winter of 2018, while nitrate increased sharply from 18% to 34%, becoming the most abundant composition in $PM_{2.5}$.

2.3 Meteorological conditions favorable for secondary formation

The rapid increases of $PM_{2.5}$ during haze episodes over the BTH region are facilitated under specific meteorological conditions, e.g. higher relative humidities (Zhao et al., 2013; Zhang et al., 2014; Han et al., 2016a), increased atmospheric stability (Zheng et al., 2015), weak cyclone and convection, and lower planetary boundary layer (PBL) (Liu et al., 2013; Guo et al., 2014). Such high atmospheric stability phenomenon is typically induced by climatological anomalies in the anticyclonic activities during winter season in north-eastern Asia (Zhong et al., 2019), and the large-scale temperature inversion in the eastern slope of the Tibetan Plateau (i.e. the harbor effect) (Xu et al., 2015). The high levels and aging of $PM_{2.5}$ can lead to meteorological feedbacks, reducing downward shortwave radiation at the surface by 26% and planetary boundary layer height by 15%–25%, and increasing the humidity of air (Wang et al., 2014d; Peng et al., 2016; Gao et al., 2017; Tie et al., 2017; Zhao et al., 2019). This feedback mechanism can be an important factor in the enhancement of secondary aerosol mass loading (Wang et al., 2020). Long range transport is another important process influencing pollution levels. During polluted days in Beijing, air was mainly transported from the polluted areas in southern Hebei (Zhao et al., 2013; Zhang et al., 2014; Zhang et al., 2019a), and such regional transport dominated Beijing local emissions in terms of $PM_{2.5}$ contributions in the winter (Ge et al., 2018; Zhai et al., 2018). Lastly, climate change may increase the frequency of meteorological conditions conducive to pollution accumulation (Cai et al., 2017; Hong et al., 2019), but the influence is limited with emission controls (Shen et al., 2018).

According to model simulations, meteorology processes contributed 7.9%–42.6% to the incremental levels of $PM_{2.5}$ pollution in the BTH region (Bei et al., 2017; Xu et al., 2018). While the decreases in the annual mean $PM_{2.5}$ have been mainly contributed by reductions in anthropogenic emissions (Cheng et al., 2019; Vu et al., 2019; Zhai et al., 2019; Zhang et al., 2019c) as a result of the China Action Plan on Prevention and Control of Air Pollution, case studies have found that extreme pollution episodes are driven by meteorological conditions, and that the effects from emission controls on the extremely polluted days during 2013–2017 are relatively small (Zhang et al., 2018).

3 Progress in aerosol chemistry in haze formation over the BTH region

As shown in Fig. 2, there are two main chemical pathways forming secondary components in aerosol particles: photochemical reactions among gas phase species and aqueous phase reactions in cloud droplets or particles. At the initial stage of pollution, the photochemical reactions produce products of low volatility which dominate the formation of secondary components. As pollution level increases, the radiation intensity decreases by light scattering and probably absorption from high aerosol loadings, reducing the formation of gas phase photochemical oxidants. On the other hand, the increased relative humidity during pollution episodes enhances heterogeneous reactions in in aerosol particles. Thus, aqueous reaction may become the dominant process in secondary aerosol formation during heavy pollution episodes.

3.1 Gas phase reaction, nucleation and condensation

During photochemical reactions, gaseous precursors (SO_2, NO_x and VOCs) are oxidized by radicals (OH, HO_2, NO_3) and ozone. The photochemical process over the BTH region during winter haze episodes is effective since: 1) the atmosphere in Beijing during winter exhibits a strong oxidation capacity. The OH and HO_2 concentrations in Beijing have been reported to be 1.5×10^6 cm^{-3} and 0.3×10^8 cm^{-3}, respectively, during pollution episodes in winter (Ma et al., 2019). The total loss rate of the OH radical in winter in Beijing is comparable with peak values observed in summer (Lu et al., 2019) indicating high levels of winter OH reactivity. 2) Ozone photolysis is the main OH production pathway, and can be produced through the oxidation of VOCs and NO_x (Lu et al., 2018). 3) Photochemical aging of $PM_{2.5}$ in Beijing can contribute to the production of nitrous acid (HONO) (Bao et al., 2018; Qu et al., 2019; Zhang et al., 2019b). The photolysis of HONO is an important source of OH, especially during heavy haze episodes with elevated HONO concentrations (Ma et al., 2019).

The photochemical process always leads to products with higher oxidation states, e.g. H_2SO_4 and oxidized organic molecules. These gas phase oxidation products have lower volatilities and further transfer into the particle phase via two paths: nucleation occurring at the cluster size range (< 1 nm) and gas-particle partitioning (condensation) occurring in all particle size ranges.

Nucleation is the first step of new particle formation, in which the ~1 nm clusters are formed by hydrogen bonding of gaseous precursors under low level of pre-existing particles (Kulmala, 2003; Kulmala et al., 2013), and is considered to be one of the main sources of aerosol particles all over the world. H_2SO_4 formed by gas phase reaction of SO_2 and OH/Crigee radicals is thought to be the

most important precursor of nucleation (Kuang et al., 2008; Sipilä et al., 2010; Wang et al., 2011). In addition, the participation of other gaseous precursors, e.g. H_2O (Zollner et al., 2012), NH_3 (Xiao et al., 2015), dimethylamine (DMA) (Yao et al., 2018) and organic acids (Zhang et al., 2004), is essential to the efficient nucleation in polluted atmosphere in China (Wang et al., 2017). The oxidation products of VOCs emitted by vehicles also contribute remarkably to nucleation in atmosphere of Beijing (Guo et al., 2020). Heterogeneous nucleation between ions and gaseous molecules is found to have small contributions to the number concentrations of newly formed particles over Beijing (Jayaratne et al., 2017). The large number of nano particles formed through atmospheric nucleation can then grow into larger sizes through formation of secondary low volatility products which partition into the particulate phase and finally cause haze (Guo et al., 2014). During the beginning of particle growth and haze formation over urban atmosphere, the gas to particle partitioning of gas phase oxidation products is dominant (Qi et al., 2018). For example, the condensation of gaseous H_2SO_4 has been found contribute 19%–45% of particle phase sulfate mass, depending on the stages of new particle growth (Shao et al., 2019)

At the early stage of haze formation, SOA is formed by photochemical reaction of VOCs and further condensation of the oxidation products onto the particles. Good correlations (R^2 = 0.53–0.80) have been found between less oxidized oxygenated organic aerosols (LO-OOA) and odd oxygen ($O_x = O_3 + NO_2$) in the BTH region (Hu et al., 2017; Xu et al., 2017). Previous studies of photochemical reaction mechanisms of VOCs in the atmosphere only included products with a lower degree of oxidation. In recent years, highly oxygenated multifunctional organic molecules (HOMs) were observed in laboratory and atmospheric studies (Ehn et al., 2014; Mutzel et al., 2015). HOM compounds are formed by autoxidation of $\cdot RO_2$ radicals and can contribute to condensational growth and nucleation of particles (Riccobono et al., 2014).

For particulate nitrate, gas phase reaction between HNO_3 and NH_3 was thought as the main formation path in daytime (Wen et al., 2018), and the formation of NH_4NO_3 is highly dependent on temperature. During haze formation, higher levels of NH_3 and water vapor in the BTH region influence the thermodynamic equilibrium, and favor aqueous NH_4NO_3 formation (Liu et al., 2015). In addition, nitrate and SOA show gradual increasing trend during day time in winter in Beijing, indicating contributions from photochemical process and gas-particle partitioning at low temperatures (Sun et al., 2013b).

3.2 Heterogeneous reaction

The formation of SNA and SOA also occurs through heterogeneous processes, including the uptake of SO_2, NO_x and VOCs and other gaseous pollutants by cloud droplets ("in-cloud process") or particles ("heterogeneous process"), and then oxidation by H_2O_2, O_3 and NO_2 in aqueous phase (Zhu et al., 2011; Zhang et al., 2015a). According to recent studies in the BTH region, the uptake and oxidation process can occur rapidly in liquid water content of particles (LWCP) (Wang et al., 2016). During haze formation, relative humidity increases to over 60% to 80%, sub micrometer particles were deliquescent during heavy haze episodes, facilitating the mass transfer and multiphase reactions of the particles (Liu et al., 2017). The fractions of SOA, sulfate and nitrate in $PM_{2.5}$, sulfur and nitrogen oxidation ratios have positive correlations with relative humidity (RH), indicating aqueous reactions play important roles in secondary transformation in the BTH during winter haze formation (Sun et al., 2013a; Yang et al., 2015; Elser et al., 2016; Sun et al., 2016a; Wang et al., 2016; Hu et al., 2017). Due to the dependence on LWCP, the heterogeneous reactions occur mainly on larger particle size range (>100 nm).

For sulfate formation, the most important pathway is the oxidation of S(IV) in aqueous phase. Field measurements revealed that, at the accumulation stage of winter haze, RH increases to more than 60% to 80%, during which the aerosol particles deliquesce and shift from solid phase to liquid state thereby increasing LWCP (Liu et al., 2017). The phase change can further decrease the viscosity of particles and enhance the uptake of SO_2 and oxidizing agents. However, there is disagreement among studies about the main oxidizing agent during haze formation in the winter of BTH region. Some claim that the acidity of particles during aqueous reactions is close to neutral (pH = 5–6), and dissolved NO_2 (Cheng et al., 2016; Wang et al., 2016; Xue et al., 2016) is the main oxidizing agent for sulfate formation. On the other hand, some recent studies reveal that pH of particles is around 4–5 (Song et al., 2018). In this pH range, the oxidizing capacity of transition metal ions (TMIs) and O_3 can be stronger than that of NO_2 (Shao et al., 2019). Thus, SO_2 oxidation in aerosol water by O_3 catalyzed by TMI (Li et al., 2017a) and in-cloud reactions dominates sulfate production on polluted days, with a fractional contribution of up to 68% (He et al., 2018a; Shao et al., 2019). In addition, the levels of another oxidant, H_2O_2, during haze episodes have been found to be 0.90 parts per billion by volume (ppbv) (Ye et al., 2018), one order of magnitude higher than reported in previous studies (Cheng et al., 2016). Such high levels could be the result of heterogeneous formation involving NO_x (Qin et al., 2018). At H_2O_2 level of ~1 ppbv, the sulfate formation rate from the H_2O_2 oxidation pathway can be one order of magnitude higher than the rate from the NO_x oxidation pathway (Ye et al., 2018). Apart from inorganic sulfates, the concentration of particulate sulfur can also be partially explained by organic sulfates, e.g. hydroxymethansulfonic acid (HMSA) from HCHO and S(IV) reaction in cloud droplets (Moch et al., 2018; Song et al., 2019).

Heterogeneous reaction is also important for SOA

formation during haze episode in the BTH region. Model results show that heterogeneous HONO sources substantially enhance near-surface SOA formation by contributing to the OH radical level through its photolysis, increasing the regional average near-surface SOA concentration by about 46.3% during episodes. The uptake and hydrolysis of glyoxal and methylglyoxal in LWCP is another important pathway of SOA formation during haze formation, with the SOA contribution at 30.2% (Xing et al., 2019).

The heterogeneous formation of nitrate is mainly from the uptake and hydrolysis of N_2O_5 during nighttime (Liu et al., 2019b). Nighttime production of nitrate in air masses above urban Beijing (~200 m height) has been found to enhance its concentration at ground level by 28 μg/m^3 through vertical mixing (Wang et al., 2018), comprising of a 21.0% enhancement of nitrate (NO_3^-) through N_2O_5 hydrolysis and a 7.5% enhancement of ammonium (NH_4^+) (Su et al., 2017). The isotope analysis of $\Delta^{17}O$ in NO_3^- indicates that the nocturnal pathway is dominant (56%–97%) in the formation of nitrate during pollution process (He et al., 2018b).

The aqueous reactions and water content in particles have a positive feedback loop (Fig. 2). The increase in inorganic fraction and elevation of the oxidation state of organics in aerosol particles enhance the hygroscopicity and water uptake of particles, thus further promoting the aqueous reactions, resulting in more inorganic salt and SOA formation (Li et al., 2019b). Furthermore, the heterogeneous reactions between NO_2 and SO_2 in LWCP can form HONO, which would further generate hydroxyl radicals via photolysis, promoting photochemical reactions (Ge et al., 2019).

4 Challenges on aerosol chemistry of secondary formation

The studies on aerosol chemistry of haze formation in the BTH region have achieved substantive progress, but there are still many problems and unexplained phenomena that remain to be solved.

1) The unknown sources of strong oxidation capacity during polluted periods. Based on current mechanisms, the models can simulate the concentration of OH radicals during clean periods in winter, but underestimate the OH concentrations during polluted periods (Ma et al., 2019).

2) The ambiguous mechanisms of new particle formation in rural atmosphere. Due to limitation of observational data sets, the nucleation mechanisms including H_2SO_4 + DMA and H_2SO_4 + HOMs were only evaluated at a limited number of locations in the BTH region. The key precursors of the effective nucleation observed in the BTH regions remain unknown. Thus, continuous and comprehensive observations with full measurements of new particle formation parameters are needed.

3) The dominant roles of nitrate in pollution. Models, which are based on current mechanisms, are able to reproduce nitrate formation in clean and polluted period. However, the reasons of the explosive growth in particulate nitration concentrations during extreme pollution episodes still need to be understood. With continuing efforts in reducing SO_2 emissions, the concentrations of particulate sulfate have been decreasing in recent years. However, particulate nitrate concentrations have stayed at similar levels over the same period despite reductions in NO_x emissions, making it as the most important inorganic components in aerosols during pollution.

4) The different views on the main oxidation mechanisms of SO_2. Recent studies provided deeper understandings in sulfate formation by including heterogeneous reactions in LWCP. On the other hand, there are different views on the oxidation path. More studies are needed to distinguish the main oxidizing agents of SO_2 in liquid phase, among H_2O_2, transition medal, O_3 and NO_2, and to quantify their respective contributions.

5) The need to explore explicit molecular mechanisms of SOA formation. Aqueous formation of SOA is commonly considered to be important during haze formation, but this conclusion is based only on correlations between SOA concentration and RH (or LWCP). At the molecular level, current observations only find the higher O:C ratio of SOA during pollution period. Such observations can not provide detailed information on chemical reactions in aqueous formation of SOA.

5 Future outlook

5.1 Monitoring of key parameters

To meet the challenges of future aerosol chemistry studies on haze formation of BTH region, researchers need to be equipped with instruments that are able to measure additional important atmospheric parameters, such as the level of water contents in particles, H_2SO_4, HOMs, particle pH, etc. With precise and comprehensive data sets, researchers can work on the integration of different mechanisms, and find out the main pathway of SNA and SOA formations.

Such comprehensive measurements in atmosphere need to be conducted continuously in both urban and rural areas, so that researchers and policy makers can get reliable results on atmospheric chemistry, to analyze the outcomes of emission control policies (Kulmala, 2018).

5.2 Systematic understanding among different chemical and physical processes

In future studies, researchers must systematically consider the formation of different secondary aerosols in the real atmosphere. Recent studies indicate that the formation of

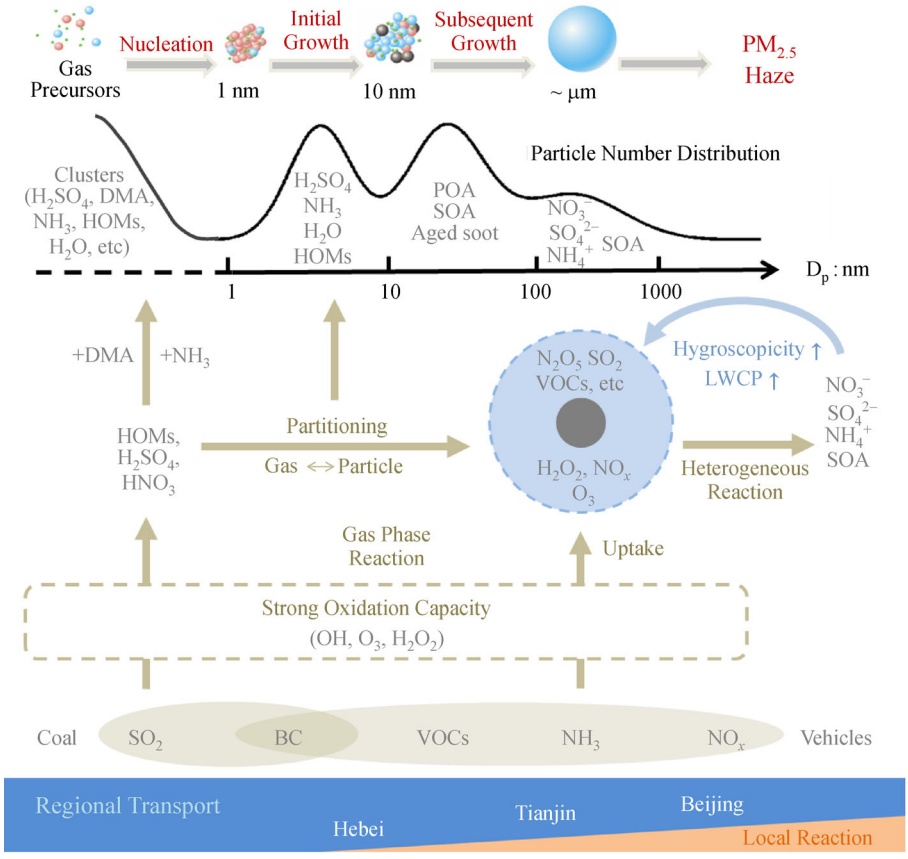


Fig. 2 Sketch map of secondary component formation by atmospheric aerosol chemical process.

SNA can enhance SOA formation during haze episode by increasing the LWCP and accelerating the uptake of VOCs on particle surface. However, the formation mechanisms of secondary components were treated separately in many previous model or laboratory studies, leading to a lack of understanding on the interactions among nitrate, sulfate and SOA formation.

Knowledge on such interactions may lay a foundation in guiding policy development. Because of the complex interactions among pollutants, the mitigation of particle pollution may have unforeseen consequences in other air pollution issues. For example, reduction of NO_x and NH_3 emissions can control secondary formation of aerosol particles, but may aggravate ozone pollution (Lu et al., 2019) and acid rain problems, respectively (Liu et al., 2019c). To achieve synergistic control of atmospheric pollutants, a comprehensive understanding of the atmospheric chemical reaction mechanism is required for effective control actions.

5.3 Quantifying the contribution of different pathway on secondary aerosol formation

Through studies conducted in recent years, researchers developed various mechanisms and characterized many parameters in aerosol chemistry during haze formation. However, there are still no consensual understandings about the relative contributions of different pathways of formation of secondary particulate components including SNA and SOA. One future task for the researchers is to integrate the mechanisms and parameters revealed in those separate studies into a comprehensive numerical model to quantify the contributions from the different pathways on SNA and SOA under certain atmospheric conditions.

5.4 Integrating measurement, laboratory and model techniques

To validate the mechanisms obtained from theoretical and laboratory studies for applications to real atmosphere, comprehensive measurements in the real atmosphere must be conducted to determine related precursor and product concentration levels. Closure studies must be done, by feeding the measured precursors into models equipped with various mechanisms, and see which mechanism can reproduce the measured products and particle properties.

Acknowledgements This research has been supported by the National Natural Science Foundation of China (Grant Nos. 91844301 and 91544214), National Research Program for Key Issues in Air Pollution Control (DQGG0103), National Key Research and Development Program of China

(No. 2016YFC0202000: Task 3). The authors want to thank Dr. Shaomeng Li for the language polishing, Nan Xu for data analysis support and Tianyi Tan for figure beautification. Xiangxinyue Meng provided the photos in the graphic abstract.

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