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Sulfur Dioxide Transported From the Residual Layer Drives Atmospheric Nucleation During Haze Periods in Beijing

Yonghong Wang[1,2,3], Yongjing Ma[4,5], Chao Yan[1,3], Lei Yao[1,3], Runlong Cai[1,3], Shuying Li[2], Zhuohui Lin[1], Xiujuan Zhao[6], Rujing Yin[7], Chenjuan Deng[7], Juha Kangasluoma[1,3], Xu-Cheng He[3], Simo Hakala[3], Xiaolong Fan[1,8], Siyu Chen[9], Qingxin Ma[2,8], Veli-Matti Kerminen[3], Tuukka Petäjä[3], Jinyuan Xin[5], Lin Wang[10], Baoxian Liu[11], Weigang Wang[12], Maofa Ge[12], Jingkun Jiang[7], Yongchun Liu[1], Federico Bianchi[3], Biwu Chu[2,8], Neil M. Donahue[13], Scot T. Martin[4], Hong He[2,8], and Markku Kulmala[1,3]

[1]Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing, China, [2]State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China, [3]Faculty of Science, Institute for Atmospheric and Earth System Research/Physics, University of Helsinki, Helsinki, Finland, [4]School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA, [5]Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China, [6]Institute of Urban Meteorology, China Meteorological Administration, Beijing, China, [7]School of Environment, Tsinghua University, Beijing, China, [8]Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China, [9]College of Atmospheric Sciences, Lanzhou University, Lanzhou, China, [10]Department of Environmental Science and Engineering, Fudan University, Shanghai, China, [11]Beijing Key Laboratory of Airborne Particulate Matter Monitoring Technology, Beijing Municipal Environmental Monitoring Center, Beijing, China, [12]Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, [13]Carnegie Mellon University Center for Atmospheric Particle Studies, Pittsburgh, PA, USA

Abstract New particle formation (NPF) is a global phenomenon that significantly influences climate. NPF also contributes to haze, with pronounced negative impacts on human health. Theory and observations both show that nucleation is favored during clean days and inhibited during haze episodes due to a high pre-existing condensation sink (CS). Here we show that the surprising occurrence of NPF during haze days in Beijing is associated with a high concentration of sulfuric acid dimers. With both field observations and model simulations, we demonstrate that downward mixing of sulfur dioxide (SO_2) from the residual layer aloft enhances ground level SO_2, which in turn elevates sulfuric acid dimer after rapid SO_2 oxidation in the polluted air. Our results address a key gap between the source of SO_2 and its atmospheric oxidation products during haze conditions in a megacity, Beijing, providing a missing link in a complete chain describing NPF in the polluted atmosphere.

Plain Language Summary New particle formation is a global phenomenon with notable effects on climate and health. Recent studies have argued that atmospheric nucleation during haze episodes with high aerosol loading should not occur. In spite of this, we have observed intensive nucleation events during haze episodes in Beijing and found an unexpected high concentration of sulfur dioxide (SO_2), along with a decreased condensation sink (CS) owing to the development of boundary layer. The SO_2 originates from emissions by tall stacks outside of Beijing and is subsequently transported downward from the morning residual layer to the surface, this contributes to peaks of SO_2 during the day. A decreased loss of sulfuric acid dimer owing to a decreased CS drives nucleation during haze episodes. As the phenomenon of a later morning SO_2 peak exactly coincide with nucleation has been widely reported in eastern China, we highlight the importance of emissions of SO_2 from tall smokestacks in atmospheric nucleation events.

Key Points:

- Sulfuric acid dimer is involved in new particle formation (NPF) events during haze episodes in Beijing
- Field observation and model simulation confirm downward mixing of sulfur dioxide from residual layer
- High formation rate of sulfuric acid dimer owing to a decreased condensation sink promotes NPF during haze

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

H. He, B. Chu and M. Kulmala,
honghe@rcees.ac.cn;
bwchu@rcees.ac.cn;
markku.kulmala@helsinki.fi

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Author Contributions:

Conceptualization: Yonghong Wang, Biwu Chu, Hong He, Markku Kulmala
Data curation: Yonghong Wang, Chao Yan, Rujing Yin, Chenjuan Deng, Juha Kangasluoma, Weigang Wang, Jingkun Jiang, Yongchun Liu, Federico Bianchi, Biwu Chu

1. Introduction

China has made great progress in mitigating fine particulate matter ($PM_{2.5}$) pollution since 2013 as a consequence of clean air policies (Ding et al., 2019; Y. Wang et al., 2020; Zhang et al., 2019; Zheng et al., 2018). For instance, the average annual $PM_{2.5}$ concentration in 338 cities of China was approximately 90 μg/m^3 in 2013 and dropped to 32 μg/m^3 in 2020. However, the level is still unhealthy as suggested by the World Health Organization (WHO) annual mean $PM_{2.5}$ target of 5 μg/m^3. New particle formation (NPF) during clean days may initiate haze formation under stagnant weather conditions by providing most of the aerosol surface area as seed for

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Investigation: Yonghong Wang, Chao Yan, Zhuohui Lin, Rujing Yin, Chenjuan Deng, Juha Kangasluoma, Xu-Cheng He, Xiaolong Fan, Yongchun Liu, Federico Bianchi, Biwu Chu
Methodology: Lin Wang, Jingkun Jiang, Markku Kulmala
Project Administration: Chao Yan, Yongchun Liu
Resources: Jinyuan Xin, Lin Wang, Weigang Wang, Maofa Ge, Jingkun Jiang, Yongchun Liu, Federico Bianchi, Hong He, Markku Kulmala
Software: Yongjing Ma, Simo Hakala, Scot T. Martin
Supervision: Veli-Matti Kerminen, Tuukka Petäjä, Neil M. Donahue, Hong He, Markku Kulmala
Validation: Baoxian Liu
Visualization: Yonghong Wang, Shuying Li, Zhuohui Lin
Writing – original draft: Yonghong Wang
Writing – review & editing: Yongjing Ma, Neil M. Donahue

haze (Guo et al., 2014). In addition, it is commonly accepted that a high aerosol loading, which results in a high condensation sink (CS), is the key factor for suppressing nucleation in polluted environments, as newly formed clusters will be rapidly scavenged by high concentrations of pre-existing aerosol particles (Cai et al., 2017; Guo et al., 2020; Kulmala et al., 2021). As a consequence, NPF is not expected to happen during haze. In spite of this, NPF events are frequently observed in Chinese megacities (e.g., Beijing, Shanghai, Nanjing and Guangzhou) (Chu et al., 2019; Deng et al., 2020; Qi et al., 2015; Wu et al., 2007; S. Xiao et al., 2015; Yue et al., 2013). Most of those studies focused on resolving the underling nucleation mechanism in the urban boundary layer. For example, a nucleation mechanism of sulfuric acid and stabilizing base compound (mainly dimethylamine, DMA) was proposed based on field measurements in Shanghai and Beijing (Cai et al., 2021; Yan et al., 2021; Yao et al., 2018), and the mechanism was confirmed in laboratory experiments with a suite of anthropogenic organic vapors (M. Xiao et al., 2021). A measurement campaign in Barcelona showed sulfuric acid—DMA nucleation but the involvement of oxygenated organic molecules could not be excluded (Brean et al., 2020). A laboratory study showed that low volatility organic vapors from vehicle emissions, rather than sulfuric acid, could be the governing component of NPF in urban Beijing (Guo et al., 2020). As this apparently contradictory literature shows it is still not known why nucleation can be observed at all under high aerosol loadings. The driving factors of the variation of vapors involved in nucleation in Beijing remains a challenge.

Diurnal boundary layer ventilation is a classic air pollution phenomenon, and studies indicate that ground-level pollution can alter the boundary layer dynamics and inhibit dilution (Petäjä et al., 2016). Primary pollution tends to be worse at night when the mixing height is low and less severe in the afternoon when the mixing height is high, which is why the morning rush hour is typically much more pronounced than the evening rush hour in time traces of pollutants such as elemental carbon and nitrogen oxides (Y. H. Wang et al., 2014). This often extends to new-particle formation because that same ventilation can dilute overall $PM_{2.5}$ and thus the CS, reducing the loss rate of vapors associated with NPF such as sulfuric acid, increasing their steady state concentrations, and so greatly increasing the particle formation rate, which typically scales as square of the sulfuric acid concentration (Dunne et al., 2016). However, sulfuric acid and nucleated clusters are both secondary pollutants, formed via chemistry in the atmosphere, and their concentrations and rates depend on a balance between their production and loss. In this case, mixing from above is not necessarily just a sink, but instead it can be a source of precursor vapors as well. Here, we report on intensive new-particle formation events during haze episodes in Beijing driven by vertical sulfur dioxide (SO_2) transport from the nocturnal residual layer (the "left over" portion of the boundary layer from the day before), which makes vertical mixing as a consequence of boundary layer development a source for both SO_2 and ultimately for particle formation.

2. Methodology

2.1. Observation Site and Instruments

Our measurements were conducted between 1 March 2018 and 30 April 2018 at the roof top of the university building at the west campus of Beijing University of Chemical Technology (39.95°N, 116.31°E). The station is located about 150 m away from the nearest road (Zizhuyuan road) and 500 m away from the West Third Ring Road, and it is surrounded by commercial properties and residential dwellings representative of an urban environment (Liu et al., 2020). The instruments and calculating methods are presented in Supporting Information S1.

2.2. Model Description

Dutch Atmospheric Large-Eddy Simulation (DALES) is a turbulence-resolved model that was originally developed since 40 years ago (Nieuwstadt & Brost, 1986). Based on the assumption of the Boussinesq approximation, DALES uses the filtered Navier-Stokes equation to resolve the filtered-scale turbulence and one-and-a-half-order closure scheme to parameterize the sub-filter-scale motions. DALES is able to simulate the complex boundary-layer motions in the closed radiation-surface-atmosphere system. The model was used to simulate the vertical transport of SO_2 in the study. The detailed settings of the model can be found in supporting information and (Ma et al., 2020).

3. Results and Discussion

3.1. Observed Intensive NPF Events During Haze

Our measurements were conducted in downtown Beijing from 1 March to 30 April 2018 (See Methods); frequent nucleation events occurred even during haze episodes. A total of 36 out of 61 days were NPF event days, and

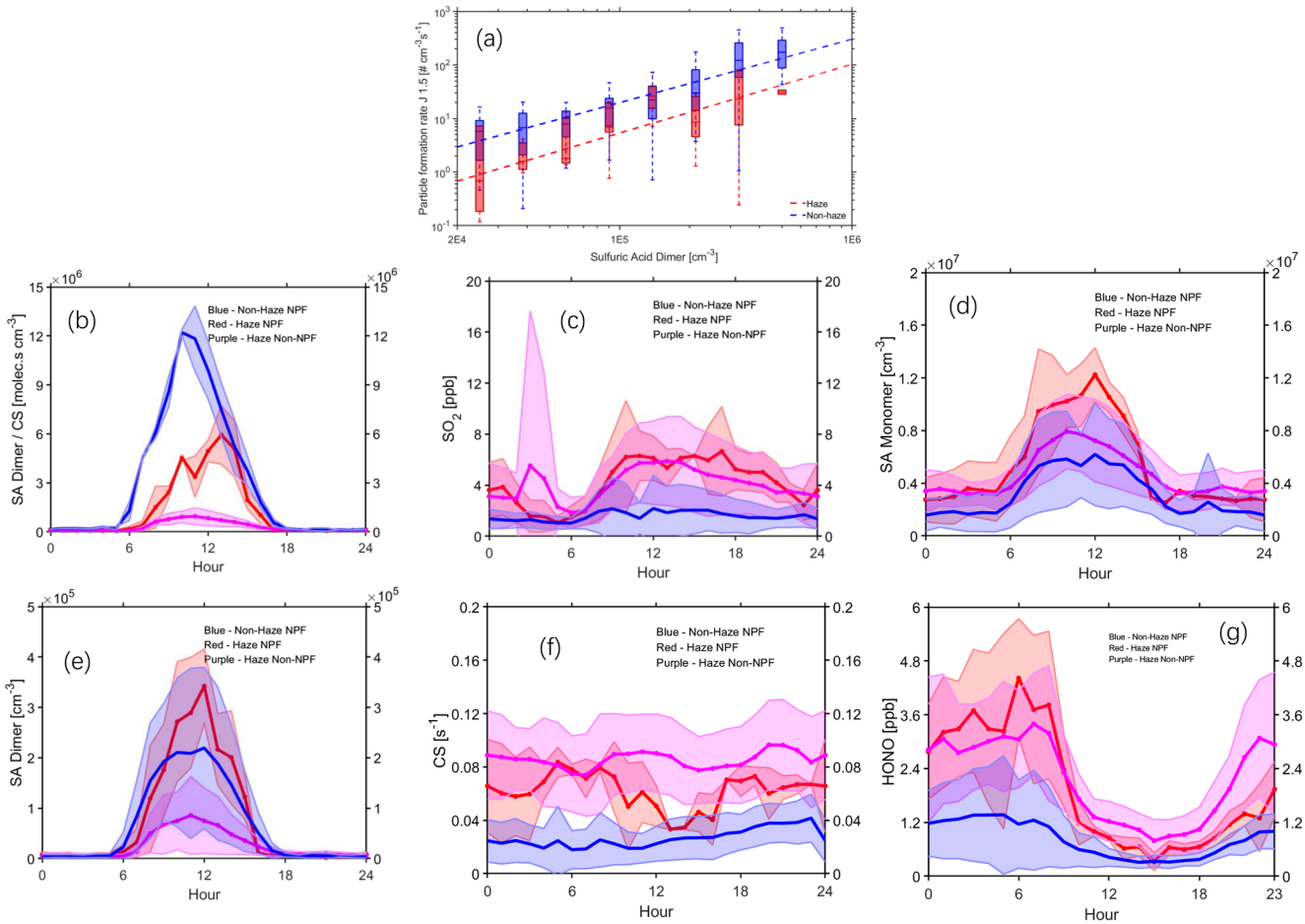

Figure 1. Factors governing observed dependency of particle formation rate $J_{1.5}$ on sulfuric acid dimer. (a) The observed dependency. The blue bars denote statistics of particle formation rates at a certain sulfuric acid dimer concentration during non-haze days, while the red bar denotes statistics of particle formation rates at the same sulfuric acid dimer concentration during haze days. The blue dashed line and red dashed line are fitted according to averaged particle formation rate versus sulfuric acid dimer concentration. The gray dashed line is a 1:1 slope, indicating a first-order dependence of $J_{1.5}$ on sulfuric acid dimer. High haze suppresses $J_{1.5}$ by roughly a factor of 3 due to decreased particle survival. The definition of haze is based on the concentration of $PM_{2.5}$, a day is defined as a haze day if the hourly $PM_{2.5}$ mass concentration is larger than 75 μg m^{-3}. Averaged diurnal variation of (b) the ratio of sulfuric acid dimer with condensation sink (CS) (c) sulfur dioxide concentrations (d) sulfuric acid monomer (e) sulfuric acid dimer (f) CS (g) HONO concentrations separated by different conditions according to the definition of haze and New particle formation event. The shaded areas denote one standard deviation.

seven of these NPF events occurred during haze episodes (see extend Figure S1 in Supporting Information S1). Overall, we classify these 36 NPF events into seven haze-NPF and 29 non-haze-NPF events, with a further 12 days during haze episodes without NPF that we classify as haze-non-NPF events.

Figure 1a presents the relationship between the measured particle formation rate ($J_{1.5}$) and the measured sulfuric acid dimer concentration during both haze-NPF and non-haze-NPF periods. $J_{1.5}$ is more strongly associated with the sulfuric acid dimer concentration than with the sulfuric acid monomer concentration (Extended Figure S2 in Supporting Information S1), and the association is approximately 1:1 in a log-log space (first order) as shown with the dashed gray line in Figure 1a; this is consistent with other observations during non-haze NPF events in Beijing and Shanghai (Cai et al., 2021; Yan et al., 2021; Yao et al., 2018). At any given sulfuric acid dimer concentration, $J_{1.5}$ is lower during haze-NPF events than during non-haze-NPF events; this is consistent with the higher CS during haze episodes reducing the survival probability of particles as they grow from dimers to 1.5 nm. Coagulation scavenging associated with the high CS is the dominant removal pathway for sulfuric acid dimer-base clusters (Cai et al., 2021). Previous studies have revealed that a sulfuric acid dimer-base cluster is formed from a sulfuric acid monomer associated with an amine monomer which then quickly stabilizes via addition of another sulfuric acid monomer (Cai et al., 2021; Petäjä et al., 2011; Yan et al., 2021; Yao et al., 2018). Thus, the measured sulfuric acid dimer is a charge separated sulfuric acid dimer-base (mainly amine) cluster before

being detected by the NO_3^--CI-APi-ToF. During ionization the NO_3^- serves as a strong base, so the stabilizing base in the ambient neutral clusters typically evaporates from the cluster before detection (see Method) (Almeida et al., 2013; Kurtén et al., 2011).

We show the balance of the production and loss of sulfuric acid dimer is the key to understanding nucleation during haze periods. This is reflected by the ratio of sulfuric acid dimers to the CS plotted in Figure 1b, separated into the three event classifications. The key feature is a high dimer/CS during NPF, with or without haze, and a low dimer/CS without NPF. The dimers form from collisions of monomers while they are lost to evaporation, the condensation (really coagulation) sink and growth toward new particles. Specifically, we can define the "apparent loss rate coefficient" as below:

$$k_{\mathrm{al}} = \left(\frac{[\mathrm{SA}]^2}{[\mathrm{dim\,er}]}\right) \cdot k_{\mathrm{collision}}$$

The parameter $k_{\mathrm{collision}}$ is the collision rate coefficient of sulfuric acid monomers with each other. We assume a value of 3×10^{-10} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ (Li et al., 2018). For a sulfuric acid monomer concentration of 1×10^7 molecule $\mathrm{cm^{-3}}$ and a dimer concentration of 3×10^5 molecule $\mathrm{cm^{-3}}$, the value of k_{al} is 0.1 $\mathrm{s^{-1}}$. The other sink for sulfuric acid dimer is coagulation with larger particles (the CS). During the measurements, the CS for sulfuric acid monomer varied between 0.01 and 0.25 $\mathrm{s^{-1}}$, but the CS for the dimers is anticipated to be slower than the monomer by nearly a half due to the larger cluster size and mass than the sulfuric acid monomer (Tuovinen et al., 2021). Evaporation is the dominant sink for dimers during clean periods (CS < 0.05 $\mathrm{s^{-1}}$). An increased effective collision of dimers with larger particles during haze makes coagulation loss of dimer as important as evaporation loss, which explains the dramatic decrease of dimers during haze seen in Figures 1a and 1b (Cai et al., 2021).

The corresponding daily profiles of SO_2, sulfuric acid monomer, sulfuric acid dimer concentrations and the CS are shown in Figure 1c–1f, respectively. While these also make sense in the context of the event classifications, none associates with NPF as profoundly as the dimer/CS relation in Figure 1b. The daytime SO_2 concentration during haze-NPF is comparable with that during haze-non-NPF, but the corresponding differences in the sulfuric acid monomer and dimer concentration are significant owing to a lower CS shown in Figure 1f and a higher atmospheric oxidation capacity in haze-NPF. A major OH source is HONO photolysis, and the HONO concentration shown in Figure 1g is higher during NPF events, even during the day, than during non-event days. The rapid photolysis of HONO produces more OH during the haze-NPF days than during haze-non-NPF days; this elevated OH, along with decreased CS, results in a much higher production rate of sulfuric acid and subsequently sulfuric acid dimers. The decrease of CS during 9:00–15:00 is owing to the increase of boundary layer height (BLH) as shown in Figure S3 in Supporting Information S1.

The phenomenon of an SO_2 peak at noon or in the later morning has been reported over both the North China Plain and the Yangtze River Delta Region, but the mechanism was attributed to diverse factors and not fully explored (A J Ding et al., 2013; Huang et al., 2020; Xu et al., 2014; L. Yang et al., 2021). SO_2 in China is predominately emitted by tall smokestacks of coal burning for steel making and electricity generation (Lu et al., 2010). The SO_2 concentration has decreased significantly in Beijing since 2013 as a consequence of the clean air policies (Y. Wang et al., 2020). In addition, SO_2 emissions from domestic heating was eliminated in Beijing after 15 March 2018. Therefore, local emissions did not build up ground-level SO_2 at our station during this measurement campaign.

3.2. Exemplary Haze-NPF Event

We presented three haze-NPF events described above in Figure 2, Figures S4 and S5 in Supporting Information S1, respectively. In particular, the mechanism behind the phenomenon for an exemplary haze-NPF event on 24 March was detailed in Figure 2. Vertical aerosol measurements from a ceilometer shown in in Figure 2a reveal that air pollutants (mainly aerosols) were concentrated within 300 m above the surface. March 23 was a haze non-NPF day with a maximum hourly averaged $PM_{2.5}$ concentration of about 182 $\mu g/m^3$. NPF started at around 08:00 (local time) on 24 March, with a $PM_{2.5}$ concentration of 188 $\mu g/m^3$ and a corresponding CS of 0.1 $\mathrm{s^{-1}}$, making this a haze NPF day. Measurements of particle formation rates showed low values of 3–27 $\mathrm{cm^{-3}\ s^{-1}}$ while the CS was as high as 0.13 $\mathrm{s^{-1}}$ during the early NPF period from 08:00–10:00 in the morning. The surface wind

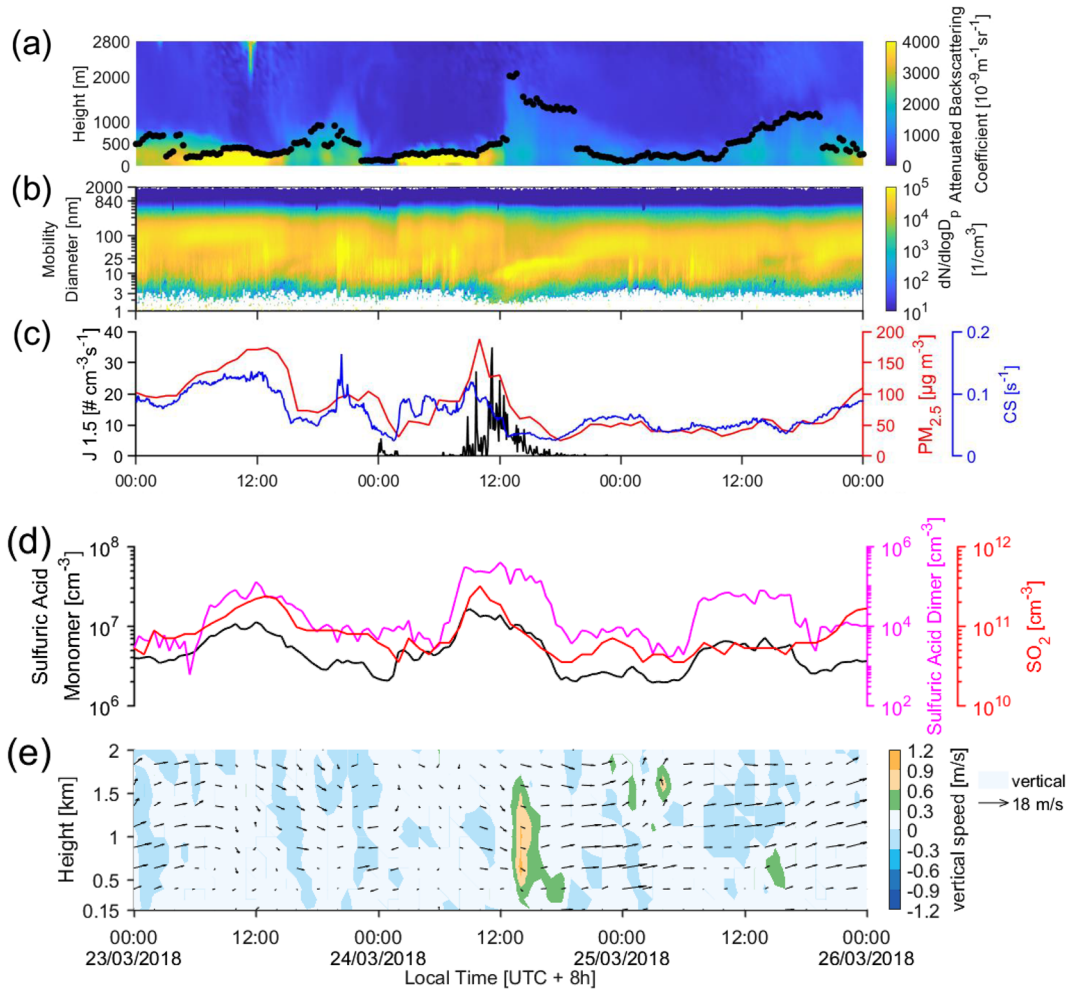

Figure 2. Analysis of an exemplary haze-NPF event. (a). Time series of (a) attenuated backscattering coefficient and boundary layer height (b) particle number concentration distribution from 1 to 2,000 nm (c) particle formation rate $J_{1.5}$, condensation sink and $PM_{2.5}$ mass concentration (d) sulfuric acid monomer, dimer and sulfur dioxide concentrations (e) vertical and horizontal wind speed and wind direction from 23 March to 25 March 2018, the warm colors (positive values) denote the vertical winds blowing from lower levels to upper levels. These parameters show new particle formation during an intensive haze day on 24 March 2018.

speed was generally low as shown in Figure 2e. In addition, both $PM_{2.5}$ mass and sulfuric acid dimer concentrations increased rapidly as the NPF proceeded. The maximum concentrations of SO_2, sulfuric acid monomer and dimers were 14.0 ppb, 1.6×10^7 cm^{-3} and 3.9×10^5 cm^{-3}, respectively, which are higher values than previous reported during nucleation in Beijing and Shanghai (Cai et al., 2021; Deng et al., 2020; Yan et al., 2021; Yao et al., 2018). These concentrations increased concurrently as NPF proceeded. All these characteristics clearly show nucleation taking place during a haze event.

3.3. Downward-Mixing of SO_2 in the Morning From the Residual Layer Aloft

Vertical transport of aerosol and gas vapors from the upper boundary layer contributes to ground-level aerosols over the continental boundary layer (Chen et al., 2009; Lampilahti et al., 2021; Y. Liu et al., 2021; J. Wang et al., 2016; Wehner et al., 2010). Frequent occurrences of higher SO_2 aloft have been reported in Beijing (Du et al., 2021; S. Yang et al., 2009). Our simultaneous measurement of SO_2 on a 325-m meteorology tower to the north of central Beijing shows that the SO_2 concentration was higher at 280 m than that at 160 m (see Extend Figure S6 in Supporting Information S1). This is because SO_2 emissions are predominately from tall smokestacks with a height of more than 120 m, which then form plumes that dilute and rise with atmospheric processes.

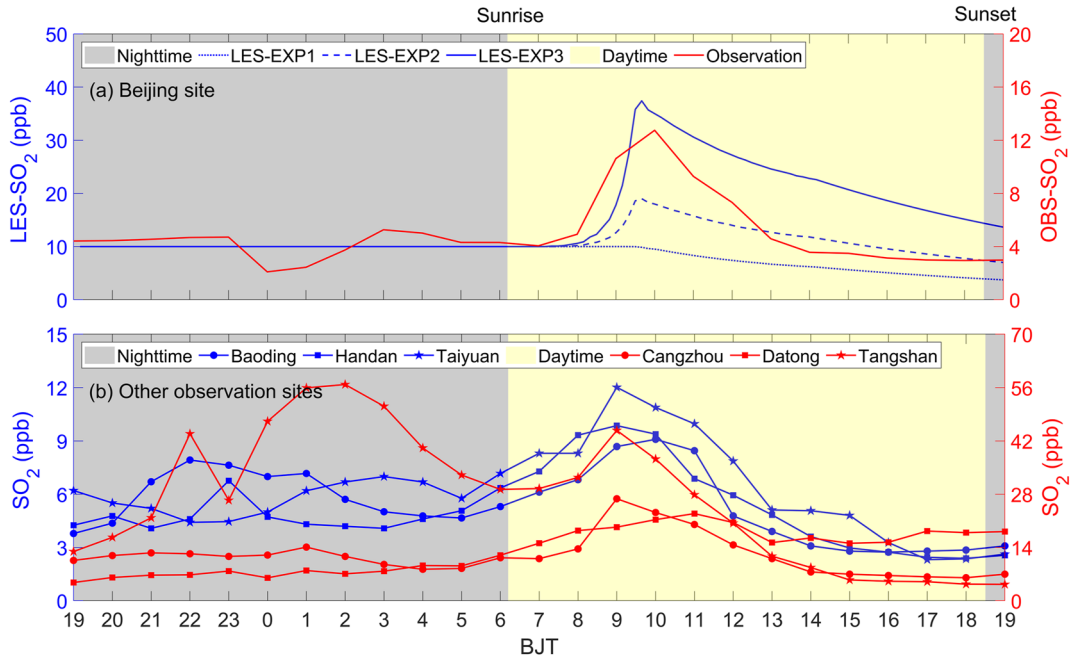

Figure 3. Comparison of large eddy simulations of vertical sulfur dioxide (SO_2) transport with regional observations during a haze-NPF event between 19:00 23 March 2018 and 19:00 24 March 2018. (a) Modeled and observed SO_2 on the surface ground in Beijing. Three simulations have different initial conditions, all with 10 ppb at the surface but with 10, 20 and 40 ppb aloft in the residual layer, as indicated. The red line is the average of the Beijing sub-observation sites. (b) Averages of daily SO_2 variation at regional observation sites as indicated, all showing a 10:00 SO_2 peak similar to the peak in Beijing. A well-mixed residual layer with a constant 293.22 K is prescribed from 110 to 910 m based on the observation of Ceilometer CL51 (see extended material) for all three simulations. Only the elevated residual layer simulations reproduce the observed peak SO_2 at 10:00, with 2 time and 4 times enhancement bracketing the observations. Noting that with limited information about vertical profile of SO_2 and temperature (an inversion layer is always favored during haze), the modeled SO_2 variation pattern cannot match exactly with observations on the surface ground.

During the haze event shown in Figure 2, air containing high SO_2 was trapped in the residual layer after sunset on 23 March as decreased solar heating and increased infrared cooling at the ground drove formation of a nocturnal boundary layer. We used the DALES model (Heus et al., 2010; Ma et al., 2020) constrained by our measurements to simulate the vertical distribution of air pollutants during this event. Based on the measured vertical inhomogeneous distribution of air pollutants, we initialized the model with SO_2 enhanced in the residual layer by a factor of 2–4 compared to the surface. With this initialization, the model reproduced the observed SO_2 behavior with a sharp peak near 10:00, as shown in Figure 3. A simulation without the vertical SO_2 gradient did not reproduce this behavior. Measurements of SO_2 at ground level on 24 March at 48 stations in Beijing, Baoding, Handan, Cangzhou, Datong, Tangshan and Taiyuan all simultaneously showed the SO_2 concentration peaking at around 10:00 (see Extended Figure S7 in Supporting Information S1), indicating a regional phenomenon. Noting that high SO_2 concentrations sustained at ground level after noontime as presented in Figure 1c, which was the time when the convection mixed layer already well developed and occupied the residue layer. Thus, it is possible that the SO_2 during this time period is because the emissions from tall smokestacks mixed downward due to the intensive vertical mixing in the mixed layer.

3.4. The Origin of Air Masses Driving NPF During Haze

With the Lagrangian particle dispersion model FLEXPART (FLEXible PARTicle dispersion model, see Methods), we further show that air masses coming to Beijing are mainly from south-west with more emissions during haze non-NPF, while the air masses from north-east and south-west are comparable during haze-NPF. This demonstrated air masses from south-west during haze non-NPF suppressed NPF owing to a higher CS (see Extend Figure S8 in Supporting Information S1). This is in line with our surface wind direction measurements during 06:00–12:00 as presented in Figure S9 in Supporting Information S1. The air masses from the south-west

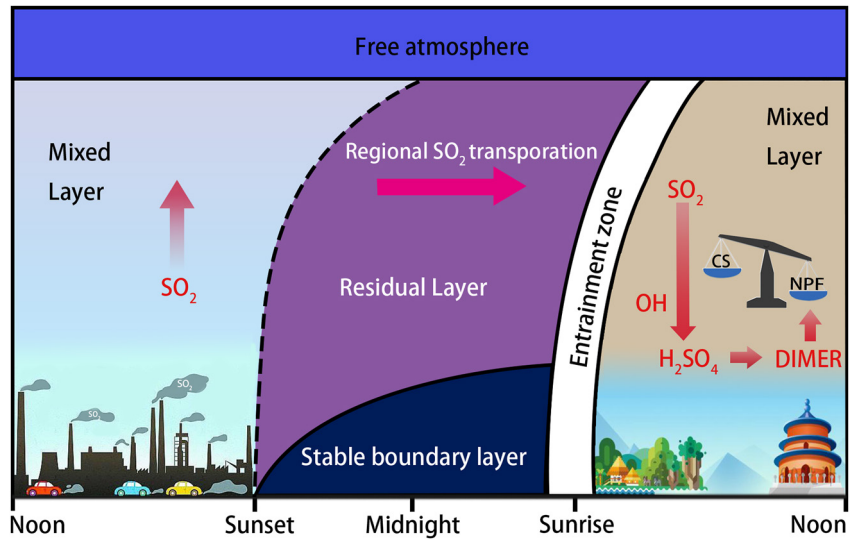

Figure 4. Schematic picture of new particle formation (NPF) in Beijing. A residual layer forms at sunset, trapping sulfur dioxide (SO_2) aloft over industrial regions with high smokestacks. Transport of SO_2 from surrounding regions to Beijing in the residual layer during the night is followed by downward mixing of high SO_2 air after sunrise during entrainment of the residual layer and mixing layer growth. NPF is enhanced by sulfuric acid formed from elevated OH and rapid SO_2 oxidation despite the high condensation sink.

are usually from megacity areas of the North China Plain, containing high concentrations of SO_2, aerosol particles, other pollutants and water vapor. In addition, the topography of Beijing, with Taihang Mountain to the west and Yan Mountain to the north (much like Los Angeles), inhibits the horizontal dispersion of air pollutants (An et al., 2019). As a consequence, air pollutants accumulate, and secondary aerosol formation is enhanced. The air masses from the north originate in desert areas and contain high concentrations of dust and some other pollutants. However, low relative humidity and strong winds do not favor secondary aerosol formation, but rather accelerate vertical mixing of air owing to a higher solar radiation associated surface heating (see Extend Figures S10 and S11 in Supporting Information S1).

4. Conclusion

In summary, we show that downward mixing of high SO_2 air from the morning residual layer to the surface is a key process leading to atmospheric nucleation during haze episodes. The origin of air mass determines the production and loss of sulfuric acid dimer clusters mediated by the coagulation sink. Overall, sulfuric acid dimers drive nucleation in Beijing. The whole process is summarized in Figure 4, where high concentrations of SO_2 originating from tall smokestacks outside of Beijing and transported by prevailing winds contribute to the haze event and the high SO_2 containing air is trapped in the residual layer after sunset. As the sun rises and surface heating is increased, the nocturnal residual layer is ventilated by vertical mixing and SO_2 is transported to the ground level gradually. The SO_2 and other pollutants on the surface, together with local air pollutants, comprise a processed chemical cocktail. As the condensation and coagulation of nucleated clusters by pre-existing aerosol (represented by CS) is less efficient than the production of sulfuric acid dimer clusters, nucleation can take place. However, if the air masses contain higher loadings of aerosols with more local production of secondary aerosol matter, nucleation is suppressed. Given the large reductions of emissions in China since 2013, a further emission reduction from those tall smokestacks is difficult even with the strictest emission standards in the world (https://www.greenpeace.org/static/planet4-mena-stateless/a372e5fe-so2-report-english.pdf). Meanwhile, China has articulated a goal to have carbon dioxide emissions peak before 2030 and to achieve carbon neutrality before 2060. Considering that both CO_2 and SO_2 are predominantly emitted from coal burning, we suggest that clean energy with low emissions of both pollutants should be used, as only this with decrease both the frequency of NPF and the emissions of carbon dioxide. As a consequence, particulate matter pollution, together with global warming, could be mitigated, with corresponding significant reductions in both local and global environmental (and human health) damages.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The data presented are available at ZENODO (https://zenodo.org/record/7344310#.Y3weUXZBwuU) with the https://doi.org/10.5281/zendo.7344310.

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