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Formation of Nighttime Sulfuric Acid from the Ozonolysis of Alkenes in Beijing

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Abstract. Gaseous sulfuric acid (SA) has received a lot of attention for its crucial role in atmospheric new particle formation (NPF), and for this reason, studies until now have mainly focused on daytime SA when most NPF events occur. While daytime SA production is driven by SO_2 oxidation of OH radicals from photochemical origin, the formation of SA during night and its potential influence on particle formation remains poorly understood. Here we present evidence for significant nighttime SA production in urban Beijing during winter, yielding concentrations between 1.0 and 3.0×10^6 cm^{-3}. We found a high frequency (~ 30%) of nighttime SA events, which are defined by the appearance of a distinct SA peak observed between 20:00 and 04:00 local time, and with the maximum concentration exceeding 1.0×10^6 cm^{-3}. These events mostly occurred during unpolluted nights with low vapor condensation sink. Furthermore, we found that under very clean conditions (visibility > 16.0 km) with abundant ozone (concentration > 2.0×10^{11} cm^{-3}, ~ 7 ppb), the overall sink of SA was strongly correlated with the products of O_3, alkenes and SO_2 concentrations, suggesting that the ozonolysis of alkenes played a major role in nighttime SA formation under such conditions. This is in light with previous studies showing that the ozonolysis of alkenes can form OH radical and stabilized Criegee intermediate (sCI), both of which are able to oxidize SO_2 leading to SA formation. However, we also need to point out that there exist additional sources of SA under more polluted condition, which are not investigated in this study. Moreover, there was a strong correlation between SA concentration and the number concentration of sub-3 nm particles in both clean and polluted nights. Different from forest environments, where oxidized biogenic vapors are the main driver of nighttime clustering, our study demonstrates that the formation of nighttime cluster mode particles in urban environments is mainly driven by nighttime SA production.

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1. Introduction

Atmospheric aerosol particles have considerable impact on global climate by directly affecting the radiation balance of the earth and by indirectly acting as cloud condensation nuclei (Stocker et al., 2014). The number concentration of these aerosol particles depends to a large extent on the atmospheric new particle formation (NPF), which includes gas-phase nucleation and subsequent growth of newly formed particles. Studies over the past twenty years have shown that the SA is the major gaseous precursor of NPF in most environments inside the continental boundary layer. Sulfuric acid driven NPF can proceed as SA-water binary nucleation, SA-water-ammonia ternary nucleation (Kirkby et al., 2011), SA-amine-water nucleation (Almeida et al., 2013;Kuerten et al., 2014), SA-organics nucleation (Riccobono et al., 2014), and SA-organics-amonia nucleation (Lehtipalo et al., 2018) and H_2SO_4-H_2O-NH_3-amine nucleation (Myllys et al., 2019). Both the nucleation rate (J_{nuc}) and the initial growth rate of newly formed particles tends to have a power-law relationship with the SA concentration: $J_{nuc} = k \times SA^{\alpha}$, where the activation nucleation is dominant when $\alpha \approx 1$ (Kulmala et al., 2006), the kinetic nucleation is dominant when $\alpha \approx 2$ (Riipinen et al., 2007;Paasonen et al., 2009;Erupe et al., 2010) and the thermodynamic nucleation becomes more crucial when α is larger than 2.5 (Wang et al., 2011).

Due to the importance of SA for NPF, accurate and reliable measurement of SA is of great importance. Up to now, ambient SA concentrations have been reported for many sites (Weber et al., 1997;Weber et al., 1998;Weber et al., 1999;Paasonen et al., 2010;Jokinen et al., 2018;Fiedler et al., 2005;Eisele et al., 2006;Boy et al., 2008;Iida et al., 2008;Wang et al., 2011;Kuerten et al., 2016;Yao et al., 2018;Mauldin et al., 2001). These studies indicate that the concentration level of SA in the atmosphere is closely related to human activities. In general, daytime SA concentration is around 10^5 cm^{-3} in pristine Antarctica region (Mauldin et al., 2001), 10^6 cm^{-3} in remote continental, remote marine and forest regions (which are less affected by human activities) and 10^7 cm^{-3} in urban and rural agricultural lands (which are influenced dominantly by human activities). SA generally shows a distinct diurnal pattern correlating with radiation (Lu et al., 2019) with typical concentrations between 10^6 to 10^7 cm^{-3} during daytime and 10^4 to 10^6 cm^{-3} during nighttime. The seasonal variation of SA is only reported in very few studies, showing higher concentrations during spring and summer than in winter and autumn (Erupe et al., 2010).

Due to the strong connection between SA and NPF, previous studies mostly focused on understanding the SA formation in the daytime. However, recent observation on the formation of sub-3 nm particles have shown that these cluster mode particles also exist with high concentration during the night (Junninen et al., 2008;Lehtipalo et al., 2011;Kulmala et al., 2013;Kecorius et al., 2015;Mazon et al., 2016) and sometimes even nighttime particle nucleation events can be clearly distinguished. In boreal forest environments, nighttime cluster formation can be attributed to highly oxygenated organic molecules (HOMs) (Kammer et al., 2018;Rose et al., 2018). However, the sources of SA and its role in the particle formation during the nighttime remain largely unresolved, both of which are the focus of this work. In this study, we show frequent and noticeable increase of SA during the nighttime in urban Beijing. We further investigate the main sources of SA and demonstrate its role in the nocturnal formation of sub-3nm clusters.

2. Nighttime Sulfuric Acid Formation

During the daytime, gaseous SA is primarily a photochemical product, generated from the oxidation of SO_2 by OH radical, while at nighttime, SA is highly associated with non-photochemical oxidants, most likely non-photochemical OH radical and stabilized Criegee intermediate (sCI) (Mauldin et al., 2012;Taipale et al., 2014). The non-photochemical oxidation pathway mainly includes the following five reactions. First, the production of (stabilized) Criegee Intermediates by the ozonolysis of alkenes:

$$\mathrm{Alkene} + \mathrm{O_3} \xrightarrow{k_1} \varphi \mathrm{sCI} + (1-\varphi)\mathrm{CI} + \mathrm{RCHO} \qquad \mathrm{R1}$$

Then, the direct oxidation of SO_2 by long lived sCI:

$$\mathrm{sCI} + \mathrm{SO_2} \xrightarrow{k_2} \mathrm{SO_3} + \mathrm{RCHO} \qquad \mathrm{R2}$$

Or the alternative oxidation of SO_2 by OH radicals formed from decomposition of (stabilized) Criegee Intermediates:

$$\mathrm{sCI} \xrightarrow{k_3} \cdot \mathrm{OH} + \mathrm{R_1COR_2} \qquad \mathrm{R3}$$

$$\mathrm{CI} \xrightarrow{k_4} \cdot \mathrm{OH} + \mathrm{R_1COR_2} \qquad \mathrm{R4}$$

$$\mathrm{SO_2} + \cdot \mathrm{OH} + \mathrm{O_2} \xrightarrow{k_5} \mathrm{HO_2} \cdot + \mathrm{SO_3} \qquad \mathrm{R5}$$

where k_i is the rate constant of each reaction, φ is the yield of sCI in the ozonolysis of alkenes, and CI is the chemically activated Criegee intermediate. Currently, only limited types of sCI has been studied: isoprene-derived sCI (Neeb et al., 1997;Zhang et al., 2002;Atkinson et al., 2006;Newland et al., 2015b), monoterpene-derived sCI (Hatakeyama et al., 1984;Rickard et al., 1999;Zhang and Zhang, 2005;Mauldin et al., 2012;Sipila et al., 2014;Vereecken et al., 2017) and the simplest sCI including CH_2COO, CH_3CHOO and $(CH_3)_2COO$ (Hatakeyama et al., 1984;Hasson et al., 2001;Welz et al., 2012;Taatjes et al., 2013;Welz et al., 2014;Newland et al., 2015a;Vereecken et al., 2017). Based on the aforementioned studied, the yield φ of sCI can vary from 0.1 to 0.65 and the rate constants for different reactions span over several orders of magnitude, for k_1 from 1.6×10^{-18} to 2.5×10^{-16} $\mathrm{cm^3 s^{-1}}$ and for k_2 from 1.4×10^{-13} to $2.2 \times 10^{-10} \mathrm{cm^3 s^{-1}}$. Moreover, the bimolecular reaction and decomposition reactivity of sCI is highly structure-dependent. sCI with more complicated substituent groups tend to react with H_2O more slowly (Huang et al., 2015), decompose faster (Fenske et al., 2000;Hasson et al., 2001) and more likely to react with SO_2. There were also studies showing that the reactions between sCI and SO_2 were pressure and temperature dependent and were commonly affected by the presence of water and other constituents (Kotzias et al., 1990;Sipila et al., 2014).

3. Ambient Observations

The continuous and comprehensive measurements were conducted at the west campus of Beijing University of Chemical Technology (39.95 ℕ′, 116.31 ℇ′). Here we investigate the time period from 18th January to 16th March 2019. The measuring

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instruments are located on the fifth floor, which is about 15 m above the ground level. This station is a typical urban site, which is around 130 m to the nearest Zizhuyuan Road, 550 m to the West Third Ring Road, and surrounded by commercial properties and residential dwellings.

3.1 Measurement of Sulfuric Acid with CI-APi-TOF

Sulfuric acid is measured by a long time-of-flight chemical ionization mass specter (LTOF-CIMS, Aerodyne Research, Inc.) equipped with a nitrate chemical ionization source. The basic working principle of this instrument can be found elsewhere (Jokinen et al., 2012). In our measurement, we draw air through a stainless-steel tube with a length of 1.6 m and a diameter of 3/4 inch with a flowrate at 7.2 L min^{-1}. In addition, we have implemented a flush plate (Karsa Inc.) to effectively remove water molecules entering the instrument, which is found necessary to maintain a continuous measurement.

The sulfuric acid concentration is calibrated with known concentrations of gaseous sulfuric acid produced by the reaction of SO_2 and OH radicals formed by UV photolysis of water vapor, and the detailed method has been described by (Kurten et al., 2012). We obtain a calibration coefficient of 6.07×10^9 cm^{-3} as the final calibration coefficient after taking into account the diffusion loss in the 1.6 m sampling line.

3.2 Measurement of Alkenes with SPI-MS

Six alkenes are analyzed in this study, i.e., including propylene, butylene, butadiene, isoprene, pentene and hexene, which were detected by a single photon ionization time-of-flight mass spectrometer (SPI-MS 3000, Guangzhou Hexin Instrument Co., Ltd., China) (Gao et al., 2013). It should be mentioned that this instrument cannot distinguish conformers, and therefore the pentene and haxene could also be cyclopentane and cyclohexane, respectively. A polydimethylsiloxane (PDMS) membrane sampling system is used. As the PDMS membrane has better selective adsorption to volatile organic compounds (VOCs), VOC molecules can be concentrated after diffusing and desorbing from the membrane under vacuum sampling condition. In this way, the detection limit of VOCs can be improved. Then the gas molecules are guided to an ionization chamber through a 2 mm-diameter stainless steel capillary, where VOC molecules are ionized by the vacuum ultraviolet (VUV) light with an ionization energy smaller than 10.8eV. For the detection of positive ions, two microchannel plates (MCPs, Hamamatsu, Japan) assembled with a chevron-type configuration are employed. An analog to digital converter (ADC) was used to measure and record the output current signal from the MCPs.

Alkenes concentrations are quantified by performing a direct calibration. The PAMS (Photochemical Assessment Monitoring Stations) and TO-15 environmental gases (including 57 and 65 types of VOCs separately, Linde Gas North America LLC, USA) are used as two standard gases with ultra-high-purity nitrogen as the carrier gas. Gas with different concentrations of VOC standards is produced by mixing a constant carrier gas with standard gas of varying flow rates. The calibration coefficient is further calculated from the ratio between the actual concentration and the ion intensity.

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3.3 Other Ancillary Measurements

The number concentration of clusters with the size range of 1.30~2.45 nm is measured with a Particle Sizer Magnifier (PSM) (Vanhanen et al., 2011). The number size distributions of aerosol particles from 6 to 840 nm and from 0.52 to 19.81 μm are measured by the Differential Mobility Particle Sizer (DMPS) (Aalto et al., 2001) and the Aerodynamic Particle Sizer (APS) (Armendariz and Leith, 2002) respectively. Meteorological parameters are measured with a weather station (AWS310, Vaisala Inc.) located on the rooftop of the building. These parameters include the ambient temperature, relative humidity (RH), pressure, visibility, UVB radiation, as well as horizontal wind speed and direction. Trace gas concentrations of carbon monoxide (CO), sulfur dioxide (SO_2) nitrogen oxides (NO_x) and ozone (O_3) are monitored using four Thermo Environmental Instruments (models 48i, 43i-TLE, 42i, 49i, respectively). Calibration of these instruments are performed monthly using the standard gases of known concentrations. The mass concentration of $PM_{2.5}$ is directly measured with a Tapered Element Oscillating Microbalance Dichotomous Ambient Particulate Monitor (TEOM 1405-DF, Thermo Fisher Scientific Inc, USA) with a total flow rate of 16.67 L/min. In addition, the loss rate of gas-phase sulfuric acid described by condensation sink (CS) is calculated based on the size distribution data from DMPS and APS (Kulmala et al., 2001).

4. Results and Discussions

4.1 Definition of Nighttime Sulfuric Acid Event

An overview of our measurements during 18th January to 16th March 2019 is shown in Fig. S1 in the Supplement. As our measurement period overlaps with the heating period in Beijing (from 15th November 2018 to 15th March 2019), the SO_2 level during the measurement period was higher than that of other periods in one year (from 16th March to 31st May 2019) (Fig. S2 in the Supplement).

In this work, the nighttime window is defined between 20:00 and 04:00 (following day) to exclude any possible influence of photochemistry. Fig. 1 shows the diurnal variation of SA concentration on one typical SA event night (14 March 2019) and one typical SA non-event night (3 February 2019). Overall, nighttime SA concentrations vary between 3.0×10^5 and 3.0×10^6 cm^{-3} in our measurement period. The nighttime event in Fig. 1 shows a distinct SA peak at around 22:00 with a maximum SA concentration of around 3.0×10^6 cm^{-3}, which is almost half of the daily maximum value. While in the non-event case, SA continues decreasing throughout the evening, reaching a minimal value of 3.0×10^5 cm^{-3}. A nighttime SA event is defined when both of the following two criteria are both met: (a) there is a distinct peak during the nighttime hours, (b) the SA concentration exceeds 1.0×10^6 cm^{-3}. The nights without distinct peaks are classified as SA non-event nights, and if a peak is identified but it does not meet criterion (b), the night is classified as an undefined night. Out of all 56 nights studied, there are in total 18 SA event nights, 16 non-event nights, and 22 undefined nights (listed in Table. S1). Thus, the overall frequency of nighttime SA events during our observation period is 32%, which means that nearly a third of nights during our observation period had distinct nighttime sulfuric acid peaks.

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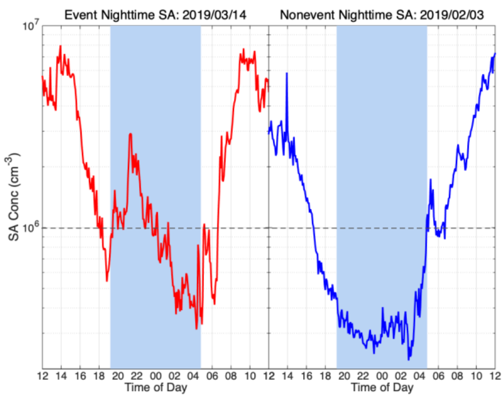

Fig. 1. Daily variation of SA concentration on a typical day with a nighttime SA event (red line, 14 March 2019) and on a non-event day (blue line, 3 February 2019). The shaded blue area shows the period that is considered as nighttime in our analysis.

4.2 Features of Nighttime Sulfuric Acid Event

We further analyzed the features of nighttime SA event nights based on the above mentioned 18 event nights and 16 non-event nights (Fig. 2). On SA event nights, the mass concentration of $PM_{2.5}$, the mixing ratio of NO_x, CS and RH were clearly lower, and visibility was clearly higher than on non-event nights. This suggests that nighttime SA events tend to occur under clean conditions. In addition, higher concentrations of O_3 were associated with SA event nights, whereas the concentration of SO_2 did not vary as much between SA event and non-event nights. This indicates that at most of the time, the concentration of SO_2 is not the dominant factor that explains the variation of nighttime SA.

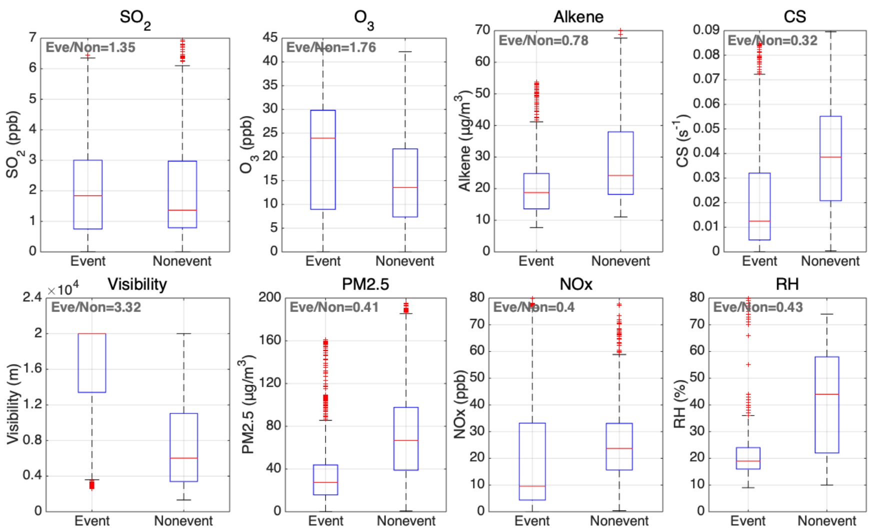

Fig. 2. Boxplots for the concentrations of SO_2, O_3 and alkenes, CS, visibility, $PM_{2.5}$, NO_x concentration and RH during nighttime SA event and non-event nights. In each plot, the middle line in the box is the median, the bottom and the top are the 25 and 75 percentiles, the whiskers are the 5 and 95 percentiles and the red points are the outliers. The dark gray values on the top left corners are the ratios between median values of event and non-event days.

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We further investigated the determining factor for the occurrence of SA events by looking into different variables during the SA event nights. CS measurements were available for 13 event nights, during which 15 SA peaks were observed. In general, we found that eight events (53%) were mainly associated with the decrease of CS. This is demonstrated in Fig. 3, where the nighttime events as well as the simultaneous decrease of CS are highlighted with green dots. Four other cases (27%) were mostly due to the increase of SO_2 concentration (Fig. S3), and the remaining three cases were likely synergistically caused by SO_2, O_3, alkenes, CS and other parameters. More details are provided in Table S2.

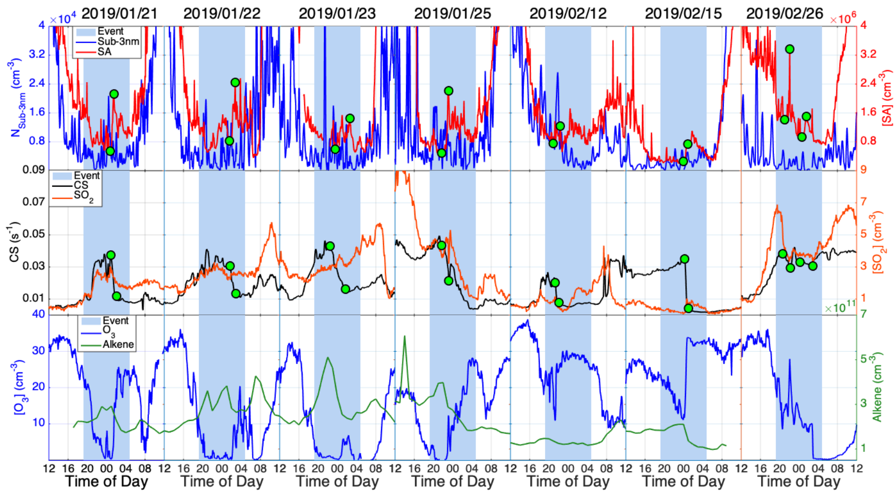

Fig. 3. Daily time-series of different variables on nighttime SA event days when SA events occurred under CS decrease conditions. The top panel shows the number concentration of sub-3nm particles ($N_{Sub-3nm}$) and SA concentration, the middle panel shows CS and SO_2 concentration, and the bottom panel shows the concentration of O_3 and alkenes. Green dots show times when CS started to drop and reached its minimum value.

4.3 Source and Sink Balance for Nighttime Sulfuric Acid: Importance of Alkene Ozonolysis

As discussed above, nighttime SA events mainly occurred under clean conditions with low CS values. Therefore, we classified all the nighttime data set into three groups according to the air pollution level, which is assessed by the visibility. The final division standards for cleanliness is explained in detail in the Supplement (Fig. S4). The clean (Clean-1), mildly polluted and heavy polluted conditions are defined by visibility values which are larger than 12.0 km, in the range of 4.0 ~ 12.0 km and smaller than 4.0 km respectively. In total, data points under each condition take up 48%, 25% and 27% of all data points.

After classifying the data set into groups based on the pollution level, we investigated the balance between SA source and sink for each group separately. A good correlation between source and sink suggests that the assumed source and sink processes are the major factors controlling the SA concentration. Both OH radical and sCI in dark conditions are products from the ozonolysis of alkenes, and their yields are largely unquantified. Therefore, we do not attempt to quantify their individual contribution to the formation of SA, but we treat them as a "bulk oxidant". Accordingly, the source term of SA can be expressed as k_{app} $[SO_2]\cdot[O_3]$ {Alkene], where k_{app} is an overall empirical parameter that takes into account the yields of OH radical and sCI and the rate constants of their reactions with SO_2 into account. The sink term consists of two parts: the condensation of

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SA onto particles ([SA]·CS) and the collision of SA monomers with each other to form SA dimers ($\beta\cdot[SA]^2$). In reality, SA monomer also collides with SA dimers and larger clusters, but due to the low concentration of SA clusters, these collisions are negligible compared to other losses. In a polluted environment where strong stabilizers of SA may exist, the formation rate of stable SA dimer is close to the collision limit (Yao et al., 2018). Therefore, β can be taken as the hard-sphere collision rate, which can be calculated as 3.46×10^{-10} cm^3 s^{-1} (Seinfeld and Pandis, 2016). Under pseudo steady-state conditions, the source-sink balance of SA can be expressed as follows:

$$k_{app} \cdot [\mathrm{Alkene}] \cdot [O_3] \cdot [SO_2] = [SA] \cdot CS + \beta \cdot [SA]^2$$

Fig. 4 shows the nighttime correlation between SA source term and sink term under different pollution levels, with the data binned into different SA sources strengths. It can be found that the ranges of the source terms are similar under all pollution levels, but the range of sink terms exhibit a large difference for different pollution levels, with days with lower visibility having much larger sink. If the source and the sink term correlate, the slope represents the overall apparent rate constant (k_{app}) of the reaction between oxidants (OH radical and sCI) from the ozonolysis of alkenes and SO_2 to produce SA for a specific pollution level.

Under Clean-1 conditions (Fig. 4 (a)), the source term and sink term have a good linear correlation in the source range of 1.0×10^{33} - 4.5×10^{33} $(cm^{-3})^3$, while the balance is broken up outside of this range. These uncorrelated data points outside of this range appear when the visibility is smaller than 16.0 km (Fig. S5 (a)) and when NO_x as well as NO concentrations are high ($[NO_x] > \sim 40$ ppb, Fig. S5 (b) and ($[NO] > \sim 3$ ppb, Fig. S5 (c)). High NO_x levels always relate to pollution and NO will consume O_3, leading to much lower O_3 concentration (marked by blue empty circles in Fig. S5 (a)). Thus, we redefined the criterion for clean condition (Clean-2) so that visibility needs to be larger than 16.0 km and $[O_3]$ higher than 2.0×10^{11} cm^{-3} (~ 7 ppb). These conditions account for 38% of all data. Fig. 4 (b) shows the good correlation between $[SO_2]\cdot[O_3]\cdot[\mathrm{Alkene}]$ source term and $[SA]\cdot CS+\beta\cdot[SA]^2$ sink term (R^2=0.97) under the redefined clean condition over the entire source range. This suggests that the ozonolysis of alkenes indeed have a dominant contribution to the formation of SA during nighttime under very clean conditions. Generally, the sink term of SA condensation onto particles takes up 95.54% for Clean-2 condition and increase to 99.67% for heavy polluted condition.

In order to have a general understanding of the apparent rate constant of sCI-SO_2 reaction obtained from our measurement, we can roughly get an upper limit value by considering all nighttime SA is produced from the sCI mechanism. From the above discussion, the slope k_{app} can be expressed as $k_1\cdot k_2\cdot\varphi\cdot f$, where f is the fraction of sCI which undergo the reaction with SO_2. It should be pointed out that k_2 is also an apparent rate constant which results from the combination of different measurement efficiency of alkenes (including undetected ones), different yields of sCI, and different rate constants of sCI reacting with SO_2. The fitted k_{app} is 2.618×10^{-30} cm^6 s^{-2}. If considering k_1 to be 1.0×10^{-17} cm^3s^{-1} (an intermediate value in the range of previous studies, which has been explained in Section 2), then $k_2\cdot\varphi\cdot f = 2.618\times10^{-13}$ cm^3s^{-1}. As the real atmospheric chemical composition is far more complex than experimental ones, the value of $\varphi\cdot f$ should be smaller. Thus, if further considering $\varphi\cdot f$ to be 0.05, then the rate constant k_2 in this real atmospheric condition is approximate 5.236×10^{-12} cm^3s^{-1}, which is in the same order of magnitude as measured values in experiments (see Section 2). If we compare the SA source and sink correlation between the Clean-1 (Fig. 4 (a)) and Clean-2 (Fig. 4 (b)) condition (which better corresponds to the real clean condition), it is obvious that

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the slope (2.678×10^{-30} $cm^6\ s^{-2}$) of the linear region of Clean-1 condition data points matches well with the slope (2.618×10^{-30} $cm^6 s^{-2}$) of Clean-2 condition data points, which proves the reliability of the balance between $[SO_2]\cdot[O_3]$ {Alkene] source term and [SA] CS+ β $\{SA]^2$ sink term under clean condition.

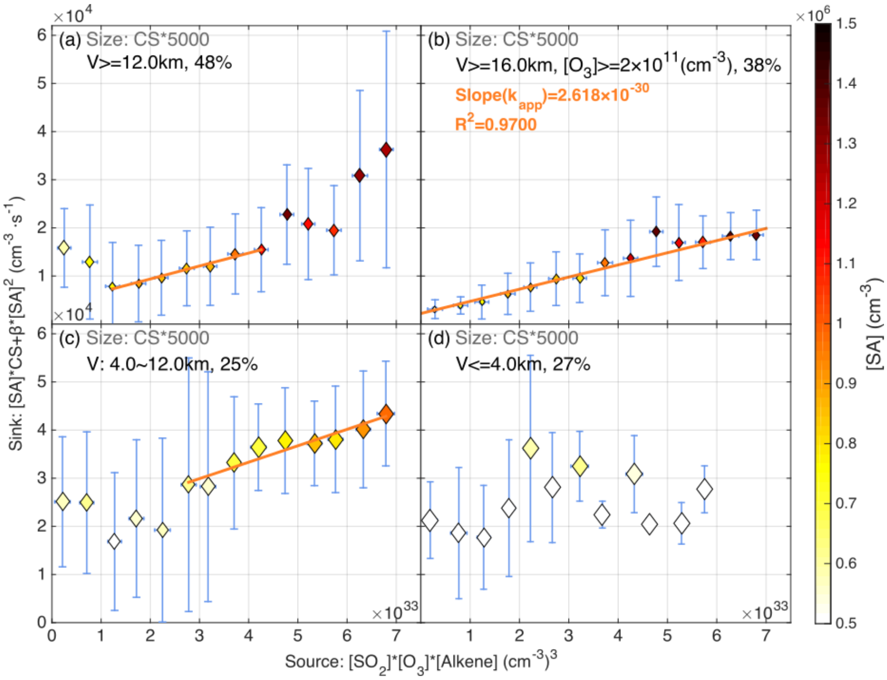

Fig. 4. Nighttime correlation between the source term ($[SO_2]$ $\{O_3]$ {Alkene]) and sink term ([SA] CS+β $\{SA]^2$) of SA under pseudo-steady-state for (a) Clean-1 condition, (b) Clean-2 condition, (c) mildly polluted condition and (d) heavy polluted condition. Note that the data points are based on data mean averaged and binned to different source ranges instead of the original, high time resolution data (Fig. S6). The error bars are the standard deviation of all data points in each bin.

Then we then took data from another period to further evaluate the reliability of the proposed source and sink balance. For summer period from 2019/03/20 to 2019/05/20 (Fig.S7 (b)), there is also a good linear correlation (R^2=0.98) when source term is smaller than 6.0×10^{33} $(cm^{-3})^3$ with k_{app} of ~ 1.496×10^{-30} cm^6s^{-2}. Although the fitted k_{app} values deviate beween these two periods, they are in the same order of magnitude. Besides, during summer period, apart from the above-mentioned six alkenes, biogenic emitted monoterpenes and isoprene start to have a bigger contribution, which cannot be measured by our instrument and therefore not included in the source term. In addition, the yield of sCI and the reaction rate constant between sCI and SO_2 appeared to be temperature-dependent (Berndt et al., 2014). They may explain at least a part of the difference of k_{app} between winter and summer observations.

Under mildly polluted conditions (Fig 4 (c)), the source term and sink term also have a good linear correlation (R^2=0.86) when source value exceeds 2.5×10^{33} $(cm^{-3})^3$. Interestingly, the slope for the mildly polluted conditions (3.393×10^{-30} cm^6s^{-2}, marked by orange line) is very close to that of the clean conditions within their linear correlation regions. This suggests that the ozonolysis of alkenes also contributes to the source of SA on mildly polluted days, and that the alkene distribution, thus the k_{app}, may be similar under those two pollution levels.

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Under heavy polluted conditions, however, the $[SO_2]\cdot[O_3]\cdot[Alkene]$ source term and $[SA]\cdot CS+\beta\cdot[SA]^2$ sink term do not show a strong correlation (Fig. 4 (d)),. Most likely, this suggested that the source terms cannot fully represent the actual SA source and sink for heavy polluted conditions. For instance, there are likely additional sources of SA, such as direct emission from diesel vehicles, oil refineries, SA plants, and any other factories that use coal as heating or power supply (Srivastava et al., 2004;Arnold et al., 2006;Ahn et al., 2011;Roy et al., 2014;Sarnela et al., 2015;Godunov et al., 2017). Another possible cause for deviations from the correlation between our proposed source and sink terms under polluted, and to some extent also under mildly polluted conditions, is that the distribution of alkenes may not be constant for all measurements classified into the same pollution level, i.e. the k_{app} is not constant. In turn, in very clean nights, in which alkene sources are considered more local and stable, dramatic changes in alkene distribution are not expected. This is also supported by the good correlation between the source and loss terms of SA. We cannot further deconvolute the contribution of OH radicals and sCI, as we cannot resolve the complicated formation pathways of sCI from different alkene precursors and thus we cannot determine e.g. a possible different atmospheric fate of different sCI and their impact on SA formation. Moreover, our instrument is only capable of measuring a limited amount of alkene species, and thus the fitted parameter k_{app} may be generally overestimated.

4.4 Atmospheric Implication: Contribution of Nighttime Sulfuric Acid to Sub-3nm Particles

We show that the ozonolysis of alkenes is the major source for the considerable amount of SA that exists during the nighttime, at least under unpolluted conditions. Furthermore, it is found that increasing SA concentrations coincide with increasing number concentrations of sub-3nm particles (Fig. 5), suggesting a strong enhancement in the formation of newly formed particles, which is consistent with previous study (Cai et al., 2017). Nighttime cluster formation events have been previously reported, most of which were observed in forest areas (Lee et al., 2008;Junninen et al., 2008;Lehtipalo et al., 2011;Mazon et al., 2016;Kammer et al., 2018). Rose et al. (2018) concluded that the high oxygenated organic molecules (HOMs) are the vapors triggering these nighttime NPF events in a boreal forest, whereas SA plays a minor role. However, in our study, the number concentration of sub-3 nm particles shows no dependence on HOM concentration (Fig. 5), indicating that nighttime SA production is the crucial step in nighttime cluster formation in an urban environment.

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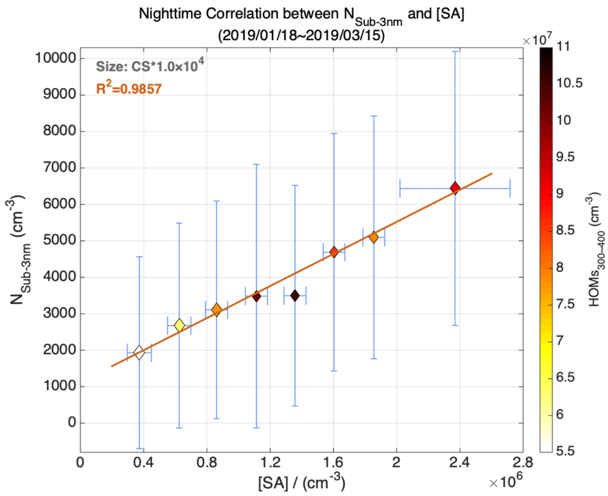

Fig. 5. Nighttime correlation between number concentration of sub-3nm particles ($N_{Sub\text{-}3nm}$, measured by PSM) and [SA] during nighttime. The data points are colored with HOM concentration and the size is related to CS. Note that the data points are based on the binned data instead of the original one.

5. Conclusions

We conducted continuous SA measurement during the heating-supply period in urban Beijing. We found frequent nighttime SA events, accounting for about 32 % of the total measurement nights. Most nighttime SA events were observed under unpolluted conditions and associated with a distinct drop in CS. We show that the SA source corresponding to alkene ozonolysis correlates well with the SA sink for clean conditions, and to some extent also for mildly polluted conditions. Thereby, we suggest that nighttime SA formation under these conditions can be largely attributed to the ozonolysis of alkenes leading to production of OH radicals or sCI which can act as oxidants for SO_2. However, further deconvolution of the contribution of OH radicals, sCI and of each possible alkene precursor was not possible within this study due to the inability to directly measure OH, sCI and the entire range of alkene precursors. It should also be pointed out that, under polluted conditions, there are very likely additional SA sources other than the ozonolysis of alkenes, such as direct emission from diesel vehicles, oil refineries and SA plants. Furthermore, we showed that these elevated SA levels have a dominant contribution to the formation of sub-3nm particles in the nighttime of winter Beijing.

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