1 Variation and Trend of Nitrate radical reactivity towards

2 volatile organic compounds in Beijing, China

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ABSTRACT. Nitrate radical (NO₃) is an important nocturnal atmospheric oxidant in the troposphere, 22 which significantly affects the lifetime of pollutants emitted by anthropogenic and biogenic activities, 23 especially volatile organic compounds (VOC). Here, we used one-year VOC observation data 24 obtained in urban Beijing in 2019 to look into the level, compositions, and seasonal variation of NO₃ 25 reactivity (k_{NO3}). We show that hourly k_{NO3} towards measured VOC highly varied from $<10^{-4}$ to 26 0.083 s⁻¹ with a campaign-averaged value (\pm standard deviation) of 0.0032 \pm 0.0042 s⁻¹. There was 27 large seasonal difference in NO₃ reactivity towards VOC with the average of 0.0024 ± 0.0026 s⁻¹, 28 $0.0067 \pm 0.0066 \text{ s}^{-1}$, $0.0042 \pm 0.0037 \text{ s}^{-1}$, $0.0027 \pm 0.0028 \text{ s}^{-1}$ from spring to winter. Alkenes such as 29 isoprene and styrene accounted for the majority. Isoprene was the dominant species in spring, 30 summer, and autumn, accounting for 40.0%, 77.2%, and 43.2%, respectively. Styrene only played a 31 leading role in winter, with a percentage of 39.8%. A sensitivity study shows monoterpenes, the 32 species we did not measure, may account for a large fraction of k_{NO3} . Based on the correlation 33 between the calculated k_{NO3} and VOC concentrations in 2019, we established localized 34 parameterization schemes for predicting the reactivity by only using a part of VOC species. The 35 historically published VOC data was collected using the parameterization method to reconstruct the 36 long-term k_{NO3} in Beijing. The lower k_{NO3} during 2014-2021 compared with that during 2005-2013 37 may attribute to anthropogenic VOC emission reduction. At last, we revealed that NO3 dominated the 38 nocturnal VOC oxidation with 83% on the annual average in Beijing in 2019, which varied 39

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 knowledge

42 of nocturnal VOC oxidation and secondary organic pollution.

43

44 **1. Introduction**

A large amount of NO emitted in cities is oxidized into NO₂ by O₃ in the atmosphere (R1), and NO₂ 45 continues to be oxidized into nitrate radical (NO₃) by O₃ (R2). NO₃ is the main nocturnal 46 tropospheric oxidant (Brown and Stutz, 2012; Wayne et al., 1991) with a relatively high 47 concentration level at night due to it has rapid loss by photolysis (R3) and the reaction with NO 48 during the daytime (Stark et al., 2007). These two reactions return NO_3 back to NO_x and thus cannot 49 contribute to effective NO_x removal. In addition, NO₃ reacts with NO₂ to form nitrous pentoxide 50 (N_2O_5) (R5), and N_2O_5 can be decomposed to NO₃ and NO₂ (R6), establishing a 51 temperature-dependent equilibrium. 52

53 NO+O ₃ \rightarrow NO ₂ +O ₂	(R1)
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54	$NO_2+O_3 \rightarrow NO_3+O_2$	(R2)
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$NO_3+hv \rightarrow NO+O_2$	(R3)
	$NO_3+hv \rightarrow NO+O_2$

- 56 $NO_3+hv \rightarrow NO_2+O^1D$ (R4)
- 57 $NO_3 + NO \rightarrow 2NO_2$ (R5)
- 58 $NO_2+NO_3+M \rightarrow N_2O_5+M$ (R6)
- 59 $N_2O_5+M \rightarrow NO_2+NO_3+M$ (R7)

During the nighttime, there are two kinds of reactions that have a large impact on air pollution and 60 regulate the lifetime and budget of many trace gas species. One is NO₃ oxidizes volatile organic 61 compounds and forms complex products (R8). The other is NO₃ be transformed into N₂O₅ and 62 removed by heterogeneous hydrolysis (R9), providing an effective way to remove NO_x and produce 63 nitrate aerosol and nitryl chloride (Brown et al., 2004; Dentener and Crutz, 1993; Osthoff et al., 64 2008). The competition between R8 and R9 determines the fate of nocturnal nitrogen oxidation 65 chemistry, which leads to the formation of different secondary pollutants (Bertram and Thornton, 66 2009; Brown et al., 2006). In particular, the degradation of VOC by NO₃, especially biogenic VOC 67 68 (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). 69

70 $NO_3+VOC \rightarrow products$ (R8)

71
$$N_2O_5+H_2O_{(aq)}/Cl^{\rightarrow}HNO_3 + \varphi ClNO_2$$
 (R9)

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

76 $k_{NO3} = \sum k_i \times [VOC_i]$ Eq. 1

where the $[VOC_i]$ is VOC concentrations and k_i is the corresponding reaction rate coefficients. Table 77 S1 gives the reaction rate coefficients of NO₃ with VOC (Atkinson and Arey, 2003). The contribution 78 of VOC to the NO₃ reactivity with respect to different VOC varies greatly, which is caused by the 79 abundance of species and the reaction rate coefficients. Thus, NO₃ reactivity towards VOC is also 80 affected by temperature since temperature affects not only the temperature-dependent reaction rate 81 coefficients but also the VOC emissions in the atmosphere, especially for the emission of biogenic 82 VOC like isoprene and monoterpenes (Wu et al., 2020), leading to the variations of VOC species that 83 dominate k_{NO3} towards VOC in different seasons. 84

Previous works showed that the VOC species which dominate the NO₃ reactivity vary greatly 85 between different regions. In forests and rural areas, such as Pabstchum outside Berlin, Germany, the 86 lush forests emitted a large number of monoterpenes and isoprene, accounting for the majority of 87 $k_{\rm NO3}$, which ranged from 0.0025 to 0.01 s⁻¹ (Asaf et al., 2009). In semi-arid urban areas such as 88 Jerusalem, the emissions of BVOC are less due to the sparser vegetation, and the maximum of NO3 89 reactivity was about 0.01 s⁻¹, in which the phenol, cresol and some monoolefins emitted by road 90 traffic were the main contributors (Asaf et al., 2009). In urban regions like Houston, industrial 91 emissions, including isoprene and other alkenes, dominated the NO₃ reactivity (Stutz et al., 2010). In 92 93 the city's suburbs, the $k_{\rm NO3}$ may be jointly affected by anthropogenic and biogenic volatile organic compounds. For example, the NO₃ reactivity towards VOC in Xianghe, Beijing reached $0.024 \pm$ 94 $0.030 \,\mathrm{s}^{-1}$, with a maximum value of 0.3 s^{-1} and minimum value of 0.0011 s^{-1} . Isoprene, styrene, and 95 2-butene contributed to most of the k_{NO3} (Yang et al., 2020). 96

The above NO₃ reactivities are all calculated by the measurement of VOC concentrations. In addition 97 to this method, an instrument was developed to measure k_{NO3} in the atmosphere directly (Liebmann 98 et al., 2017). They presented the first direct measurement of NO₃ reactivity in the Finnish boreal 99 forest in 2017. They concluded that the NO₃ reactivity was generally high, with a maximum value of 100 0.94 s^{-1} , displaying a strong diel variation with a nighttime mean value of 0.11 s^{-1} and daytime value 101 of 0.04 s⁻¹ (Liebmann et al., 2018a). In 2018, they presented the direct measurement in and above the 102 boundary layer of a mountain site, with daytime values of up to 0.3 s⁻¹ and nighttime values close to 103 0.005 s⁻¹ (Liebmann et al., 2018b). Most importantly, the direct measurement revealed the existence 104 of missing NO₃ reactivity in various regions, which indicated the missing NO₃ oxidation mechanisms. 105 These results largely improved the understanding of nighttime chemistry. 106

Nevertheless, the direct field determination of k_{NO3} is still extremely lacking, especially in urban regions at the current stage. Until now, most works about the VOC oxidation by NO₃ 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. 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 112 and total NO₃ reactivity on a long-time scale are also rarely studied. Our recent work reported that 113 the increasing trend of the NO₃ production rate is caused by anthropogenic emission changes, while 114 the long-term and detailed NO₃ loss budget is still uncertain to some extent (Wang et al., 2023). Here, 115 we attempt to look for insight into the level, variations, and impacts of NO₃ reactivity by using the 116 one-year measurement of VOC in an urban site in Beijing, the role of unmeasured VOC species 117 (monoterpenes) in the contributions of NO₃ reactivity is also discussed. The long-term trend of NO₃ 118 reactivity is estimated by collecting the published VOC data and the newly proposed 119 parameterization method. At last, the nocturnal VOC oxidation by NO₃ during different seasons was 120 further evaluated. 121

122 **2. Method**

123 **2.1** Site description and instrumentation

The measurement was conducted at the campus of Peking University (39° 99' N, 116° 30' E) during 124 the whole year of 2019. The site is situated northeast of the Beijing city center and near two traffic 125 roads, which represent a typical urban and polluted area with fresh, anthropogenic emissions (Wang 126 et al., 2017a). The measurements were made on a building roof with a height of 20 m above the 127 ground. Measurements of VOC concentrations were performed using an automated gas 128 chromatograph equipped with mass spectrometry or flame ionization detectors (GC-MS/FID). The 129 volatile organic compounds were pretreated by pre-freezing and collected in the deactivated quartz 130 empty capillary at extreme-low temperature (-150 °C), then heated and delivered into the analysis 131 system. After separation by the double chromatographic column, the low-carbon compounds C₂-C₄ 132 were detected by the FID detector, and the high-carbon compounds C₅-C₁₀ were detected by the MS 133 detector. There are 56 kinds of VOC measured in total (listed in Table S1 and the concentrations are 134 135 depicted in Figure S1), in which monoterpenes measurement are not valid. NOx and O3 were monitored by chemiluminescence (Thermo Scientific, 42i-TLE) and UV photometric methods 136 (Thermo Scientific, 49i), respectively. A Tapered Element Oscillating Microbalance analyzer 137 (TianHong, TH-2000Z1) was used to measure the mass concentration of PM_{2.5}. The quality 138 assurance and quality controls of data were implemented regularly (Chen et al., 2020). Photolysis 139 frequencies were obtained by the Tropospheric Ultraviolet and Visible (TUV) model simulation. 140 Hourly data were processed and used in the following analysis. 141

142 **2.2 Estimation of monoterpenes**

Since the measurement data did not include monoterpenes (MNT), we, therefore, use the measured isoprene and 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.

156 $Factor = \frac{[MNT_{sim}]}{[ISO + 1]}$ Eq. 2

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

We used the Factor to estimate monoterpenes level rather than modeled monoterpene concentrations 158 due to the modeled isoprene is systematically higher than that of observation (Fig. S2). Thus the 159 using of the modeled Factor may be more reasonable. In Beijing, α -pinene and β -pinene were 160 reported to have the highest abundance among monoterpenes (Cheng et al., 2018), with higher 161 emissions in summer (Wang et al., 2018b; Xia and Xiao, 2019). Therefore, we use a weighted 162 reaction rate coefficient approximated by the average value of α -pinene and β -pinene with NO₃ in the 163 following calculations. Since the emissions of sesquiterpenes in BVOC are much lower than that of 164 isoprene, monoterpenes, and other BVOC, thus we did not consider the contribution of 165 sesquiterpenes to the reactivity. The detailed average diurnal variations of Factor are listed in Table 166 S2. 167

168 2.3 VOC oxidation rate by NO₃

To study the reaction of NO₃ and VOC during the nighttime, we estimated the NO₃ concentrations by 169 steady-state calculation. This method is widely used to estimate the concentrations of short-lived 170 substances, by assuming its production and loss rates are balanced in a specific time range. Given 171 sufficient time, the steady state can be reached for NO₃ at night, in which the production and loss 172 terms are approximately balanced (Brown, 2003; Crowley et al., 2010). Here the production terms of 173 NO3 are the reaction of NO2 and O3, and the loss terms of NO3 include reactions with VOC, reaction 174 with NO, heterogeneous reaction, and photolysis. The steady-state NO₃ mixing ratios are expressed 175 by Eq. 4 (Brown and Stutz, 2012). 176

177
$$[NO_3]_{ss} = \frac{k_{NO_2+O_3}[NO_2][O_3]}{\sum k_i \times [VOC_i] + k_{NO+NO_3}[NO] + J_{NO_3} + k_{het}K_{eq}[NO_2]}$$
Eq. 4

Where J_{NO3} is the sum of the photolysis coefficients of the two photolysis reactions of NO₃. The k_{het} is the heterogeneous uptake rate of N₂O₅ on the aerosol surface, which can be calculated by Eq. 5.

180
$$k_{het} = 0.25 \times \gamma \times S_a \times c$$
 Eq. 5

181 Where γ is the dimensionless uptake coefficient of N₂O₅ parameterized by Eq. 6 (Evans and Jacob, 182 2005; Hallquist et al., 2003; Kane et al., 2001), Sa (m² m⁻³) is the aerosol surface area density 183 estimated by the level of PM_{2.5} (Wang et al., 2021), and *c* is the mean molecular velocity of N₂O₅. 184 $\gamma = \alpha \times 10^{\beta}$

185
$$\alpha = 2.79 \times 10^{-4} + 1.3 \times 10^{-4} \times RH - 3.43 \times 10^{-6} \times RH^2 + 7.52 \times 10^{-8} \times RH^3$$

186 $\beta = 4 \times 10^{-2} \times (T - 294) \ (T > 282K)$

187 $\beta = -0.48 \ (T < 282K)$ Eq. 6

The reaction rate coefficients of NO₂ and O₃, NO and NO₃, and the equilibrium constant for the 188 forward and reverse Reactions (R4) and (R5) are temperature dependent. We have adopted JPL 189 evaluation reports for the reaction rate coefficients. The time series of hourly-related parameters in 190 estimating the steady-state NO₃ and the diurnal cycle of NO₃ concentrations were shown in Fig. S3 191 and Fig. S4. To compare the VOC oxidation by NO₃ with other oxidants, we estimated OH 192 concentrations by the slope extracted from the measured OH and J_{O1D} (s⁻¹) in North China (Tan et al., 193 2017)) (Eq. 7), where J_{0^1D} used in this study was obtained by the TUV model simulations. The 194 VOC oxidation rate (R_{NO3}) and the ratio of VOC oxidized by NO₃ to the total oxidation rate can be 195 calculated by Eq. 8. 196

197 $[OH] = 4.1 \times 10^{11} cm^{-3} s^{-1} \times J_{O^{1}D}$ Eq. 7

198
$$R_{NO_3} \approx \frac{\sum k_i \times [VOC_i][NO_3]}{\sum k_i \times [VOC_i][OH] + \sum k_i \times [VOC_i][NO_3] + \sum k_i \times [VOC_i][O_3]} \qquad \text{Eq. 8}$$

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

200 3. Results and discussion

3.1 NO₃ reactivity calculated by measured VOC

During the campaign, the hourly k_{NO3} towards measured VOC (named as $k_{NO3 mea}$) highly varied 202 from $<10^{-4}$ to 0.083 s⁻¹ with campaign-averaged value (± standard deviation) of 0.0032 ± 0.0042 s⁻¹. 203 The $k_{\text{NO3 mea}}$ displayed a strong diel variation on the annual average (Fig. S5). In previous studies, 204 the NO₃ reactivity towards VOC was reported to be 0.024 ± 0.030 s⁻¹ on average in a suburban site in 205 summer in North China (Yang et al., 2020); and highly varied between 0.005 - 0.3 s⁻¹ in the 206 mountaintop site in summer (Liebmann et al., 2018c). Our result is one order of magnitude lower, 207 which may reflect the huge difference of $k_{\rm NO3 mea}$ in different environments and sampling time. 208 Certainly, it may be attributed to the reason that calculated k_{NO3} here did not include some species, 209 such as monoterpenes, phenol, cresol and so on. The diurnal variations of $k_{\rm NO3\ mea}$ had strong 210 seasonal variability (Fig. S6). The diurnal variations in winter and spring were relatively weak, and 211 in summer and autumn were strong, with clear peaks at 9:00-10:00 and 15:00, respectively. The 212 $k_{\rm NO3\ mea}$ in spring, summer, and autumn reached the daily maximum value between 8:00 a.m. and 213 10:00 a.m. (spring: 0.0034 s⁻¹, summer: 0.0083 s⁻¹, autumn: 0.0057 s⁻¹). In winter, it reached the 214 maximum value of 0.0033 s^{-1} at about 22:00. 215

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 217 reactivity in August. The $k_{\rm NO3 mea}$ towards isoprene reached the maximum in August and the 218 minimum in February, which was consistent with the previously reported change in isoprene 219 concentrations in Beijing (Cheng et al., 2018). The $k_{NO3 mea}$ shows a large seasonal difference with 220 the average value of $0.0024 \pm 0.0026 \text{ s}^{-1}$, $0.0067 \pm 0.0066 \text{ s}^{-1}$, $0.0042 \pm 0.0037 \text{ s}^{-1}$, $0.0027 \pm 0.0028 \text{ s}^{-1}$ 221 s⁻¹ from spring to winter. Table S3 shows the specific contributions of the top six species to $k_{\rm NO3\ mea}$ 222 in different seasons. Isoprene was the dominant species, accounting for 40.0%, 77.2%, and 43.2% in 223 spring, summer, and autumn. By comparison, styrene only played a leading role in winter, 224 accounting for 39.8%. Among the species which contributed to $k_{\rm NO3 mea}$ in Beijing, isoprene and 225 styrene contributed most to the overall $k_{\rm NO3 mea}$ (60%~90%), followed by cis-2-butene, 226 trans-2-butene, trans-2-pentene, and proplyene (5%~15%) with another VOC less than 2%. Our 227 results are consistent with previous studies in Beijing that $k_{\rm NO3}$ was mainly contributed by isoprene 228 (Yang et al., 2020), indicating the critical role of isoprene in NO₃ reactivity in Beijing. From summer 229 to autumn, the dominant species changed from isoprene to styrene, while from winter to spring, the 230 dominant species changed from styrene to isoprene. This indicated the AVOC and BVOC control 231 $k_{\rm NO3\ mea}$ alternately. Overall, the $k_{\rm NO3\ mea}$ displayed a characteristic of high in summer and autumn 232 233 and low in winter and spring.



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

Figure 1b-c shows the k_{NO3_mea} towards measured VOC display clear day-night differences in summer and winter, especially in summer. The NO₃ 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 biogenic sources, which the 245 anthropogenic sources of isoprene are mainly traffic emissions (Li et al., 2013; Riba et al., 1987; Zou 246 et al., 2015). The isoprene emissions from biogenic sources in Beijing were one order of magnitude 247 larger than that of anthropogenic sources (Yuan et al., 2009). This indicates the concentrations of 248 isoprene at the environmental level in the urban areas of Beijing are not affected by the traffic 249 vehicles but mainly by plants (Cheng et al., 2018). As an aromatic hydrocarbon, styrene origins from 250 251 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 252 flame of engine fuel (Meng et al., 2016), industrial production (Radica et al., 2021) and other human 253 activities. The dominant source of styrene in Beijing is the local vehicle emissions (Li et al., 2014). 254 255 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 256 biogenic styrene compared with isoprene, we believe that the styrene in the atmosphere in Beijing is 257 mainly resulted from anthropogenic origins. It is believed that human activities in winter, such as 258 heating, gasoline, and diesel combustion, increased, meanwhile, the reduction of temperature and 259 radiation resulted in the reduction of biogenic isoprene emissions, explained the conversion of 260 dominance of NO₃ reactivity from summer to winter. 261

The NO₃ reactivity towards MNTs (named as $k_{NO3 MNTs}$) was estimated by the method mentioned in 262 section 2.2. After taking MNTs into account, the total k_{NO3} (named as $k_{NO3 \text{ total}}$) was greatly enlarged, 263 with the campaign-averaged value of 0.0061 ± 0.0088 s⁻¹, resulting in our results comparable with 264 previous research results. The NO₃ reactivity towards MNTs was higher in autumn and winter and 265 lower in spring and summer (Fig. S7). Considering the corresponding reactivity towards 266 monoterpenes, the total NO₃ reactivity towards VOC changed from (summer > autumn > winter > 267 spring) to (autumn > winter > summer > spring), highlighting the impact of the monoterpene 268 269 variations on the reactivity. The NO₃ reactivity towards MNTs displayed significant differences between daytime and nighttime (Fig. S7c-d). The reactivity at night in all months was higher than 270 that in the daytime, especially from October to January, highlighting the role of biogenic 271 monoterpenes in nocturnal NO₃ chemistry (Li et al., 2013; Riba et al., 1987). To evaluate the 272 contribution of monoterpenes to the total k_{NO3} , we calculated the fraction (F_{MNTs}) by Eq. 9. 273

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$$F_{MNTs} = \frac{k_{NO_3_MNTs}}{k_{NO_3_total}} \qquad \text{Eq. 9}$$

Figure 2a displays the differences between the k_{NO3_mea} and k_{NO3_total} . Monoterpenes were very important for NO₃ reactivity, and the F_{MNTs} varied from 40% to 80%, with strong seasonal variations. The MNTs accounted for NO₃ 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.



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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 NO₃ reactivity towards MNTs.

289 3.2 Parameterization of NO₃ reactivity

We examined the correlation of key VOC concentrations and k_{NO3} mea. Figure. S8 gives the case in 290 January, for example. To a certain extent, the variations of $k_{\rm NO3\ mea}$ were closely linked to the 291 variations of the concentrations of main contributors. It is worth noting that in January, 292 trans-2-butene had a higher correlation coefficient with $k_{\rm NO3\ mea}$, which exceeded that of isoprene and 293 styrene. This indicates that higher contributions may not imply a stronger correlation. Fig. 3 shows 294 the correlation coefficients and the fitting equations between VOC concentrations and k_{NO3} in each 295 month (detailed in Table S4). According to the correlation coefficients, we can select the strongest 296 indicator corresponding to a certain month as the variable of the parameterization method. Here we 297 didn't import the VOC with small contributions into the parameterization method because these 298 299 indicators had no practical significance for $k_{\rm NO3 mea}$. In this way, we established the first parameterization method (Method 1) by using the strongest indicator in each month which can be 300 found in Table S4 (Eq. 10): 301

$$NO_3 reactivity_{sim1} = a \times [VOC] + b$$
 Eq. 10

Where, a, b, and [VOC] respectively represent the slope, the intercept, and the VOC species concentrations (ppbv) used for parameterization each month. The correlation coefficients between isoprene concentrations and k_{NO3_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 display the indication of these two species (isoprene and styrene) in different seasons.



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Figure 3. The 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 NO₃ reactivity towards total VOC to the reactivity towards these top 6 species: 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} = $\sum_{i=1}^{6} k_i \times [VOC_i]$ Eq. 11

where $[VOC_i]$ is the VOC concentrations and k_i is the corresponding reaction rate coefficients with NO₃. It should be noted that this parameterization method of NO₃ reactivity towards VOC may be localized.

To evaluate the effectiveness of the two parameterization methods established above, we estimated 322 the $k_{\rm NO3}$ in the different time scales, and compared them with the determined $k_{\rm NO3\ mea}$ by all 323 measured VOC. As shown in Fig. S9, both methods can well capture the level and variations of 324 $k_{\rm NO3\ mea}$, indicating the parametrization feasibility. Method 1 can easily and quickly estimate NO₃ 325 reactivity towards VOC using a single indicator. In areas where a single VOC specie dominates NO3 326 reactivity towards VOC for a long time, such as forest areas, suburbs, and rural areas (BVOC 327 dominant), this method would have a good performance. Method 2 had a better performance, while 328 more VOC species are needed. In urban areas, especially in urban areas where the contributors had 329 different chemo diversity with strong seasonality, this method should be more suitable. Since the two 330 methods lower the bar for estimating NO₃ reactivity by using VOC measurement data, we can 331 investigate the level of NO₃ reactivity using the reported VOC measurement data in the past. 332

We collected the historical measurement data of VOC concentrations in Beijing (Supporting file. S1) 333 and estimated NO₃ reactivity using parameterization methods. We found the level of NO₃ reactivity 334 mainly ranged from 0.001 to 0.1 s⁻¹ in Beijing in the past decades (Fig. 4). During 2014-2020, a large 335 amount of VOC data in urban Beijing presented and be collected in this study. We calculated the 336 $k_{\rm NO3\ mea}$ by detailed VOC concerning the data provided by the literature, and estimated the NO₃ 337 reactivity by parameterization methods if the reported data in the literatures are limited. As shown in 338 Fig. 4, NO₃ reactivity was relatively lower after 2014 than before. We inferred that the level of 339 isoprene during this period may be varied small since the change of biogenic emission may not be 340 significant. Thus, we proposed that the lower NO₃ reactivity during the past decade may be attributed 341 to the anthropogenic emission reduction of anthropogenic VOC. It should be noted that this 342 estimation suffers from uncertainty, nevertheless, this trend and characterization of NO₃ reactivity in 343 Beijing is helpful to understand the nighttime chemistry in Beijing. 344



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Figure 4. The reported VOC concentrations in Beijing calculated the reconstructed NO₃ reactivity record from 2005-2021. The averaged NO₃ reactivity calculated by the reported VOC data in each campaign is plotted as the star. The median values of NO₃ reactivity (black dot) 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.

351 After considering MNTs, we updated the parameterization method established before by using the relationship between reactivity and VOC concentrations, including monoterpenes. The updated 352 parameterization Method 1 used the same principle introduced in Sect 3.2, with fitting slopes 353 changing significantly (Figure. S10). Table S5 shows the correlation coefficients between six key 354 VOC concentrations and $k_{\rm NO3 \ total}$. The updated Method 2 considered the sum contributions of six 355 VOC and the estimated MNTs by isoprene concentration. We reevaluated the two updated 356 parameterization methods (single VOC and six VOC, respectively). Overall, the performance of the 357 two methods is reasonable, and the updated Method 1 is better than that of Method 2 in general (Fig. 358 S11). We evaluated this parameterization on datasets of other years (shown in Fig S12) and showed a 359 robust performance. 360

361 **3.3** Nighttime VOC oxidation

Here we examined the role of NO₃ in VOC oxidation in Beijing 2019. As shown in Fig. S13, OH 362 oxidized most of VOC during the daytime, with the oxidation rate reaching the maximum value of 363 0.6 pptv s⁻¹ in the afternoon. Compared with OH, the VOC oxidation rates by O₃ and NO₃ in the 364 daytime were remarkably lower. From 18:00 to 6:00, the ratios of VOC oxidized by NO₃ kept above 365 80%, and the contribution of O₃ was relatively weak, which is consistent with that reported in high 366 NOx regions(Chen et al., 2019; Edwards et al., 2017; Wang et al., 2018a). The VOC oxidation rate 367 by NO₃ presented a single peak at 19:00 with the value of 0.25 pptv s⁻¹, which is the same magnitude 368 as that by OH in the daytime, illustrating the importance of NO₃ in VOC oxidation as shown in the 369 previous studies (Wang et al., 2017a), implying the importance of nocturnal chemistry for organic 370 nitrate and SOA formation. 371

The VOC oxidation rate by NO₃ and oxidation fractions had strong seasonal variabilities in Beijing. 372 As shown in Fig. 5, the nighttime oxidation rate (summer > spring > autumn > winter) was affected 373 by NO₃ concentrations and the total NO₃ reactivity towards VOC. In summer, the NO₃ oxidation rate 374 presented a single peak, with a maximum value of 0.7 pptv s⁻¹ at 20:00, and remained around 0.1 375 pptv s⁻¹ at the rest of the night. The rate at 21:00-5:00 was relatively constant. The rate in winter was 376 lower, with the two maximum values of 0.06 pptv s⁻¹ presented at 19:00 and 4:00, which were further 377 lower than the average value of the other three seasons. The results agreed with the previous studies, 378 in which the VOC oxidation rate by NO₃ concentrations was high from 19:00-23:00 (Wang et al., 379 2017b). There was a competition between NO₃ and O₃ in the nighttime VOC oxidation in Beijing. 380 Although the NO₃ oxidation rate at night was higher than that of O₃ throughout the year, the changes 381 in O₃ oxidation rate significantly impacted the ratios of VOC oxidized by NO₃. The ratios of 382 nighttime VOC oxidized by NO₃ in Beijing were higher in autumn and spring, summer, and winter. 383 Although the O₃ concentrations in winter decreased, the competitiveness of NO₃ in VOC oxidation 384 decreased more due to the decline of NO₃ concentrations. The competitiveness of O₃ in VOC 385 oxidation was relatively enhanced, resulting in a significant decline in the ratios of VOC oxidized by 386 NO₃. 387



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, NO₃, and O₃ during different seasons, with the averaged values and standard deviations.

393 3.4 Relationship between O₃/NO_x and nocturnal VOC oxidation by NO₃

To understand the importance of nighttime VOC oxidized by NO₃, we defined the fraction of VOC 394 oxidation rate by NO₃ to the total oxidation rate as nocturnal VOC oxidation ratio by NO₃ (R_{NO3}, see 395 Section 2.3 for its calculation) and explored the relationship between the ratio and the nighttime 396 concentrations of O₃ and NO_x. It is found that a strong nonlinear relationship between them (shown 397 in Figure 6). The R_{NO3} had negative correlation coefficients with NO concentrations. With the 398 increase of NO concentrations at night, the ratios decreased exponentially. When the NO 399 concentrations increased at low NO conditions, it could cause a significant decline in the ratios of 400 VOC oxidized by NO₃. While at high NO condition, the ratios were not sensitive to the increase of 401 NO concentrations (Fig. S14), indicating that the nighttime NO concentrations in Beijing strongly 402 controlled the ratios effectively. It can be expected since the increase of NO concentrations controlled 403

the NO₃ loss term, then caused the decrease of NO₃ concentration. When the NO concentrations
 exceeded a threshold value (7 ppbv), the NO₃ loss was dominated by NO.



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Figure 6. Fitting diagrams between the ratios of nighttime VOC oxidized by NO₃ and the 407 concentrations of NO (a), O_3 (b), and NO_x (c). The light pink scattered dots represent the oxidation 408 ratios at different concentrations, and the solid dots represent the median value of each bin of 409 oxidation ratios corresponding to each concentration range. Colored dot lines represent the fitting 410 results of the solid median dots. And the black dot line in each panel shows a threshold to divide the 411 412 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 (O₃) limited and 413 saturated regimes. The results showed in (b) and (c) are representative of low NO condition (< 7 414 ppbv). 415

The ratios of nighttime VOC oxidized by NO₃ also had a strong nonlinear relationship with O₃ and 416 NO_x concentrations. O₃ concentrations have one positive and one negative contribution to the R_{NO3} . 417 The positive effect is that increasing O₃ concentration increases the NO₃ production rate, which 418 increases the NO₃ steady-state concentrations and then increase the ratios. And the negative is 419 increasing O₃ concentrations increases the reaction rate between VOC and O₃, which increase the 420 competitiveness of O₃ in VOC oxidation and then decrease the ratios. Figure. S14 also shows the 421 relationship between the R_{NO3} and the concentrations of O₃. While O₃ concentrations were below 25 422 ppbv, the ratios were very sensitive to O₃ level, which fast increased with O₃ concentrations. While 423 424 the ratio became not sensitive and remained relatively constant when the O₃ concentrations exceeded 25 ppbv. It can be explained that when the O₃ concentrations were low, the NO₃ production rate was 425 426 more sensitive to the increase in O₃ concentrations. In this case, O₃ mainly affects the ratios positively. When the O₃ concentrations were high, the positive effect of O₃ tended to be constant, 427 indicating the two opposite effects kept in balance. 428

When the NO_x concentrations were low (i.e., <25 ppbv), the R_{NO3} was less sensitive to NO_x, remaining relatively constant with further increase. The increase of NO₃ loss rates through the N₂O₅ heterogeneous reaction and the NO reaction was believed to be kept in balance with the NO₃ production rate increased by NO₂ concentrations. At high NO_x conditions, the ratios sensitively decreased with the increase of NO_x concentrations, which is explained by the increase of NO₃ loss 434 rates by NO, resulting in a decline in the ratios.

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. S15, in higher concentrations of NO_2 , the threshold of lower O_3 concentrations was required for the R_{NO3} to become constant, which reflected the couple 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.

441 **4.** Conclusions and implications

In this study, we showed that the NO₃ reactivity towards measured VOC highly varied with big 442 seasonal differences, mainly driven by isoprene concentrations. The top 6 contributors to the 443 measured NO₃ reactivity towards VOC were isoprene, styrene, cis-2-butene, trans-2-butene, 444 trans-2-pentene, and propylene. Among them, isoprene and styrene contributed most of the reactivity. 445 In addition, monoterpenes are proposed to be a significant source of NO₃ reactivity. Recently studies 446 showed that anthropogenic emissions contribute significantly to the ambient MNTs concentrations 447 through biomass burning, traffic and volatile chemical product emissions in the urban regions, it 448 would further enhance the importance of nocturnal NO₃ oxidation (Coggon et al., 2021; Nelson et al., 449 2021; Peng et al., 2022; Qin et al., 2020; Wang et al., 2022). It should be noted that the estimated 450 451 contributions of MNTs only considered the biogenic emissions and may represent the lower bias. Thus we highlight the importance of field observation of MNTs for advancing the understanding the 452 nighttime NO₃ chemistry. In addition, it should be noted that we didn't take the contributions of 453 OVOC into account since the reaction rate coefficients of OVOC with NO3 are small (Ambrose et al., 454 2007). 455

Looking for insight to the trend and evolution of detailed NO₃ chemistry is very scare, but it can be 456 helpful to understand the response of the nocturnal chemistry on the emission change at a large time 457 scale. Limited by the non-extensive and non-continuous observation, we cannot obtain the long-time 458 measurement of all the VOC species in multiple sites. Since isoprene and styrene are good indicators 459 of NO₃ reactivity in different seasons, at least as we showed in urban Beijing, those can be used to 460 estimate the NO₃ reactivity towards VOC to reestablish the long-term trend of NO₃ reactivity in 461 urban regions for further evaluation of its history of nighttime chemistry. We admitted that the 462 463 estimation of the NO₃ reactivity trend might be highly uncertain, but this attempt may be very helpful to know the level and overall change of nighttime chemistry. 464

We showed that NO₃ dominated the nighttime VOC oxidation in Beijing, but the oxidation ratio had a strong nonlinear relationship with O₃ and NO_x concentrations. With the NO₂ concentrations decreasing, the threshold values of O₃ between the sensitive regime and non-sensitive regime tended to increase, indicative of the nighttime oxidation by NO₃ would be more easily affected by the level of O₃ with the implementation of sustaining NO_x reduction in the future. The threshold values of O₃ can provide an effective basis for the measures to control nocturnal chemical and secondary organic aerosol pollution in the typical urban region.

472 **Code/Data availability.** The datasets used in this study are available from the corresponding author

473 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., and S.J.F., W.X.F. provided the modeled
monoterpene and isoprene data, X.L., L.M.Z., M.H., and Y.H.Z. organized this field campaign and
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- 484 **Reference**.

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