https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

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

Hejun Hu[1], Haichao Wang[1, 2 *], Keding Lu[3*], Jie Wang[1], Zelong Zheng[1], Xuezhen Xu[1], Tianyu Zhai[3], Xiaorui Chen[4], Xiao Lu[1, 2], Momei Qin[5], Xin Li[3], Limin Zeng[3], Min Hu[3], Yuanhang Zhang[3]

[1]School of Atmospheric Sciences, Sun Yat-sen University, and Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, 519082, China
[2]Guangdong Provincial Observation and Research Station for Climate Environment and Air Quality Change in the Pearl River Estuary, Key Laboratory of Tropical Atmosphere-Ocean System (Sun Yat-sen University), Ministry of Education, Zhuhai, 519082, China
[3]State Key Joint Laboratory of Environmental Simulation and Pollution Control, The State Environmental Protection Key Laboratory of Atmospheric Ozone Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China.
[4]Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China
[5]Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Nanjing University of Information Science and Technology, Nanjing, China

Correspondence to: Haichao Wang (wanghch27@mail.sysu.edu.cn), Keding Lu (k.lu@pku.edu.cn)

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 activities, especially volatile organic compounds (VOC). Here, we used one-year VOC observation data obtained in urban Beijing in 2019 to look insight to the level, compositions and seasonal variation of NO_3 reactivity (k_{NO3}). We show the hourly k_{NO3} towards measured VOC highly varied from $<10^{-4}$ to 0.083 s^{-1} with 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 percentage of 39.8%. Sensitivity study shows monoterpenes, the species we did not measure, may account 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 published VOC data was collected to reconstruct the long-term NO_3 reactivity in Beijing by the parameterization method. The downward trend of k_{NO3} during 2011-2020 may be responded to the reduction of anthropogenic VOC emission. At last, we revealed 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

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

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 large amount of NO emitted by cities is oxidized into NO_2 by ozone and released into the atmosphere (R1), and NO_2 continues to be oxidized into NO_3 by O_3 (R2). NO_3 only presents a high concentration level at night because it has a rapid photolysis rate 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 form nitrous pentoxide (N_2O_5) (R4), and N_2O_5 can be decomposed to NO_3 and NO_2 (R5), establishing a temperature-dependent equilibrium.

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

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

$$NO_3+NO \rightarrow 2NO_2 \quad (R3)$$

$$NO_2+NO_3+M \rightarrow N_2O_5+M \quad (R4)$$

$$N_2O_5+M \rightarrow NO_2+NO_3+M \quad (R5)$$

The main removal of NO_3 from the gas phase is the reaction with NO (R3), solar photolysis (R6, R7), and volatile organic compounds oxidation (R8), forming complex products. In addition, NO_3 can be transformed into N_2O_5 and removed by heterogeneous hydrolysis (R9), providing an effective way to remove 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, 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).

$$NO_3+h\nu \rightarrow NO+O_2 \quad (R6)$$

$$NO_3+h\nu \rightarrow NO_2+O^1D \quad (R7)$$

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

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

The high NO_3 concentration and fast reaction rate make NO_3 responsible for the sink of many

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

unsaturated hydrocarbons at night (Edwards et al., 2017; Ng et al., 2017; Yang et al., 2020). The NO_3 reactivity (k_{NO3}) towards VOC can be calculated by Eq. 1.

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

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). The NO_3 reactivity towards different VOC varies greatly, which is affected by the abundance of species and the reaction rate coefficients. NO_3 reactivity towards VOC is also affected by temperature. Since temperature not only affects the reaction rate coefficients but also the VOC concentrations in the atmosphere, especially for the emission of biogenic VOC like isoprene and monoterpenes (Wu et al., 2020), causing the variations of VOC species which dominate k_{NO3} towards VOC in different seasons.

The VOC species which dominant the NO_3 reactivity vary greatly between different regions. In forests and rural areas, such as Pabstchum outside Berlin, Germany, the lush forests emit a large amount 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); 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, cresol and some monoolefins emitted by road traffic are the main contributors (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, the k_{NO3} may be jointly affected by anthropogenic and biological volatile organic compounds. For example, the NO_3 reactivity towards VOC in Xianghe, Beijing reached 0.024 ± 0.030 s^{-1}, with the maximum value of 0.3 s^{-1} and minimum value of 0.0011 s^{-1}. Isoprene, styrene and 2-butene contributed to the majority 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 reactivity was generally high with a maximum value of 0.94 s^{-1}, displaying a strong diel variation with 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 regions, which indicated the missing NO_3 oxidation mechanisms, and largely improved the understanding of nighttime chemistry.

Nevertheless, the field direct determination of k_{NO3} is still extremely lacked, especially in urban regions. Until now, most works about the VOC oxidation by NO_3 was usually based on short-term investigations, and the analysis of nocturnal chemical process or reactivity was carried out based on the data of a few weeks or several months. The studies of nighttime chemistry based on long-term measurement data are 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 a long-time scale are rarely studied. Our recent work reported that the increasing trend

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

of NO_3 production rate 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). Here, we attempt to look insight to 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 proposed parameterization method. At last, the regulation of NO_3 oxidation of nocturnal VOC in different seasons is further evaluated.

2. Methods

2.1 Site description and instrumentation

The measurement was conducted at the campus of Peking University (39° 99' N, 116° 30' E). The site is situated northeast of the Beijing city center and near two traffic roads, which represents 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. NO_x 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.

2.2 Estimation of monoterpenes

Since the measurement data did not include monoterpenes (MNTs), we therefore use the measured isoprene and modelled concentration ratio of monoterpene to isoprene in the same region of measurement site (named as Factor, Eq. 2) to estimate the ambient monoterpene concentrations (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). We used the Factor to estimate monoterpenes level rather than modelled monoterpene concentrations is due to the modelled isoprene is systematically higher than that of observation (Fig. S1), thus the using of the modelled 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 approximated the averaged 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, we didn't consider NO_3 reactivity towards sesquiterpenes.

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

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

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

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, 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 production terms of NO_3 is the reaction of NO_2 and O_3, and the loss terms of NO_3 includes 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).

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

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 and Fig. S3. To compare the oxidation of 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} was obtained by the TUV model simulations. The VOC oxidation rate 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.

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

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 annual average (Fig. S4). 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 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 and sampling time. Certainly, it may be attributed to the calculated k_{NO3} here did not include some species, such as monoterpenes. The diurnal variations of k_{NO3_mea} had strong seasonal variability (Fig. S5). The diurnal variations in winter and spring were relatively weak, and the variations in summer and autumn were large, 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 reported change of isoprene concentrations in Beijing (Cheng et al., 2018). Figure 1b 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 shows the specific contributions of 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 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 k_{NO3_mea} alternately. Overall, the k_{NO3_mea} displayed a characteristic of high in summer and autumn and low in winter and spring.

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

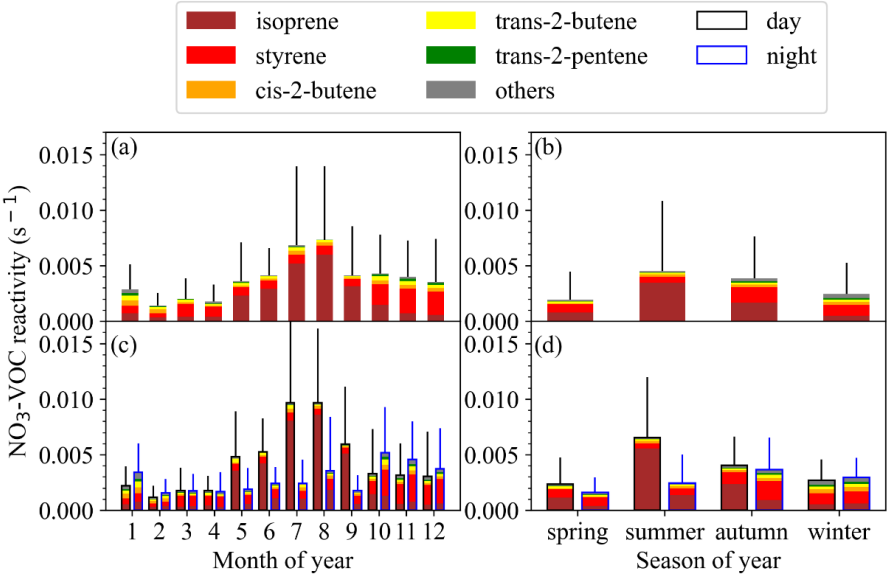


Figure 1. (a-b) Histograms of monthly and seasonal-averaged k_{NO3_mea} and the compositions. (c-d) Histograms of monthly and seasonal-averaged k_{NO3_mea} and the compositions divided into daytime (black frames) and nighttime (blue frames). The color denotes the contributions of different VOC species.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

Figure 1c-d showed 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 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 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 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 emissions (Li et al., 2014). Some vegetation, such as evergreen and oleander, can release natural

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

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 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.

3.2 Parameterization of NO_3 reactivity

We examined the correlation of key VOC concentrations and k_{NO3_mea}. Figure S6 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 stronger correlation. Fig. 2 shows the correlation coefficients and the fitting equations between VOC concentrations and k_{NO3} in each month (detailed in Table S3). According to the correlation coefficients, we can select the strongest indicator corresponding to the 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 by using the strongest indicator in each month and can be found in Table S3 (Eq. 10):

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

where, a_i, b_i and $[VOC_i]$ respectively represent the slope, the intercept and the VOC species concentrations (ppbv) used for parameterization in each month. Throughout the year, the correlation coefficients between isoprene concentrations and k_{NO3_mea} were high, 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.

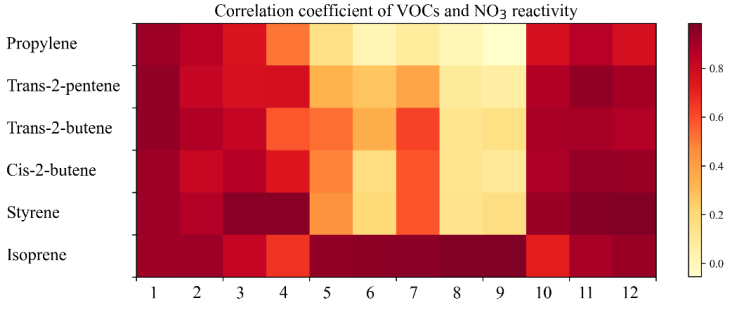


Figure 2. The thermodynamic diagram of the correlation between VOC concentrations and k_{NO3_mea}. Colored blocks indicate different correlations, by which the best indicator can be selected for parameterization method of each month.

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

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 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, and compared them with the determined k_{NO3_mea} by all measured VOC. As shown in Fig. S7, 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 NO_3 reactivity towards VOC is dominated by a single VOC specie for a long time, such as forest areas, suburbs, 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 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 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, 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 the data provided by the literatures, and estimated the NO_3 reactivity by parameterization methods if the reported data in the literatures is limited. As shown in Fig. 3, an overall decrease trend of NO_3 reactivity can be found during 2011-2020. We inferred that the level of isoprene during this period may be varied small, since the biogenic emission unlikely to change much. Thus, we proposed that the decrease of 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.

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

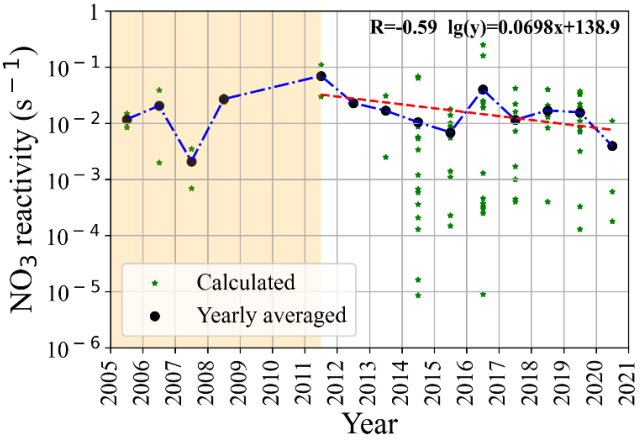


Figure 3. The reconstructed NO_3 reactivity calculated by the reported VOC concentrations in Beijing. The averaged NO_3 reactivity calculated by the reported VOC data in each campaign plotted as star. The yearly averaged NO_3 reactivity (black dot) between 2011-2019 shows a decline. It should be noted 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.

$$F_{MNTs} = \frac{k\text{NO3\_MNTs}}{k\text{NO3\_total}} \qquad \text{Eq. 12}$$

Figure 4a 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 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

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

reactivity towards MNTs accounted for a large fraction of reactivity at night.

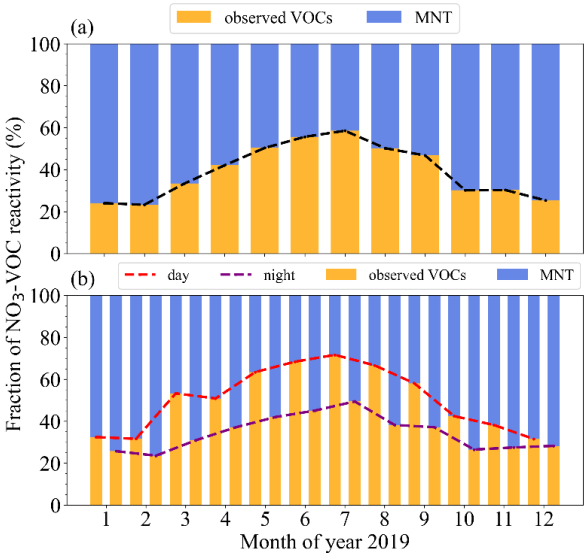


Figure 4. (a) Fractions of the k_{NO3_total}. (b) Fractions of the k_{NO3_total} divided into daytime (left) and nighttime (right). The colors on the stacked bar plot indicate the different fractions as they are donated in the legend. The lines represent the monthly-averaged variations of the NO_3 reactivity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

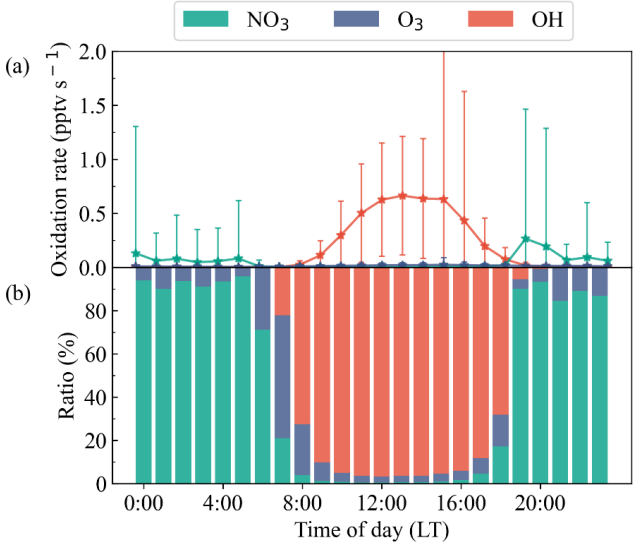
We updated the parameterization method established before by using the relationship between reactivity and VOC concentrations including monoterpenes. The updated parameterization Method 1 used the same principle as introduced in Sect 3.2, with fitting slopes changing significantly (Fig. S9). Table S4 gives the specific correlation 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 two methods are reasonable and the updated Method 1 is better than that of Method 2 in general (Fig. S10).

3.4 Nighttime VOC oxidation

Here we examined the role of NO_3 in the VOC oxidation in Beijing 2019. As shown in Fig. 5, OH oxidized most of VOC during the daytime, with the oxidation rate reached 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%, 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.,

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

352 2017a), highlight the importance of nocturnal chemistry for organic nitrate and SOA formation.



353

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

356 The VOC oxidation rate by NO_3 and oxidation fractions had strong seasonal variabilities in Beijing.
357 As shown in Fig. S11, the nighttime oxidation rate (summer > spring > autumn > winter) was
358 affected by NO_3 concentrations and the total NO_3 reactivity towards VOC. In summer, the NO_3
359 oxidation rate presented a single peak, with a maximum value of 0.7 pptv s^{-1} at 20:00, and remained
360 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
361 winter was lower, with the two maximum values of 0.06 pptv s^{-1} presented at 19:00 and 4:00, which
362 were further lower than the average value of other three seasons. The results were good agreement
363 with the previous studies, in which the VOC oxidation rate by NO_3 concentrations contained high
364 from 19:00-23:00 (Wang et al., 2017b). There was a competition between NO_3 and O_3 in the
365 nighttime VOC oxidation in Beijing. Although the NO_3 oxidation rate at night was higher than that
366 of O_3 throughout the year, the changes of O_3 oxidation rate had a significant impact on the ratios of
367 VOC oxidized by NO_3. The ratios of nighttime VOC oxidized by NO_3 in Beijing were higher in
368 autumn, and then in spring, summer and winter. Although the O_3 concentrations in winter decreased,
369 the competitiveness of NO_3 in VOC oxidation decreased more due to the decline of NO_3
370 concentrations. The competitiveness of O_3 in VOC oxidation was relatively enhanced, resulting in a
371 significant decline in the ratios of VOC oxidized by NO_3.

372 **3.5 Regulation of nighttime VOC oxidation**

373 To understand the importance of nighttime VOC oxidized by NO_3, we explored the relationship
374 between the nocturnal oxidation ratios of NO_3 (R_{NO3}) and the nighttime concentrations of NO, O_3
375 and NO_X. It is found that a strong nonlinear relationship between them (shown in Figure 6). The

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

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, 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), 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, the NO_3 loss was totally dominated by NO.

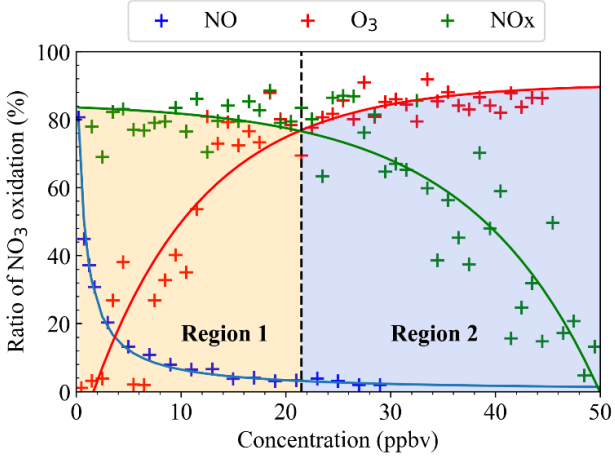


Figure 6. Fitting diagrams between the ratios of nighttime VOC oxidized by NO_3 and the concentrations of NO, O_3 and NO_X. In Region 1, the ratio is more sensitive to O_3, while less sensitive to NO_X. In Region 2, it is more sensitive to NO_X, while less sensitive to O_3.

The ratios of nighttime VOC oxidized by NO_3 also had a strong nonlinear relationship with O_3 and NOx 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 the NO_3 production rate, which increase the NO_3 steady-state concentrations then increase the ratios. And the negative is increasing O_3 concentrations increase the reaction rate between VOC and O_3, which increase the competitiveness of O_3 in VOC oxidation then decrease the ratios. Figure. S12 also shows the relationship between the R_{NO3} and the concentrations of O_3. While O_3 concentrations below 21.5 ppbv, the ratios were very sensitive to O_3 level, which fast increased with O_3 concentrations. While the ratio become not sensitive and remained relatively constant when the O_3 concentrations exceeded 21.5 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 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 the two opposite effects overall keep in balance.

When the NO_X concentrations were low (e.g., <21.5 ppbv), the R_{NO3} were less sensitive to NO_X, remaining relatively constant with the further increase. It is believed that the increase of NO_3 loss

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

rates through the N_2O_5 heterogeneous reaction and the NO reaction were kept in balance with the NO_3 production rate increased by NO_2 concentrations. At high NOx condition, the ratios sensitively decreased with the increase of NO_X concentrations, which is explained that the increase of NO_3 loss 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. S13, in higher concentrations of NO_2, the threshold of lower O_3 concentrations were required for the R_{NO3} to become constant, which reflected the couple influence 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 the NO_3 reactivity towards measured VOC highly varied with strong 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 anthropogenic emissions contributes significantly to the ambient MNTs concentrations by 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 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 insight to the trend and evolution of detailed NO_3 chemistry is very scare, but it can really helpful to understand 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 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 NO_3 reactivity trend may 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 NO_X concentrations. With the NO_2 concentrations decrease, the threshold values of O_3 between 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 of sustaining NOx 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

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

aerosols pollution in the typical urban region.

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. provided the modelled 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.

Acknowledgments. This project is supported by the National Natural Science Foundation of China (42175111, 21976006). Thanks for the data contributed by field campaign team.

Reference.

Ambrose JL, Mao H, Mayne HR, Stutz J, Talbot R, Sive BC. Nighttime nitrate radical chemistry at Appledore island, Maine during the 2004 international consortium for atmospheric research on transport and transformation. Journal of Geophysical Research-Atmospheres 2007; 112: 19.

Asaf D, Pedersen D, Matveev V, Peleg M, Kern C, Zingler J, et al. Long-Term Measurements of NO3 Radical at a Semiarid Urban Site: 1. Extreme Concentration Events and Their Oxidation Capacity. Environmental Science & Technology 2009; 43: 9117-9123.

Atkinson R, Arey J. Atmospheric degradation of volatile organic compounds. Chemical Reviews 2003; 103: 4605-4638.

Bertram TH, Thornton JA. Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride. Atmospheric Chemistry and Physics 2009; 9: 8351-8363.

Brown SS. Applicability of the steady state approximation to the interpretation of atmospheric observations of NO3and N2O5. Journal of Geophysical Research 2003; 108.

Brown SS, Dibb JE, Stark H, Aldener M, Vozella M, Whitlow S, et al. Nighttime removal of NOx in the summer marine boundary layer. Geophysical Research Letters 2004; 31: 5.

Brown SS, Ryerson TB, Wollny AG, Brock CA, Peltier R, Sullivan AP, et al. Variability in nocturnal nitrogen oxide processing and its role in regional air quality. Science 2006; 311: 67-70.

Brown SS, Stutz J. Nighttime radical observations and chemistry. Chemical Society Reviews 2012; 41: 6405-6447.

Chen X, Wang H, Liu Y, Su R, Wang H, Lou S, et al. Spatial characteristics of the nighttime oxidation capacity in the Yangtze River Delta, China. Atmospheric Environment 2019; 208: 150-157.

Cheng X, Li H, Zhang YJ, Li YP, Zhang WQ, Wang XZ, et al. Atmospheric isoprene and monoterpenes in a typical urban area of Beijing: Pollution characterization, chemical reactivity and source identification. Journal of Environmental Sciences 2018; 71: 150-167.

Coggon MM, Gkatzelis GI, McDonald BC, Gilman JB, Schwantes RH, Abuhassan N, et al. Volatile chemical product emissions enhance ozone and modulate urban chemistry. Proceedings of the National Academy of Sciences of the United States of America 2021; 118.

Crowley JN, Schuster G, Pouvesle N, Parchatka U, Fischer H, Bonn B, et al. Nocturnal nitrogen oxides at a rural mountain-site in south-western Germany. Atmospheric Chemistry and Physics 2010; 10: 2795-2812.

Dentener FJ, Crutz PJ. Reaction of N2O5on tropospheric aerosols: impact on the global distributions of NOx, O3, OH. Journal of Geophysical Research 1993; 98: 7149-7163.

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

Edwards PM, Aikin KC, Dube WP, Fry JL, Gilman JB, de Gouw JA, et al. Transition from high- to low-NOx control of night-time oxidation in the southeastern US. Nature Geoscience 2017; 10: 490-+.

Evans MJ, Jacob DJ. Impact of new laboratory studies of N2O5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH. Geophysical Research Letters 2005; 32: 4.

Goldstein AH, Galbally IE. Known and unexplored organic constituents in the Earth's atmosphere. Geochimica Et Cosmochimica Acta 2009; 73: A449-A449.

Hallquist M, Stewart DJ, Stephenson SK, Cox RA. Hydrolysis of N2O5 on sub-micron sulfate aerosols. Physical Chemistry Chemical Physics 2003; 5: 3453-3463.

Kane SM, Caloz F, Leu MT. Heterogeneous Uptake of Gaseous N_2O_5 by $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4 Aerosols. The Journal of Physical Chemistry A 2001; 105: 6465-6470.

Kiendler-Scharr A, Mensah AA, Friese E, Topping D, Nemitz E, Prevot ASH, et al. Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol. Geophysical Research Letters 2016; 43: 7735-7744.

Lee BS, Wang JL. Concentration variation of isoprene and its implications for peak ozone concentration. Atmospheric Environment 2006; 40: 5486-5495.

Li L, Li H, Zhang XM, Wang L, Xu LH, Wang XZ, et al. Pollution characteristics and health risk assessment of benzene homologues in ambient air in the northeastern urban area of Beijing, China. Journal of Environmental Sciences 2014; 26: 214-223.

Li L, Wu F, Meng X. Seasonal and Diurnal Variation of Isoprene in the Atmosphere of Beijing. Environmental Monitoring in China 2013; 29: 120-124.

Liebmann J, Karu E, Sobanski N, Schuladen J, Ehn M, Schallhart S, et al. Direct measurement of NO3 radical reactivity in a boreal forest. Atmospheric Chemistry and Physics 2018a; 18: 3799-3815.

Liebmann JM, Muller JBA, Kubistin D, Claude A, Holla R, Plass-Dulmer C, et al. Direct measurements of NO3 reactivity in and above the boundary layer of a mountaintop site: identification of reactive trace gases and comparison with OH reactivity. Atmospheric Chemistry and Physics 2018b; 18: 12045-12059.

Liebmann JM, Muller JBA, Kubistin D, Claude A, Holla R, Plass-Dülmer C, et al. Direct measurements of NO₃ reactivity in and above the boundary layer of a mountaintop site: identification of reactive trace gases and comparison with OH reactivity. Atmospheric Chemistry and Physics 2018c; 18: 12045-12059.

Liebmann JM, Schuster G, Schuladen JB, Sobanski N, Lelieveld J, Crowley JN. Measurement of ambient NO3 reactivity: design, characterization and first deployment of a new instrument. Atmospheric Measurement Techniques 2017; 10: 1241-1258.

Mao J, Li L, Li J, Sulaymon ID, Xiong K, Wang K, et al. Evaluation of Long-Term Modeling Fine Particulate Matter and Ozone in China During 2013–2019. Frontiers in Environmental Science 2022; 10.

Meng X, Hu EJ, Li XT, Huang ZH. Experimental and kinetic study on laminar flame speeds of styrene and ethylbenzene. Fuel 2016; 185: 916-924.

Miller RR, Newhook R, Poole A. Styrene production, use and human exposure. Critical Reviews in Toxicology 1994; 24: S1-S10.

Mogel I, Baumann S, Bohme A, Kohajda T, von Bergen M, Simon JC, et al. The aromatic volatile organic compounds toluene, benzene and styrene induce COX-2 and prostaglandins in human lung epithelial cells via oxidative stress and p38 MAPK activation. Toxicology 2011; 289: 28-37.

Nelson BS, Stewart GJ, Drysdale WS, Newland MJ, Vaughan AR, Dunmore RE, et al. In situ ozone production is highly sensitive to volatile organic compounds in Delhi, India. Atmospheric Chemistry and Physics 2021; 21: 13609-13630.

Ng NL, Brown SS, Archibald AT, Atlas E, Cohen RC, Crowley JN, et al. Nitrate radicals and biogenic volatile organic

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

compounds: oxidation, mechanisms, and organic aerosol. Atmospheric Chemistry and Physics 2017; 17: 2103-2162.

Osthoff HD, Roberts JM, Ravishankara AR, Williams EJ, Lerner BM, Sommariva R, et al. High levels of nitryl chloride in the polluted subtropical marine boundary layer. Nature Geoscience 2008; 1: 324-328.

Peng Y, Mouat AP, Hu Y, Li M, McDonald BC, Kaiser J. Source appointment of volatile organic compounds and evaluation of anthropogenic monoterpene emission estimates in Atlanta, Georgia. Atmospheric Environment 2022; 288.

Qin M, Murphy BN, Isaacs KK, McDonald BC, Lu Q, McKeen SA, et al. Criteria pollutant impacts of volatile chemical products informed by near-field modelling. Nature Sustainability 2020; 4: 129-137.

Radica F, Della Ventura G, Malfatti L, Guidi MC, D'Arco A, Grilli A, et al. Real-time quantitative detection of styrene in atmosphere in presence of other volatile-organic compounds using a portable device. Talanta 2021; 233: 7.

Riba ML, Tathy JP, Tsiropoulos N, Monsarrat B, Torres L. Diurnal variation in the concentration of α- and β-pinene in the landes forest (France). Atmospheric Environment 1987; 21: 191-193.

Schaeffer V, Bhooshan B, Chen S, Sonenthal J, Hodgson A. Characterization of Volatile Organic Chemical Emissions From Carpet Cushions. Journal of the Air & Waste Management Association (1995) 1996; 46: 813-820.

Stark H, Lerner BM, Schmitt R, Jakoubek R, Williams EJ, Ryerson TB, et al. Atmospheric in situ measurement of nitrate radical (NO3) and other photolysis rates using spectroradiometry and filter radiometry. Journal of Geophysical Research-Atmospheres 2007; 112: 11.

Stutz J, Wong KW, Lawrence L, Ziemba L, Flynn JH, Rappengluck B, et al. Nocturnal NO3 radical chemistry in Houston, TX. Atmospheric Environment 2010; 44: 4099-4106.

Tan ZF, Fuchs H, Lu KD, Hofzumahaus A, Bohn B, Broch S, et al. Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO2 and RO2 radicals. Atmospheric Chemistry and Physics 2017; 17: 663-690.

Tang WC, Hemm I, Eisenbrand G. Estimation of human exposure to styrene and ethylbenzene. Toxicology 2000; 144: 39-50.

Vrekoussis M, Mihalopoulos N, Gerasopoulos E, Kanakidou M, Crutzen PJ, Lelieveld J. Two-years of NO3 radical observations in the boundary layer over the Eastern Mediterranean. Atmospheric Chemistry and Physics 2007; 7: 315-327.

Wang H, Lu K, Chen X, Zhu Q, Chen Q, Guo S, et al. High N2O5 Concentrations Observed in Urban Beijing: Implications of a Large Nitrate Formation Pathway. Environmental Science & Technology Letters 2017a; 4: 416-420.

Wang H, Lu K, Guo S, Wu Z, Shang D, Tan Z, et al. Efficient N2O5 uptake and NO3 oxidation in the outflow of urban Beijing. Atmospheric Chemistry and Physics 2018a; 18: 9705-9721.

Wang H, Ma X, Tan Z, Wang H, Chen X, Chen S, et al. Anthropogenic monoterpenes aggravating ozone pollution. National Science Review 2022.

Wang H, Wang H, Lu X, Lu K, Zhang L, Tham YJ, et al. Increased night-time oxidation over China despite widespread decrease across the globe. Nature Geoscience 2023.

Wang HC, Lu KD, Chen SY, Li X, Zeng LM, Hu M, et al. Characterizing nitrate radical budget trends in Beijing during 2013-2019. Science of the Total Environment 2021; 795: 9.

Wang HC, Lu KD, Guo S, Wu ZJ, Shang DJ, Tan ZF, et al. Efficient N2O5 uptake and NO3 oxidation in the outflow of urban Beijing. Atmospheric Chemistry and Physics 2018b; 18: 9705-9721.

Wang HC, Lu KD, Tan ZF, Sun K, Li X, Hu M, et al. Model simulation of NO3, N2O5 and ClNO2 at a rural site in Beijing during CAREBeijing-2006. Atmospheric Research 2017b; 196: 97-107.

Wayne RP, Barnes I, Biggs P, Burrows JP, Canosa-Mas CE, Hjorth J, et al. The nitrate radical: physics, chemistry, and the atmosphere. Atmospheric Environment, Part A (General Topics) 1991; 25A: 1-203.

Wu K, Yang X, Chen D, Gu S, Lu Y, Jiang Q, et al. Estimation of biogenic VOC emissions and their corresponding impact on

https://doi.org/10.5194/egusphere-2023-622
Preprint. Discussion started: 17 April 2023

ozone and secondary organic aerosol formation in China. Atmospheric Research 2020; 231.

Wu L, Sun Y, Tian Y, Su D. Composition Spectrum of Biogenic Volatile Organic Compounds Released by Typical Flowers in Beijing. Enuivonmental Science and Technology 2014; 37: 154-158.

Xia C, Xiao L. Estimation of biogenic volatile organic compounds emissions in Jing-Jin-Ji. Acta Scientiae Circumstantiae 2019; 39: 2680-2689.

Yang Y, Wang YH, Zhou PT, Yao D, Ji DS, Sun J, et al. Atmospheric reactivity and oxidation capacity during summer at a suburban site between Beijing and Tianjin. Atmospheric Chemistry and Physics 2020; 20: 8181-8200.

Yuan ZB, Lau AKH, Shao M, Louie PKK, Liu SC, Zhu T. Source analysis of volatile organic compounds by positive matrix factorization in urban and rural environments in Beijing. Journal of Geophysical Research-Atmospheres 2009; 114: 14.

Zhu J, Wang S, Zhang S, Xue R, Gu C, Zhou B. Changes in NO3 Radical and Its Nocturnal Chemistry in Shanghai From 2014 to 2021 Revealed by Long‐Term Observation and a Stacking Model: Impact of China's Clean Air Action Plan. Journal of Geophysical Research: Atmospheres 2022; 127.

Zielinska B, Sagebiel JC, Harshfield G, Gertler AW, Pierson WR. Volatile organic compounds up to C-20 emitted from motor vehicles; Measurement methods. Atmospheric Environment 1996; 30: 2269-2286.

Zilli M, Palazzi E, Sene L, Converti A, Del Borghi M. Toluene and styrene removal from air in biofilters. Process Biochemistry 2001; 37: 423-429.

Zou Y, Deng X, Li F, Wang B, Tan H, Deng T, et al. Variation characteristics,chemical reactivity and sources of isoprene in the atmosphere of Guangzhou. Acta Scientiae Circumstantiae 2015; 35: 647-655.