Variation and Trend of Nitrate radical reactivity towards volatile organic compounds in Beijing, China

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ABSTRACT. Nitrate radical (NO_3) is an important nocturnal atmospheric oxidant in the troposphere, which significantly affects the lifetime of pollutants emitted by anthropogenic and ~~biological~~biogenic activities, especially volatile organic compounds (VOC). Here, we used one-year VOC observation data obtained in urban Beijing in 2019 to look ~~insight to~~into the level, compositions, and seasonal variation of NO_3 reactivity (k_{NO3}). We show ~~the~~that hourly k_{NO3} towards measured VOC highly varied from $<10^{-4}$ to 0.083 s^{-1} with a campaign-averaged value (± standard deviation) of 0.0032 ± 0.0042 s^{-1}. There was large seasonal difference in NO_3 reactivity towards VOC with the average of 0.0024 ± 0.0026 s^{-1}, 0.0067 ± 0.0066 s^{-1}, 0.0042 ± 0.0037 s^{-1}, 0.0027 ± 0.0028 s^{-1} from spring to winter. Alkenes such as isoprene and styrene accounted for the majority. Isoprene was the dominant species in spring, summer, and autumn, accounting for 40.0%, 77.2~~%~~%, and 43.2%, respectively. Styrene only played a leading role in winter, with ~~the~~a percentage of 39.8%. ~~Sensitivity~~A sensitivity study shows monoterpenes, the species we did not measure, may account for a large fraction of k_{NO3}. Based on the correlation between the calculated k_{NO3} and VOC concentrations in 2019, we established localized parameterization schemes for predicting the reactivity by only using a part of VOC species. The ~~historical~~historically published VOC data was collected using the parameterization method to reconstruct the long-term ~~NO_3 reactivity~~ k_{NO3} in Beijing~~ by the parameterization method.~~. The ~~downward trend of~~lower k_{NO3} during ~~2011-2020~~2014-2021 compared with that during 2005-2013 may ~~be responded~~attribute to ~~the reduction of~~ anthropogenic VOC emission reduction. At last, we revealed

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that NO_3 dominated the nocturnal VOC oxidation with 83% on the annual average in Beijing in 2019, which varied seasonally and was strongly regulated by the level of k_{NO3}, nitrogen oxide, and ozone. Our results improve the understanding of nocturnal atmospheric oxidation in urban regions, and gain the knowledge of nocturnal VOC oxidation and secondary organic pollution.

1. Introduction

Nitrate radical (NO_3) is the main nocturnal tropospheric oxidant (Brown and Stutz, 2012; Wayne et al., 1991), which is mainly formed in the reaction of NO_2 and O_3. During the daytime, a A large amount of NO emitted by in cities is oxidized into NO_2 by ozone and released into O_3 in the atmosphere (R1), and NO_2 continues to be oxidized into nitrate radical (NO_3) by O_3 (R2). NO_3 only presents a NO_3 is the main nocturnal tropospheric oxidant (Brown and Stutz, 2012; Wayne et al., 1991) with a relatively high concentration level at night because due to it has a rapid loss by photolysis rate (R3) and the reaction with NO during the daytime (Stark et al., 2007), NO_3 can oxidize NO into NO_2 (R3). During the nighttime, NO_3 and NO_2 react to These two reactions return NO_3 back to NO_x and thus cannot contribute to effective NO_x removal. In addition, NO_3 reacts with NO_2 to form nitrous pentoxide (N_2O_5) (R4R5), and N_2O_5 can be decomposed to NO_3 and NO_2 (R5R6), establishing a temperature-dependent equilibrium.

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$$NO+O_3 \rightarrow NO_2+O_2 \quad (R1)$$

$$NO_2+O_3 \rightarrow NO_3+O_2 \quad (R2)$$

$$NO_3+h\nu \rightarrow NO+O_2 \quad (R3)$$

$$NO_3+h\nu \rightarrow NO_2+O^1D \quad (R4)$$

$$NO_3+NO \rightarrow 2NO_2 \quad (R3R5)$$

$$NO_2+NO_3+M \rightarrow N_2O_5+M \quad (R4R6)$$

$$N_2O_5+M \rightarrow NO_2+NO_3+M \quad (R5R7)$$

The main removal of NO_3 from During the nighttime, there are two kinds of reactions that have a large impact on air pollution and regulate the lifetime and budget of many trace gas phase species. One is the reaction with NO (R3), solar photolysis (R6, R7), and NO_3 oxidizes volatile organic compounds oxidation (R8), forming and forms complex products. In addition, (R8). The other is NO_3 can be transformed into N_2O_5 and removed by heterogeneous hydrolysis (R9), providing an effective way to remove NO_x NO_x and produce nitrate aerosol and nitryl chloride (Brown et al., 2004; Dentener and Crutz, 1993; Osthoff et al., 2008). The competition between R8 and R9 determines the fate of nocturnal nitrogen oxidation chemistry, which leads to the formation of different type secondary pollutants (Bertram and Thornton, 2009; Brown et al., 2006). Specifically In particular, the degradation of VOC by NO_3, especially biogenic VOC (Ng et al., 2017), has been proven to be related to the formation of

organic nitrate and secondary organic aerosols (SOA) (Goldstein and Galbally, 2009; Kiendler-Scharr et al., 2016).

~~$NO_3+hv \rightarrow NO+O_2$ (R6)~~

~~$NO_3+hv \rightarrow NO_2+O^1D$ (R7)~~

$NO_3+VOC \rightarrow products$ (R8)

$N_2O_5+H_2O_{(aq)}/Cl^- \rightarrow HNO_3 + \varphi ClNO_2$ (R9)

The high NO_3 concentration and fast reaction rate make NO_3 responsible for the ~~sink~~sinking of many unsaturated hydrocarbons at night (Edwards et al., 2017; Ng et al., 2017; Yang et al., 2020). The NO_3 reactivity (k_{NO3}) towards VOC, defined as the consuming capacity of NO_3 by ambient VOC, can be calculated by Eq. 1.

$$k_{NO3} = \sum k_i \times [VOC_i] \quad \text{Eq. 1}$$

where the $[VOC_i]$ is VOC concentrations and k_i is the corresponding reaction rate coefficients. Table S1 gives the reaction rate coefficients of NO_3 with VOC ~~(Atkinson and Arey, 2003)~~(Atkinson and Arey, 2003). The contribution of VOC to the NO_3 reactivity ~~towards~~with respect to different VOC varies greatly, which is ~~affected~~caused by the abundance of species and the reaction rate coefficients. Thus, NO_3 reactivity towards VOC is also affected by temperature~~. Since~~ since temperature affects not only ~~affects~~ the temperature-dependent reaction rate coefficients but also the VOC ~~concentrations~~emissions in the atmosphere, especially for the emission of biogenic VOC like isoprene and monoterpenes (Wu et al., 2020), ~~causing~~leading to the variations of VOC species ~~which~~that dominate k_{NO3} towards VOC in different seasons.

~~The~~ Previous works showed that the VOC species which ~~dominant~~dominate the NO_3 reactivity vary greatly between different regions. In forests and rural areas, such as Pabstchum outside Berlin, Germany, the lush forests ~~emit~~emitted a large ~~amount~~number of monoterpenes and isoprene, accounting for the majority of k_{NO3}, which ranged from 0.0025 to 0.01 s^{-1} ~~(Asaf et al., 2009);~~(Asaf et al., 2009). In semi-arid urban areas such as Jerusalem, the emissions of BVOC are less due to the sparser vegetation, and the maximum of NO_3 reactivity was about 0.01 s^{-1}~~. Phenol~~, in which the phenol, cresol and some monoolefins emitted by road traffic ~~are~~were the main contributors ~~(Asaf et al., 2009)~~(Asaf et al., 2009). In ~~the~~ urban regions like Houston, ~~the~~ industrial emissions, including isoprene and other alkenes, dominated the NO_3 reactivity (Stutz et al., 2010). In ~~the suburbs of~~ the city's suburbs, the k_{NO3} may be jointly affected by anthropogenic and ~~biological~~biogenic volatile organic compounds. For example, the NO_3 reactivity towards VOC in Xianghe, Beijing reached 0.024 ± 0.030 s^{-1}, with ~~the~~a maximum value of 0.3 s^{-1} and minimum value of 0.0011 s^{-1}. Isoprene, styrene, and 2-butene contributed to ~~the majority~~most of the k_{NO3} (Yang et al., 2020).

~~In addition to calculating k_{NO3} by the measured VOC, an instrument was developed to directly measure k_{NO3} in the atmosphere (Liebmann et al., 2017). On this basis, they presented the first direct measurement of NO_3 reactivity in the Finnish boreal forest in 2017 and concluded that the NO_3~~

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~~reactivity was generally high with a maximum value of 0.94 s^{-1}, displaying a strong diel variation with~~The above NO_3 reactivities are all calculated by the measurement of VOC concentrations. In addition to this method, an instrument was developed to measure k_{NO3} in the atmosphere directly (Liebmann et al., 2017). They presented the first direct measurement of NO_3 reactivity in the Finnish boreal forest in 2017. They concluded that the NO_3 reactivity was generally high, with a maximum value of 0.94 s^{-1}, displaying a strong diel variation with a nighttime mean value of 0.11 s^{-1} and daytime value of 0.04 s^{-1} (Liebmann et al., 2018a). In 2018, they presented the direct measurement in and above the boundary layer of a mountain site, with daytime values of up to 0.3 s^{-1} and nighttime values close to 0.005 s^{-1} (Liebmann et al., 2018b). Most importantly, the direct measurement revealed the existence of missing NO_3 reactivity in ~~varies~~various regions, which indicated the missing NO_3 oxidation mechanisms~~, and~~. These results largely improved the understanding of nighttime chemistry.

Nevertheless, the ~~field~~ direct field determination of k_{NO3} is still extremely ~~lacked~~lacking, especially in urban regions~~.~~ at the current stage. Until now, most works about the VOC oxidation by NO_3 ~~was~~were usually based on short-term investigations, and the analysis of the nocturnal chemical process or reactivity was carried out based on the data of a few weeks or several months. ~~The studies~~Studies of nighttime chemistry based on long-term measurement data are very scarce (Vrekoussis et al., 2007; Wang et al., 2023; Zhu et al., 2022). The detailed VOC contributions to k_{NO3}, and the relationship between certain VOC and total NO_3 reactivity ~~in~~on a long-time scale are also rarely studied. Our recent work reported that the increasing trend of the NO_3 production rate is caused by ~~the~~ anthropogenic emission changes, while the long-term and detailed NO_3 loss budget is still uncertain to some extent ~~(Wang et al., 2023).~~(Wang et al., 2023). Here, we attempt to look for insight ~~to~~into the level, variations, and impacts of NO_3 reactivity by using the one-year measurement of VOC in an urban site in Beijing, the role of unmeasured VOC species (monoterpenes) in the contributions of NO_3 reactivity is also discussed. The long-term trend of NO_3 reactivity is estimated by collecting the published VOC data and the newly proposed parameterization method. At last, the ~~regulation of NO_3 oxidation of~~ nocturnal VOC ~~in~~oxidation by NO_3 during different seasons ~~is~~was further evaluated.

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~~2. Methods~~

2. Method

2.1 Site description and instrumentation

The measurement was conducted at the campus of Peking University (39° 99' N, 116° 30' E~~).~~) during the whole year of 2019. The site is situated northeast of the Beijing city center and near two traffic roads, which ~~represents~~represent a typical urban and polluted area with fresh, anthropogenic emissions (Wang et al., 2017a). The measurements were made on a building roof with a height of 20 m above the ground. Measurements of VOC concentrations were performed using an automated gas chromatograph equipped with mass spectrometry or flame ionization detectors (GC-MS/FID). ~~There are 56 kinds of VOC are measured in total, in which monoterpenes are not valid.~~The volatile organic compounds were pretreated by pre-freezing and collected in the deactivated quartz empty capillary at extreme-low temperature (-150 °C), then heated and delivered into the analysis system. After separation by the double chromatographic column, the low-carbon compounds C_2-C_4 were detected

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by the FID detector, and the high-carbon compounds C_5-C_{10} were detected by the MS detector. There are 56 kinds of VOC measured in total (listed in Table S1 and the concentrations are depicted in Figure S1), in which monoterpenes measurement are not valid. NOx and O_3 were monitored by chemiluminescence (Thermo Scientific, 42i-TLE) and UV photometric methods (Thermo Scientific, 49i), respectively. A Tapered Element Oscillating Microbalance analyzer (TianHong, TH-2000Z1) was used to measure the mass concentration of $PM_{2.5}$. The quality assurance and quality controls of data were implemented regularly (Chen et al., 2020). Photolysis frequencies were obtained by the Tropospheric Ultraviolet and Visible (TUV) model simulation. Hourly data were processed and used in the following analysis.

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2.2 Estimation of monoterpenes

Since the measurement data did not include monoterpenes (~~MNTs~~MNT), we, therefore, use the measured isoprene and ~~modelled~~modeled concentration ratio of monoterpene to isoprene in the same region of the measurement site (named as Factor, Eq. 2) to estimate the ambient monoterpene concentrations (named as MNT_{obs}, Eq. 3). The Factor was obtained by the regional model (WRF/CMAQ), more details of the model simulation setup can be found in Mao et al. (2022). Briefly, the regional model CMAQ (Community Multiscale Air Quality) version 5.2 was applied to simulate air quality in eastern China, with a horizontal resolution of 36 km. Specifically, the gas-phase mechanism of SAPRC-07 and aerosol module AERO6 were used. The meteorological fields were provided by Weather Research & Forecasting (WRF) Model version 4.2. The biogenic emissions were simulated by the MEGANv2.1, which was driven by WRF as well, and the emissions of open burning were estimated with FINN. The MEIC emission inventory for 2019 (obtained via private communication) was used to represent anthropogenic emissions over China, while the emissions in the areas outside China were provided by the REAS v3.2 inventory simulation.

$$Factor = \frac{[MNT_{sim}]}{[ISO_{sim}]} \quad \text{Eq. 2}$$

$$[MNT_{obs}] = [ISO_{obs}] \times Factor \quad \text{Eq. 3}$$

We used the Factor to estimate monoterpenes level rather than ~~modelled~~modeled monoterpene concentrations ~~is~~ due to the ~~modelled~~modeled isoprene is systematically higher than that of observation (Fig. ~~S1), thus~~S2). Thus the using of the ~~modelled~~modeled Factor may be more reasonable. In Beijing, α-pinene and β-pinene were reported to have the highest abundance among monoterpenes (Cheng et al., 2018), with higher emissions in summer (Wang et al., 2018b; Xia and Xiao, 2019). Therefore, we use a weighted reaction rate coefficient approximated by the ~~averaged~~average value of α-pinene and β-pinene~~ reaction rate coefficients~~ with NO_3 in the following calculations. Since the emissions of sesquiterpenes in BVOC are much lower than that of isoprene, monoterpenes, and other BVOC, thus we ~~didn't~~did not consider ~~NO_3 reactivity towards~~the contribution of sesquiterpenes to the reactivity. The detailed average diurnal variations of Factor are listed in Table S2.

~~$$Factor = \frac{[MNT_{sim}]}{[ISO_{sim}]} \quad \text{Eq. 2}$$~~

~~$$[MNT_{obs}] = [ISO_{obs}] \times Factor \quad \text{Eq. 3}$$~~

2.3 VOC oxidation rate by NO_3

To study the reaction of NO_3 and VOC during the nighttime, we estimated the NO_3 concentrations by steady-state calculation. This method is widely used to estimate the concentrations of short-lived substances ~~like NO_3~~, by assuming its production and loss rates are balanced in a specific time range. Given sufficient time, the steady state can be reached for NO_3 at night, in which the production and loss terms are approximately balanced (Brown, 2003; Crowley et al., 2010). ~~The~~Here the production terms of NO_3 ~~is~~are the reaction of NO_2 and O_3, and the loss terms of NO_3 ~~includes~~include reactions with VOC, reaction with NO, heterogeneous reaction, and photolysis. The steady-state NO_3 mixing ratios are expressed by Eq. ~~4 (Brown and Stutz, 2012)~~4 (Brown and Stutz, 2012).

$$[NO_3]_{ss} = \frac{k_{NO_2+O_3}[NO_2][O_3]}{\sum k_i \times [VOC_i] + k_{NO+NO_3}[NO] + J_{NO_3} + k_{het}K_{eq}[NO_2]} \quad \text{Eq. 4}$$

Where J_{NO3} is the sum of the photolysis coefficients of the two photolysis reactions of NO_3. The k_{het} is the heterogeneous uptake rate of N_2O_5 on the aerosol surface, which can be calculated by Eq. 5.

$$k_{het} = 0.25 \times \gamma \times S_a \times c \quad \text{Eq. 5}$$

Where γ is the dimensionless uptake coefficient of N_2O_5 parameterized by Eq. 6 (Evans and Jacob, 2005; Hallquist et al., 2003; Kane et al., 2001), Sa ($m^2\ m^{-3}$) is the aerosol surface area density estimated by the level of $PM_{2.5}$ (Wang et al., 2021), and c is the mean molecular velocity of N_2O_5.

$$\gamma = \alpha \times 10^{\beta}$$

$$\alpha = 2.79 \times 10^{-4} + 1.3 \times 10^{-4} \times RH - 3.43 \times 10^{-6} \times RH^2 + 7.52 \times 10^{-8} \times RH^3$$

$$\beta = 4 \times 10^{-2} \times (T - 294)\ \ (T > 282K)$$

$$\beta = -0.48\ \ (T < 282K) \quad \text{Eq. 6}$$

The reaction rate coefficients of NO_2 and O_3, NO and NO_3, and the equilibrium constant for the forward and reverse Reactions (R4) and (R5) are temperature dependent. We have adopted JPL evaluation reports for the reaction rate coefficients. The time series of hourly ~~-~~related parameters in estimating the steady-state NO_3 and the diurnal cycle of NO_3 concentrations were shown in Fig. ~~S2~~S3 and Fig. ~~S3~~S4. To compare the VOC oxidation ~~of~~by NO_3 ~~towards VOC~~ with other oxidants, we estimated OH concentrations by the slope ~~that~~ extracted from the measured OH and J_{O1D} (s^{-1}) in North China (Tan et al., 2017)) (Eq. 7), where J_{O^1D} used in this study was obtained by the TUV model simulations. The VOC oxidation rate (R_{NO3}) and the ratio of VOC oxidized by NO_3 to the total oxidation rate can be calculated by Eq. 8.

$$[OH] = 4.1 \times 10^{11} cm^{-3} s^{-1} \times J_{O^1D} \quad \text{Eq. 7}$$

$$R_{NO_3} \approx \frac{\sum k_i \times [VOC_i][NO_3]}{\sum k_i \times [VOC_i][OH] + \sum k_i \times [VOC_i][NO_3] + \sum k_i \times [VOC_i][O_3]} \quad \text{Eq. 8}$$

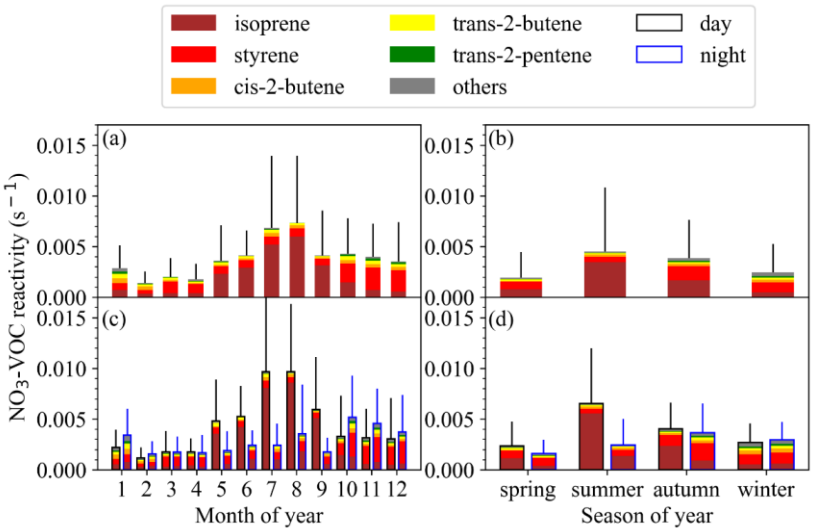
where k_i represents the corresponding reaction rate coefficients of different VOC with oxidants.

3. Results and discussion

3.1 NO_3 reactivity calculated by measured VOC

During the campaign, the hourly k_{NO3} towards measured VOC (named as k_{NO3_mea}) highly varied from $<10^{-4}$ to 0.083 s^{-1} with campaign-averaged value (± standard deviation) of 0.0032 ± 0.0042 s^{-1}. The k_{NO3_mea} displayed a strong diel variation on the annual average (Fig. ~~S4~~S5). In previous studies, the NO_3 reactivity towards VOC was reported to be 0.024 ± 0.030 s^{-1} on average in a suburban site in summer in North China (Yang et al., 2020); and highly varied between 0.005 - 0.3 s^{-1} in the mountaintop site in summer (Liebmann et al., 2018c). Our result is one order of magnitude lower, which may reflect the huge difference of k_{NO3_mea} in different ~~environment~~environments and sampling time. Certainly, it may be attributed to the reason that calculated k_{NO3} here did not include some species, such as monoterpenes~~.~~, phenol, cresol and so on. The diurnal variations of k_{NO3_mea} had strong seasonal variability (Fig. ~~S5~~S6). The diurnal variations in winter and spring were relatively weak, and ~~the variations~~ in summer and autumn were ~~large~~strong, with clear peaks at 9:00-10:00 and 15:00, respectively. The k_{NO3_mea} in spring, summer, and autumn reached the daily maximum value between 8:00 a.m. and 10:00 a.m. (spring: 0.0034 s^{-1}, summer: 0.0083 s^{-1}, autumn: 0.0057 s^{-1}). In winter, it reached the maximum value of 0.0033 s^{-1} at about 22:00.

As shown in Fig. 1a, the k_{NO3_mea} reached the highest in August and lowest in February, which was largely affected by the level of isoprene and styrene. For example, isoprene contributed ~80% to the reactivity in August. The k_{NO3_mea} towards isoprene reached the maximum in August and the minimum in February, which was consistent with the ~~previous~~previously reported change ~~of~~in isoprene concentrations in Beijing (Cheng et al., 2018). ~~Figure 1b~~The k_{NO3_mea} shows a large seasonal difference ~~in k_{NO3_mea}~~ with the average value of 0.0024 ± 0.0026 s^{-1}, 0.0067 ± 0.0066 s^{-1}, 0.0042 ± 0.0037 s^{-1}, 0.0027 ± 0.0028 s^{-1} from spring to winter. Table ~~S2~~S3 shows the specific contributions of the top six species to k_{NO3_mea} in different seasons ~~(and Fig. S4).~~. Isoprene was the dominant species, accounting for 40.0%, 77.2~~%~~%, and 43.2% in spring, summer, and autumn. By comparison, styrene only played a leading role in winter, accounting for 39.8%. ~~Of~~Among the species which contributed to k_{NO3_mea} in Beijing, isoprene and styrene contributed most to the overall k_{NO3_mea} (60%~90~~%)~~%), followed by cis-2-butene, trans-2-butene, trans-2-pentene, and proplyene (5%~15%) with another ~~individual~~ VOC less than 2%. Our results are consistent with previous studies in Beijing that k_{NO3} was mainly contributed by isoprene (Yang et al., 2020), indicating ~~that~~ the critical role of isoprene in NO_3 reactivity in Beijing. From summer to autumn, the dominant species changed from isoprene to styrene, while from winter to spring, the dominant species changed from styrene to isoprene. This indicated the AVOC and BVOC ~~controls~~control k_{NO3_mea} alternately. Overall, the k_{NO3_mea} displayed a characteristic of high in summer and autumn and low in winter and spring.



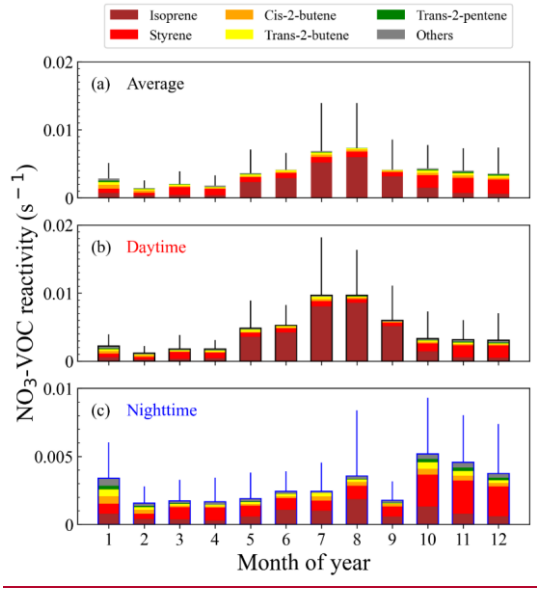


Figure 1. ~~(a-b)~~ Histograms of monthly ~~and seasonal~~-averaged k_{NO3_mea} and the compositions~~. (c-d) Histograms of monthly and seasonal-averaged k_{NO3_mea} and~~ during the ~~compositions divided into~~day (a), daytime (~~black frames~~)b), and nighttime (~~blue frames~~c). The color denotes the contributions of different VOC species. The ~~black and blue~~ lines represent the error bars of the reactivity (± standard

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deviations).

Figure ~~1c-d showed~~1b-c shows the k_{NO3_mea} towards measured VOC display clear day-night differences in summer and winter, especially in summer. The NO_3 reactivity towards VOC in the daytime reached the value of 0.010 s^{-1} in July and August, which was much higher than 0.002 s^{-1} in the nighttime. The variations were mainly caused by the diel variations of isoprene concentrations. Reversely, the reactivity was higher at night and lower in the daytime in winter, which was due to the high AVOC level in the morning and at night (Lee and Wang, 2006). Specifically, styrene concentrations at night increased significantly in the stable nocturnal boundary layer, resulting in relatively higher reactivity.

In urban areas of Beijing, isoprene origins from anthropogenic and ~~biological~~biogenic sources, ~~in~~ which the anthropogenic sources of isoprene are mainly traffic emissions (Li et al., 2013; Riba et al., 1987; Zou et al., 2015). ~~In summer, isoprene mainly origins from plant, and in winter origins from the combustion of engine fuel. In spring and autumn, there are mixed effects of anthropogenic and biological origins (Li et al., 2013). The isoprene emissions of biological~~The isoprene emissions from biogenic sources in Beijing were one order of magnitude larger than that of anthropogenic sources (Yuan et al., 2009). This indicates the concentrations of isoprene at the environmental level in the urban areas of Beijing ~~is~~are not affected by the traffic vehicles~~,~~ but mainly by plants ~~in Beijing~~ (Cheng et al., 2018). As an aromatic hydrocarbon, styrene origins from both anthropogenic and biogenic sources in the atmosphere (Miller et al., 1994; Mogel et al., 2011; Schaeffer et al., 1996; Tang et al., 2000; Zielinska et al., 1996; Zilli et al., 2001), such as the laminar flame of engine fuel (Meng et al., 2016), industrial production (Radica et al., 2021) and other human activities. The dominant source of styrene in Beijing is the local ~~vehicles~~vehicle emissions (Li et al., 2014). Some vegetation, such as evergreen and oleander, can also release natural styrene (Wu et al., 2014), however, due to the dense industrial distribution in the urban area and the much lower level of these biogenic styrene compared with isoprene, we ~~believed~~believe that the styrene in the atmosphere in Beijing is mainly resulted from anthropogenic origins. It is believed that human activities in winter, such as heating, gasoline, and diesel combustion, increased, meanwhile, the reduction of temperature and radiation resulted in the reduction of biogenic isoprene emissions, explained the conversion of dominance of NO_3 reactivity from summer to winter.

The NO_3 reactivity towards MNTs (named as k_{NO3_MNTs}) was estimated by the method mentioned in section 2.2. After taking MNTs into account, the total k_{NO3} (named as k_{NO3_total}) was greatly enlarged, with the campaign-averaged value of 0.0061 ± 0.0088 s^{-1}, resulting in our results comparable with previous research results. The NO_3 reactivity towards MNTs was higher in autumn and winter and lower in spring and summer (Fig. S7). Considering the corresponding reactivity towards monoterpenes, the total NO_3 reactivity towards VOC changed from (summer > autumn > winter > spring) to (autumn > winter > summer > spring), highlighting the impact of the monoterpene variations on the reactivity. The NO_3 reactivity towards MNTs displayed significant differences between daytime and nighttime (Fig. S7c-d). The reactivity at night in all months was higher than that in the daytime, especially from October to January, highlighting the role of biogenic monoterpenes in nocturnal NO_3 chemistry (Li et al., 2013; Riba et al., 1987). To evaluate the contribution of monoterpenes to the total k_{NO3}, we calculated the fraction (F_{MNTs}) by Eq. 9.

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$$F_{MNTs} = \frac{k_{NO_3\_MNTs}}{k_{NO_3\_total}} \quad \text{Eq. 9}$$

Figure 2a displays the differences between the k_{NO3_mea} and k_{NO3_total}. Monoterpenes were very important for NO_3 reactivity, and the F_{MNTs} varied from 40% to 80%, with strong seasonal variations. The MNTs accounted for NO_3 reactivity of nearly 80% in winter and spring. In the seasons when isoprene no longer dominated, the measured reactivity accounted for a small fraction, and the corresponding reactivity towards AVOC, such as styrene, was smaller than that of monoterpenes. As shown in Fig. 2b, the measured VOC had high fractions in the daytime and low at night, especially in May and August. The measured VOC in the daytime accounted for more than 60% of k_{NO3_total}, which was closely related to the increasing concentrations of isoprene in the summer daytime. The reactivity towards MNTs accounted for a large fraction of reactivity at night.

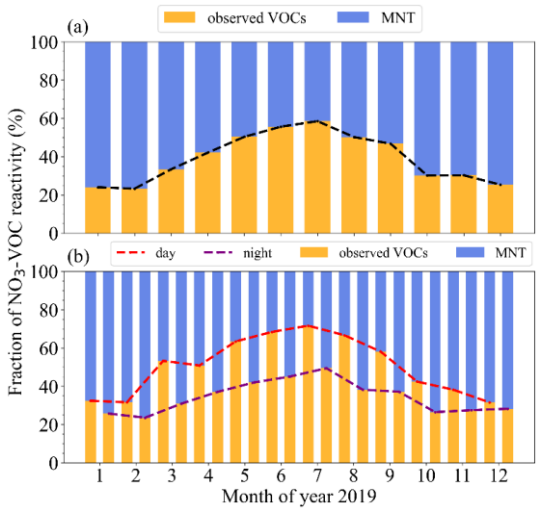

Figure 2. (a) Fractions of the k_{NO3_total}. (b) Fractions of the k_{NO3_total} divided into daytime (left) and nighttime (right). The colors on the stacked bar plot indicate the different fractions as they are donated in the legend. The lines represent the monthly-averaged variations of the NO_3 reactivity towards MNTs.

3.2 Parameterization of NO_3 reactivity

We examined the correlation of key VOC concentrations and k_{NO3_mea}. Figure ~~S6~~ S8 gives the case in January, for example. To a certain extent, the variations of k_{NO3_mea} were closely linked to the variations of the concentrations of main contributors. It is worth noting that in January, trans-2-butene had a higher correlation coefficient with k_{NO3_mea}, which exceeded that of isoprene and styrene. This indicates that higher contributions may not imply a stronger correlation. Fig. ~~2~~3 shows the correlation coefficients and the fitting equations between VOC concentrations and k_{NO3} in each month (detailed in Table ~~S3~~S4). According to the correlation coefficients, we can select the strongest indicator corresponding to ~~the~~a certain month as the variable of the parameterization method. Here we didn't

import the VOC with small contributions into the parameterization method~~,~~ because these indicators had no practical significance for k_{NO3_mea}. In this way, we established the first parameterization method (Method 1) by using the strongest indicator in each month ~~and~~which can be found in Table ~~S3~~S4 (Eq. 10):

$$NO_3\ reactivity_{sim1} = \sim\sim a_i \times [VOC_i] + b_i \sim\sim a \times [VOC] + b \qquad \text{Eq. 10}$$

~~where, a~~$_i$~~, b$_i$~~Where, a, b, and [~~VOC$_i$~~VOC] respectively represent the slope, the intercept, and the VOC species concentrations (ppbv) used for parameterization ~~in~~ each month. ~~Throughout the year, the~~The correlation coefficients between isoprene concentrations and kNO3_mea were high throughout the year, ranging from 0.67 to 0.98, especially in summer. The correlation coefficients between styrene concentrations and the reactivity reached a maximum in autumn and winter, which can ~~clearly~~ display the indication of these two species (isoprene and styrene) in different seasons.

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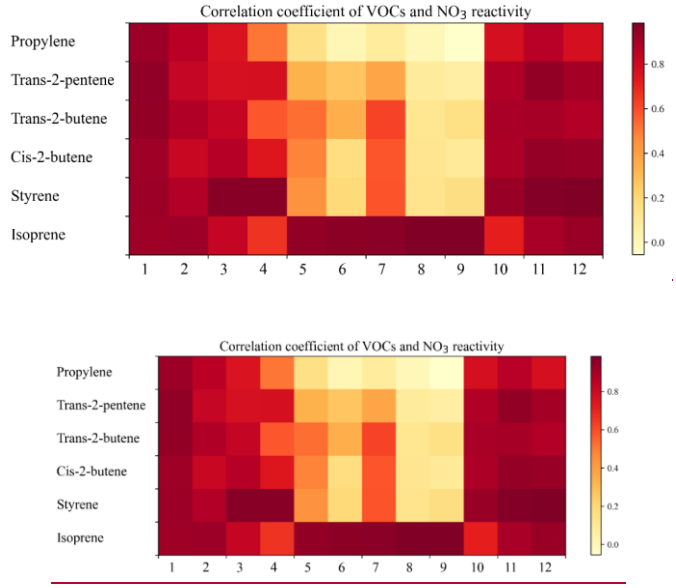


Correlation coefficient of VOCs and NO3 reactivity
Propylene
Trans-2-pentene
Trans-2-butene
Cis-2-butene
Styrene
Isoprene
1 2 3 4 5 6 7 8 9 10 11 12
0.8
0.6
0.4
0.2
0.0

Figure ~~2~~3. The ~~thermodynamic diagram~~heat map of the monthly correlation between VOC concentrations and k_{NO3_mea}. Colored blocks indicate different correlations~~,~~ by which the best indicator can be selected for the parameterization method of each month.

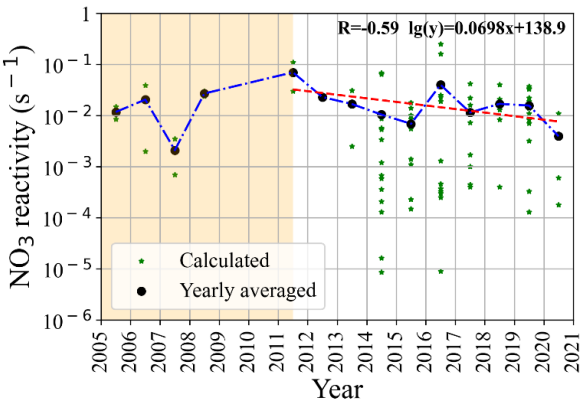
Besides the indicator parameterization method, we can also select only a part of VOC that contribute most of k_{NO3_mea} as a representative. Here we approximated NO_3 reactivity towards total VOC to the reactivity towards these top 6 species~~, namely:~~ isoprene, styrene, cis-2-butene, trans-2-butene, trans-2-pentene, and proplyene. Thus, the second parameterization method (Method 2) can be expressed by Eq. 11:

$$NO_3\ reactivity_{sim2} = \sum_{i=1}^{6} k_i \times [VOC_i] \qquad \text{Eq. 11}$$

where [VOC_i] is the VOC concentrations and k_i is the corresponding reaction rate coefficients with NO_3. It should be noted that this parameterization method of NO_3 reactivity towards VOC may be localized.

To evaluate the effectiveness of the two parameterization methods established above, we estimated the k_{NO3} in the different time ~~scale~~scales, and compared them with the determined k_{NO3_mea} by all measured VOC. As shown in Fig. ~~S7~~S9, both ~~two~~ methods can well capture the level and variations of k_{NO3_mea}, indicating the parametrization feasibility. Method 1 can easily and quickly estimate NO_3 reactivity towards VOC ~~by~~ using a single indicator. In areas where a single VOC specie dominates NO_3 reactivity towards VOC ~~is dominated by a single VOC specie~~ for a long time, such as forest areas, suburbs, and rural areas (BVOC dominant), this method would have a good performance. Method 2 had a better performance, while more VOC species are needed. In urban areas, especially in urban areas where the contributors had different chemo diversity with strong seasonality, this method should be more suitable. Since the two methods lower the bar for estimating NO_3 reactivity by using VOC measurement data, we can ~~look into~~investigate the level of NO_3 reactivity ~~by~~ using the reported VOC measurement data in the past.

We collected the historical measurement data of VOC concentrations in Beijing (Supporting file. S1) and estimated NO_3 reactivity ~~by the~~using parameterization methods. We found the level of NO_3 reactivity mainly ranged from 0.001 to 0.1 s^{-1} in Beijing in the past decades (Fig. ~~3). Due to the limitation of data, we cannot find a trend of NO_3 reactivity before 2011. While during 2011-2020,~~4). During 2014-2020, a large amount of VOC data in urban Beijing presented and be collected in this study. We calculated the k_{NO3_mea} by detailed VOC ~~with respect to~~concerning the data provided by the ~~literatures~~literature, and estimated the NO_3 reactivity by parameterization methods if the reported data in the literatures ~~is~~are limited. As shown in Fig. ~~3, an overall decrease trend of~~4, NO_3 reactivity ~~can be found during 2011-2020.~~was relatively lower after 2014 than before. We inferred that the level of isoprene during this period may be varied small~~,~~ since the change of biogenic emission ~~unlikely to change much.~~may not be significant. Thus, we proposed that the ~~decrease of~~lower NO_3 reactivity during the past decade may be attributed to the anthropogenic emission reduction of anthropogenic VOC. It should be noted that this estimation suffers from ~~the~~ uncertainty, nevertheless, this trend and characterization of NO_3 reactivity in Beijing is helpful to understand the nighttime chemistry in Beijing.



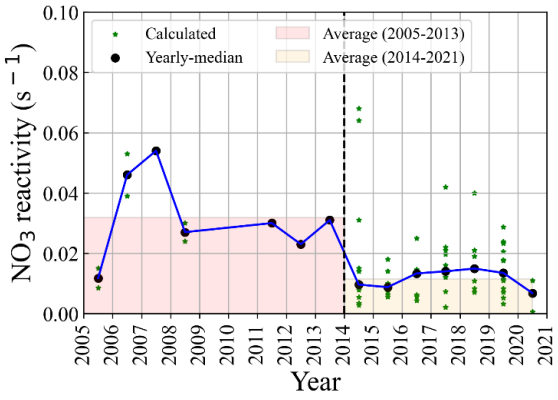


Figure ~~3~~4. The ~~reconstructed NO_3 reactivity calculated by the~~ reported VOC concentrations in Beijing calculated the reconstructed NO_3 reactivity record from 2005-2021. The averaged NO_3 reactivity calculated by the reported VOC data in each campaign is plotted as the star. The ~~yearly averaged~~ median values of NO_3 reactivity (black dot) ~~between 2011-2019 shows a decline.~~in each year show high during 2005-2013 and relatively low during 2014-2021. It should be noted that the monoterpenes are not considered here.

~~3.3 NO_3 reactivity towards monoterpenes~~

~~After taking MNTs into account, the total k_{NO3} (named as k_{NO3_total}) was greatly enlarged, with campaign-averaged value of 0.0061 ± 0.0088 s^{-1}, resulting in our results comparable with previous research results. The NO_3 reactivity towards MNTs (named as k_{NO3_MNTs}) was higher in autumn and winter and lower in spring and summer (Fig. S8). Considering the corresponding reactivity towards monoterpenes, the total NO_3 reactivity towards VOC changed from (summer > autumn > winter > spring) to (autumn > winter > summer > spring), highlights the impact of the monoterpene variations~~

on the reactivity. The NO_3 reactivity towards MNTs displayed significant differences between daytime and nighttime (Fig. S8c-d). The reactivity at night in all months was higher than that in the daytime, especially from October to January, highlights the role of biogenic monoterpenes in nocturnal NO_3 chemistry (Li et al., 2013; Riba et al., 1987). To compare the measured and the total NO_3 reactivity towards VOC, we calculated the fraction (F_{MNTs}) by Eq. 12.

$$F_{MNTs} = \frac{kNO3\_MNTs}{kNO3\_total} \quad \text{Eq. 12}$$

Figure 4a displays the differences between the k_{NO3_meas} and k_{NO3_total}. Monoterpenes were very important for NO_3 reactivity, and the F_{MNTs} varied from 40% to 80%, with strong seasonal variations. The MNTs accounted for NO_3 reactivity nearly 80% in winter and spring. In the seasons when isoprene no longer dominated, the measured reactivity accounted for a small fraction, and the corresponding reactivity towards AVOC such as styrene was smaller than that of monoterpenes. As shown in Fig. 4b, the measured VOC had high fractions in the daytime and low at night. Especially in May and August. The measured VOC in the daytime accounted for more than 60% of k_{NO3_total}, which was closely related to the increasing concentrations of isoprene in the summer daytime. The reactivity towards MNTs accounted for a large fraction of reactivity at night.

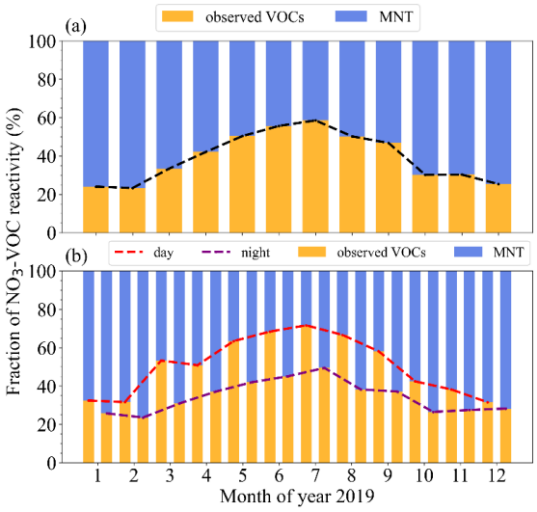


Figure 4. (a) Fractions of the k_{NO3_total}. (b) Fractions of the k_{NO3_total} divided into daytime (left) and nighttime (right). The colors on the stacked bar plot indicate the different fractions as they are donated in the legend. The lines represent the monthly-averaged variations of the NO_3 reactivity towards MNTs.

We After considering MNTs, we updated the parameterization method established before by using the relationship between reactivity and VOC concentrations, including monoterpenes. The updated parameterization Method 1 used the same principle as introduced in Sect 3.2, with fitting slopes changing significantly (Fig. S9 Figure. S10). Table S4 gives S5 shows the specific correlation

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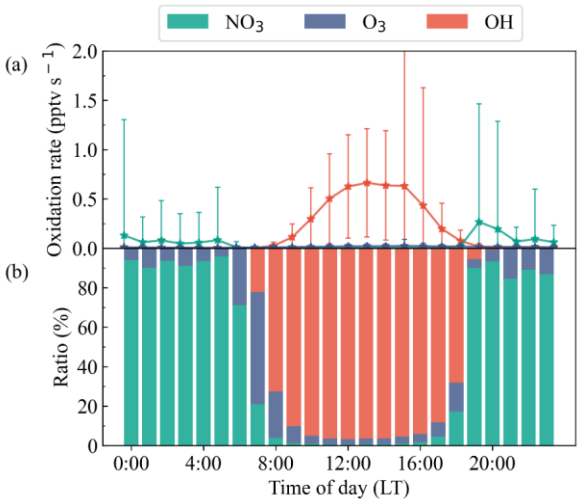
coefficients between six key VOC concentrations and k_{NO3_total}. The updated Method 2 considered the sum contributions of six VOC and the estimated MNTs by isoprene concentration. We reevaluated the two updated parameterization methods (single VOC and six VOC, respectively). Overall, the performance of the two methods ~~are~~is reasonable, and the updated Method 1 is better than that of Method 2 in general (Fig. ~~S10).~~S11). We evaluated this parameterization on datasets of other years (shown in Fig S12) and showed a robust performance.

3.~~4~~3 Nighttime VOC oxidation

Here we examined the role of NO_3 in ~~the~~ VOC oxidation in Beijing 2019. As shown in Fig. ~~5~~S13, OH oxidized most of VOC during the daytime, with the oxidation rate ~~reached~~reaching the maximum value of 0.6 pptv s^{-1} in the afternoon. Compared with OH, the VOC oxidation rates by O_3 and NO_3 in the daytime were remarkably lower. From 18:00 to 6:00, the ~~characteristics of nocturnal chemical in Beijing were significant. The~~ ratios of VOC oxidized by NO_3 kept above 80%, and the contribution of O_3 was relatively weak, which is consistent with that reported in high NOx regions(Chen et al., 2019; Edwards et al., 2017; Wang et al., 2018a). The VOC oxidation rate by NO_3 presented a single peak at 19:00 with the value of 0.25 pptv s^{-1}, which is the same magnitude as that by OH in the daytime, illustrating the importance of NO_3 in VOC oxidation as shown in the previous studies (Wang et al., 2017a), ~~highlight~~implying the importance of nocturnal chemistry for organic nitrate and SOA formation.



~~**Figure 5.** (a) Median diurnal profile of VOC oxidation rate by OH, NO_3 and O_3. The colored lines are error bars (+standard deviation). (b) Fractions of VOC oxidation rate by atmospheric oxidants.~~

The VOC oxidation rate by NO_3 and oxidation fractions had strong seasonal variabilities in Beijing. As shown in Fig. ~~S11~~5, the nighttime oxidation rate (summer > spring > autumn > winter) was affected by NO_3 concentrations and the total NO_3 reactivity towards VOC. In summer, the NO_3 oxidation rate

presented a single peak, with a maximum value of 0.7 pptv s^{-1} at 20:00, and remained around 0.1 pptv s^{-1} at the rest of the night. The rate at 21:00-5:00 was relatively constant. The rate in winter was lower, with the two maximum values of 0.06 pptv s^{-1} presented at 19:00 and 4:00, which were further lower than the average value of the other three seasons. The results ~~were good agreement~~agreed with the previous studies, in which the VOC oxidation rate by NO_3 concentrations ~~contained~~was high from 19:00-23:00 (Wang et al., 2017b). There was a competition between NO_3 and O_3 in the nighttime VOC oxidation in Beijing. Although the NO_3 oxidation rate at night was higher than that of O_3 throughout the year, the changes ~~of~~in O_3 oxidation rate ~~had a significant impact on~~significantly impacted the ratios of VOC oxidized by NO_3. The ratios of nighttime VOC oxidized by NO_3 in Beijing were higher in autumn~~,~~ and ~~then in~~ spring, summer, and winter. Although the O_3 concentrations in winter decreased, the competitiveness of NO_3 in VOC oxidation decreased more due to the decline of NO_3 concentrations. The competitiveness of O_3 in VOC oxidation was relatively enhanced, resulting in a significant decline in the ratios of VOC oxidized by NO_3.

~~3.5 Regulation of nighttime VOC oxidation~~

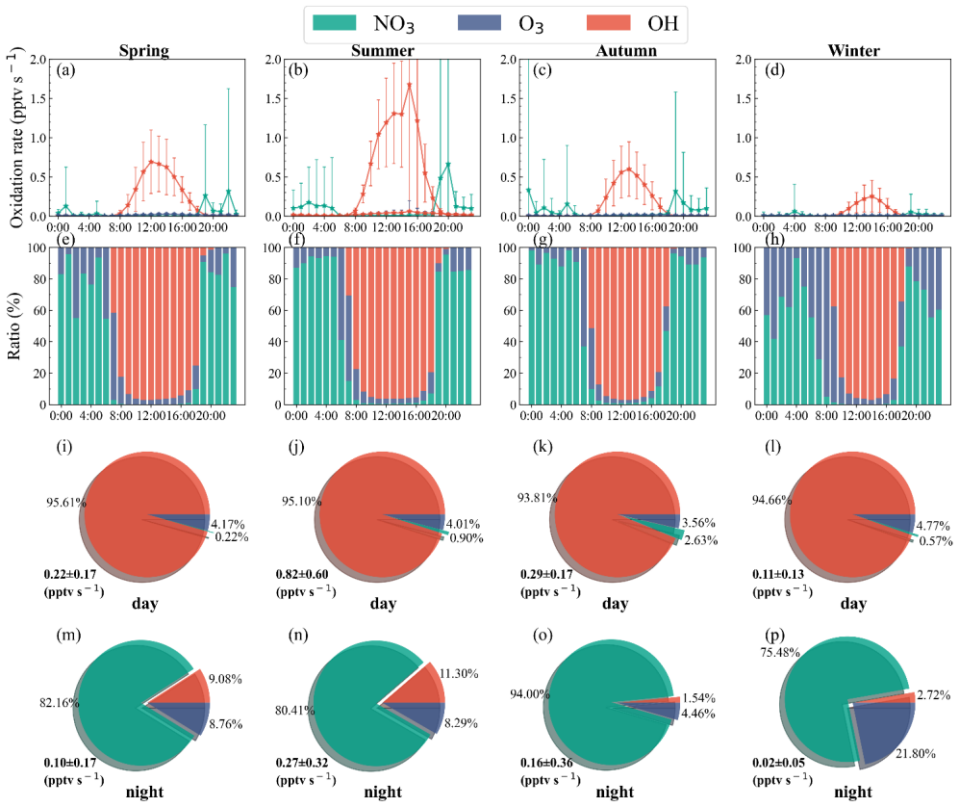
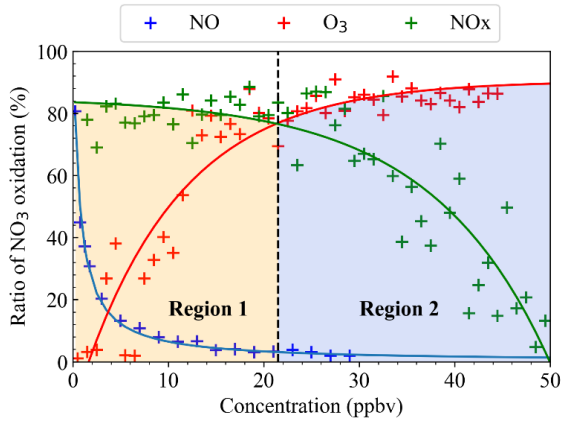


Figure 5. (a-d) Median diurnal profiles (±standard deviation) of VOC oxidation rate by atmospheric

oxidants in different seasons. (e-h) Fractions of VOC oxidation rate by atmospheric oxidants in different seasons. (i-p) Pie charts representing the daytime and the nighttime VOC oxidation rate by OH, NO_3, and O_3 during different seasons, with the averaged values and standard deviations.

3.4 Relationship between O_3/NO_x and nocturnal VOC oxidation by NO_3

To understand the importance of nighttime VOC oxidized by NO_3, we defined the fraction of VOC oxidation rate by NO_3 to the total oxidation rate as nocturnal VOC oxidation ratio by NO_3 (R_{NO3}, see Section 2.3 for its calculation) and explored the relationship between the ~~nocturnal oxidation ratios of NO_3 (R_{NO3})~~ratio and the nighttime concentrations of ~~NO,~~ O_3 and ~~NO_x~~NO_x. It is found that a strong nonlinear relationship between them (shown in Figure 6). The R_{NO3} had negative correlation coefficients with NO concentrations. With the increase of NO concentrations at night, the ratios decreased exponentially. When the NO concentrations increased at low NO ~~condition~~conditions, it could cause a significant decline in the ratios of VOC oxidized by NO_3. While at high NO condition, the ratios were not sensitive to the increase of NO concentrations (Fig. ~~S12~~S14), indicating that the nighttime NO concentrations in Beijing strongly controlled the ratios effectively. It can be expected since the increase of NO concentrations controlled the NO_3 loss term, then caused the decrease of NO_3 concentration. When the NO concentrations exceeded a threshold value~~,~~ (7 ppbv), the NO_3 loss was ~~totally~~ dominated by NO.



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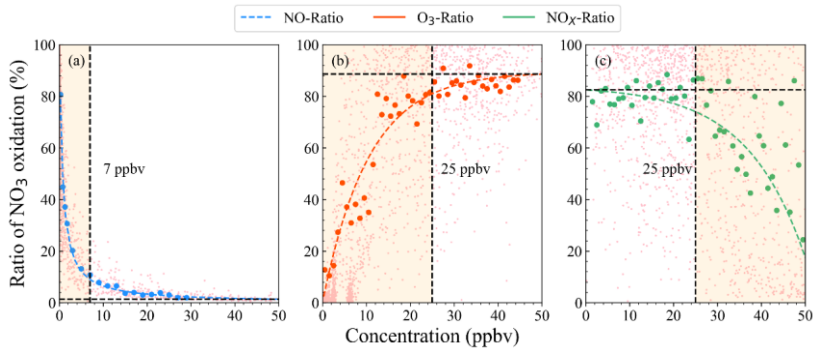

Figure 6. Fitting diagrams between the ratios of nighttime VOC oxidized by NO_3 and the concentrations of NO~~, O_3 and NO_X. In Region 1, the ratio is more sensitive to O_3, while less sensitive to NO_X. In Region 2, it is more sensitive to NO_X, while less sensitive to O_3.~~ (a), O_3 (b), and NO_x (c). The light pink scattered dots represent the oxidation ratios at different concentrations, and the solid dots represent the median value of each bin of oxidation ratios corresponding to each concentration range. Colored dot lines represent the fitting results of the solid median dots. And the black dot line in each panel shows a threshold to divide the curve into two regimes. In (a), the regime is divided into NO-limited (<7 ppbv) and NO-saturated (>7 ppbv); in (b) and (c), a threshold of 25 ppbv divide the curves into NO_x (O_3) limited and saturated regimes. The results showed in (b) and (c) are representative of low NO condition (< 7 ppbv).

The ratios of nighttime VOC oxidized by NO_3 also had a strong nonlinear relationship with O_3 and NO_x concentrations. O_3 concentrations have one positive and one negative contribution to the R_{NO3}. The positive effect is that increasing O_3 concentration ~~increase~~increases the NO_3 production rate, which ~~increase~~increases the NO_3 steady-state concentrations and then increase the ratios. And the negative is increasing O_3 concentrations ~~increase~~increases the reaction rate between VOC and O_3, which increase the competitiveness of O_3 in VOC oxidation and then decrease the ratios. Figure. ~~S12~~S14 also shows the relationship between the R_{NO3} and the concentrations of O_3. While O_3 concentrations were below ~~21.5~~25 ppbv, the ratios were very sensitive to O_3 level, which fast increased with O_3 concentrations. While the ratio ~~become~~became not sensitive and remained relatively constant when the O_3 concentrations exceeded ~~21.5~~25 ppbv. It can be explained that when the O_3 concentrations were low, the NO_3 production rate was more sensitive to the increase ~~of~~in O_3 concentrations. In this case, O_3 mainly affects the ratios positively. When the O_3 concentrations were high, the positive effect of O_3 tended to be constant, ~~indicates~~indicating the two opposite effects ~~overall keep~~kept in balance.

When the ~~NO_X~~NO_x concentrations were low (i.e~~.g., <21.5~~., <25 ppbv), the R_{NO3} ~~were~~was less sensitive to ~~NO_X~~NO_x, remaining relatively constant with ~~the~~ further increase. ~~It is believed that the~~The increase of NO_3 loss rates through the N_2O_5 heterogeneous reaction and the NO reaction ~~were~~was believed to be kept in balance with the NO_3 production rate increased by NO_2 concentrations. At high NO_x ~~condition~~conditions, the ratios sensitively decreased with the increase of ~~NO_X~~NO_x concentrations, which is explained ~~that~~by the increase of NO_3 loss rates by NO, resulting in a decline in the ratios.

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To better understand the nonlinear effect of NO_2 and O_3 on the nighttime VOC oxidation, we further explored the effect of O_3 concentration on the ratios existing in different concentrations of NO_2. As shown in Fig. ~~S13~~S15, in higher concentrations of NO_2, the threshold of lower O_3 concentrations ~~were~~was required for the R_{NO3} to become constant, which reflected the couple ~~influence~~influences of NO_2 and O_3 on nighttime VOC oxidation through the nonlinear response, and indicated that in the environment richen in NO_2, nocturnal NO_3 chemistry easily tended to be more dominant.

4. Conclusions and implications

In this study, we showed that the NO_3 reactivity towards measured VOC highly varied with ~~strong~~big seasonal differences, ~~which was~~ mainly driven by isoprene concentrations. The top 6 contributors to the measured NO_3 reactivity towards VOC were isoprene, styrene, cis-2-butene, trans-2-butene, trans-2-pentene, and propylene. Among them, isoprene and styrene contributed most of the reactivity. In addition, monoterpenes are proposed to be a significant source of NO_3 reactivity. Recently studies showed ~~the~~that anthropogenic emissions ~~contributes~~contribute significantly to the ambient MNTs concentrations ~~by~~through biomass burning, traffic and volatile chemical product emissions in the urban regions, it would further enhance the importance of nocturnal NO_3 oxidation (Coggon et al., 2021; Nelson et al., 2021; Peng et al., 2022; Qin et al., 2020; Wang et al., 2022). It should be noted that the estimated contributions of MNTs only considered the biogenic emissions and may ~~be~~ represent the lower bias~~, thus~~. Thus we highlight the importance of field observation of MNTs for advancing the understanding the nighttime NO_3 chemistry. In addition, it should be noted that we didn't take the contributions of OVOC into account~~,~~ since the reaction rate coefficients of OVOC with NO_3 are small (Ambrose et al., 2007).

Looking for insight to the trend and evolution of detailed NO_3 chemistry is very scare, but it can ~~really~~be helpful to understand the response of the nocturnal chemistry on the emission change at a large time scale. Limited by the non-extensive and non-continuous observation, we cannot obtain the long-time measurement of all the VOC species in multiple sites. Since isoprene and styrene are good indicators of NO_3 reactivity in different seasons, at least as we ~~shown~~showed in urban Beijing, those can be used to estimate the NO_3 reactivity towards VOC to reestablish the long-term trend of NO_3 reactivity in urban regions for further evaluation of its history of nighttime chemistry. We admitted that the estimation of the NO_3 reactivity trend ~~may~~might be highly uncertain, but this attempt may be very helpful to know the level and overall change of nighttime chemistry.

We showed that NO_3 dominated the nighttime VOC oxidation in Beijing, but the oxidation ratio had a strong nonlinear relationship with O_3 and ~~NOx~~NO_x concentrations. With the NO_2 concentrations ~~decrease~~decreasing, the threshold values of O_3 between the sensitive regime and non-sensitive regime tended to increase, indicative of the nighttime oxidation by NO_3 would be more easily affected by the level of O_3 with the ~~implement~~implementation of sustaining NO_x reduction in the future. The threshold values of O_3 can provide an effective basis for the measures to control nocturnal chemical and secondary organic ~~aerosols~~aerosol pollution in the typical urban region.

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Code/Data availability. The datasets used in this study are available from the corresponding author upon request (wanghch27@mail.sysu.edu.cn; k.lu@pku.edu.cn).

Author contributions. H.C.W. and K.D.L. designed the study. H.J.H. and H.C.W. analyzed the data with input from J.W., Z.L.Z., X.Z.X., T.Y.Z., X.R.C., X.L., ~~M.M.Q~~and S.J.F., W.X.F. provided the ~~modelled~~modeled monoterpene and isoprene data, X.L., L.M.Z., M.H., and Y.H.Z. organized this field campaign and provided the field measurement dataset. H.J.H. and H.C.W. wrote the paper with input from K.D.L.

Competing interests. The authors declare that they have no conflicts of interest.

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