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Atmospheric Chemistry and Physics Discussions

Characterization of nighttime formation of particulate organic nitrates based on high-resolution aerosol mass spectrometry in an urban atmosphere in China

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Abstract. Organic nitrates are important atmospheric species that significantly affect the cycling of NOx and ozone production. However, characterization of particulate organic nitrates and their sources in inorganic nitrate-abundant particles in polluted atmosphere is a big challenge, and has been little performed in the literature. In this study, an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was deployed at an urban site in South China from 2015 to 2016 to characterize particulate organic nitrates with high time resolution. Based on two different data processing methods, 13-21% of the total measured nitrates was identified to be organic nitrates in spring, 41-64% in summer and 16%-25% in autumn; however, in winter, most measured nitrates were inorganic. The good correlation between organic nitrates and fresh secondary organic aerosol identified by the positive matrix factorization method at night rather than in the daytime indicated a potentially important role of nighttime secondary formation. Therefore, we theoretically estimated nighttime NO_3 radical concentrations and SOA formation using the various VOCs measured simultaneously. Consequently, the calculated products of monoterpene reacting with NO_3 agreed well with the organic nitrates in terms of both concentration and variation, suggesting that the biogenic VOC reactions with NO_3 at night are the dominant formation pathway for particulate organic nitrates in polluted atmosphere, despite of much higher abundance of anthropogenic VOCs.

1. Introduction

Organic nitrates in aerosols have an important impact on the fate of NO_X and ozone production (Lelieveld et al., 2016), which can be formed in a minor channel of the reaction between peroxy radicals and NO (R1 and R2) (usually, an increased fraction of this reaction leads to the formation of alkoxy radicals and NO_2 (R3)) or via the NO_3-induced oxidation of unsaturated hydrocarbons (R4). Even though some recent studies have suggested that the formation of organic nitrates from

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peroxy radicals and NO may play a larger role than previously recognize unsaturated hydrocarbons (R4). Even though some recent studies have suggested that the formation of organic nitrates from peroxy radicals and NO may play a larger role than previously recognized, yields of organic nitrates via NO_3 reacting with alkenes are generally much higher (Teng et al., 2017, 2015).

$$\mathrm{RH} + \mathrm{OH} + O_2 \rightarrow RO_2 + H_2O \quad (R1)$$

$$\mathrm{R}O_2 + \mathrm{NO} \rightarrow RONO_2 \quad (R2)$$

$$\mathrm{R}O_2 + \mathrm{NO} \rightarrow RO + NO_2 \quad (R3)$$

$$\mathrm{R} = R' + \mathrm{N}O_3 \rightarrow R(ONO_2)\ R' \quad (R4)$$

Several direct methods have been developed to measure total organic nitrates (gas + particle) in the real atmosphere. For example, Rollins et al.(2012) used a thermal-dissociation laser-induced fluorescence technique (TD-LIF) to observe total organic nitrates in the United States; Sobanski et al. (2017) obtained organic nitrates in Germany using the thermal dissociation cavity ring-down spectroscopy (TD-CRDS). However, it is still difficult to identify and quantify the particle phase organic nitrates, which could contribute a large portion of secondary organic aerosol (SOA) (Rollins et al., 2012; Xu et al., 2015a; Fry et al., 2013; Ayres et al., 2015; Boyd et al., 2015; Lee et al., 2016), using these direct measurement methods. Recently, researchers have proposed some estimation methods for particle-phase organic nitrates based on aerosol mass spectrometry (AMS) with high time resolution (Farmer et al., 2010; Hao et al., 2014; Xu et al., 2015a, 2015b). Ng et al. (2017) reviewed the nitrate radical chemistry and the abundance of particulate organic nitrates at multiple sites of the world, but all of these sites are located in the region (i.e. United States and Europe) with relatively clean air. To our best knowledge, few studies have investigated the concentrations and formation pathways of particulate organic nitrates in the atmosphere with high anthropogenic pollutants (Xu et al., 2017), especially with high particulate inorganic nitrate, which would make identification of organic nitrates harder in aerosol mass spectrum.

South China is located in a subtropical region, where the photochemical reactions are extremely active (Zhang et al., 2008), and the biogenic VOCs and anthropogenic NOx are relatively high. To assess the evolution of particle-phase organic nitrates in a more polluted atmosphere, in this study, we deployed Aerodyne high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS) with other instruments over an urban site in South China from 2015 to 2016 to obtain submicron aerosols. Then, organic nitrates and their contributions to OAs in different seasons were estimated by different methods based on the HR-ToF-AMS measurements. Furthermore, we used the estimates combined with the measured VOC data to investigate the potential pathway formation for organic nitrates in South China.

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2. Experiment methods

2.1 Sampling site and period

The sampling site (22.6°N, 113.9°E; 20 m a.s.l) was on the roof of one academic building on the campus of the Peking University Shenzhen Graduate School (PKUSZ), which is located in the western urban area in Shenzhen (Figure 1). This site is mostly surrounded by subtropical plants without significant anthropogenic emission sources nearby, except for a local road that is ~100 m from the site. In this study, we use the statistical data from the Meteorological Bureau of Shenzhen Municipality (http://www.szmb.gov.cn/site/szmb/Esztq/index.html) as the reference data to determine the sampling periods to obtain more representative samples in different seasons during 2015-2016, as shown in Table 1.

Figure 1. The location of the sampling site.

Table 1. Meteorological conditions, PM_1 species concentrations and relevant parameters in the estimation of organic nitrates for different seasons in Shenzhen.

Sampling period		4.1-4.30, 2016	8.1-8.31, 2015	11.4-11.30, 2015	1.21-2.3, 2016
		Spring	Summer	Autumn	Winter
Meteorology	T (°C)	24.5±2.5	29.0±3.0	23.6±3.7	10.7±4.7
	RH (%)	78.0±12.7	71.2±17.5	68.2±15.8	75.4±18.7
	WS (m s^{-1})	1.4±0.8	1.0±0.7	1.2±0.7	1.5±0.8
Species	Org	4.3±3.2	10.0±6.9	7.8±5.9	5.1±3.5
	SO_4^{2-}	3.2±1.8	5.8±3.3	2.3±1.5	1.9±1.2
	NO_3^-	0.96±1.4	0.91±0.90	1.3±1.4	1.6±1.0

($\mu g\ m^{-3}$)	NH_4^+	1.4±0.8	2.0±1.1	1.1±0.8	1.2±0.6
	Cl^-	0.14±0.19	0.03±0.05	0.22±0.36	0.64±0.85
	BC	1.9±2.1	2.4±1.6	3.5±2.6	2.4±1.5
	PM_1	12.0±8.9	15.1±13.8	11.8±9.5	12.2±7.2
ON parameters	R_{NH4NO3}	2.80	3.20	3.32	3.48
	R_{obs}	3.74	6.14	4.30	3.55
	Fraction of positive data	99%	99%	84%	47%

2.2 Instrumentation

2.2.1 High Resolution Time-of-Flight Aerosol Mass Spectrometer

During the sampling periods, the chemical compositions and mass concentration of non-refractory PM_1 were measured by an HR-ToF-AMS, and detailed descriptions of this instrument are given in the literatures (DeCarlo et al., 2006; Canagaratna et al., 2007). In summary, the HR-ToF-AMS focuses ambient particles with vacuum aerodynamic diameter smaller than 1 μm into narrow beam via an aerodynamic lens, then the submicron particles are vaporized by impaction on a tungsten heated suface (~600 ˚C) and ionized by electron ionization (70eV). Only non-refractory species can be vaporized and detected. The setup and operation of the HR-ToF-AMS can be found in our previous studies (Huang et al., 2010, 2012; Zhu et al.,2016). To remove coarse particles, a $PM_{2.5}$ cyclone inlet was placed on the roof of the building to introduce an air stream containing the remaining particles into a room through a copper tube with a flow rate of 10 l min^{-1}. Before entering the AMS, the samples are dried by a nafion dryer (MD-070-12S-4, Perma Pure Inc.) to eliminate the potential influence of relative humidity on the particle collection (Matthew et al., 2008). The ionization efficiency (IE) calibrations wer perfomed by using pure ammonium nitrate particles on every two weeks. The relative IEs (RIEs) for organics, nitrate and chloride were assumed to be 1.4, 1.1 and 1.3, respectively. A composition-dependent collection efficiency (CE) was applied to the data based on the method of Middlebrook et al. (2012). The instrument was operated at two ion optical modes with a cycle of 4 min, including 2 min for the mass-sensitive V-mode and 2 min for the high mass resolution W-mode. The HR-ToF-AMS data analysis was performed using the software SQUIRREL (version 1.57) and PIKA (version 1.16) written in Igor Pro 6.37 (Wave Metrics Inc.)(http://cires1.colorado.edu/jimenezgroup/ToFAMSResources/ToFSoftware / index.html).

2.2.2 Other co-located instruments

In addition to the HR-ToF-AMS, a suite of instruments was deployed in the same sampling site. An aethalometer (AE-31, Magee) was simultaneously used for measurements of refractory black carbon (BC) with a temporal resolution of 5 min. VOCs concentrations were measured via an automated in-situ gas chromatograph (Agilent 5977E) equipped with a mass spectrometer

(Agilent 5971). Ozone and NO_X was measured by a 49i ozone analyzer and a 42i nitrogen oxide analyzer (Thermo Scientific, US), respectively.

2.3 Organic nitrate estimation

In this study, we use two methods to estimate the organic nitrates based on AMS organic data, following the same analysis approach in Xu et al. (2015b). The first method for estimating organic nitrates is based on the NO^+/NO_2^+ ratio (NO_X^+ ratio) in the HR-AMS spectrum. Due to their very different NO_X^+ ratios (R_{ON} and R_{NH4NO3}) (Farmer et al., 2010; Boyd et al., 2015; Fry et al., 2008; Bruns et al., 2010), the NO_2 and NO concentrations for the organic nitrates ($NO_{2,ON}$ and NO_{ON}) can be quantified with the HR-AMS data via Eqs. (1) and (2), respectively (Farmer et al., 2010):

$$NO_{2,ON} = \frac{NO_{2,obs} \times (R_{obs} - R_{NH4NO3})}{R_{ON} - R_{NH4NO3}} \quad (1)$$

$$NO_{ON} = R_{ON} \times NO_{2,ON} \quad (2)$$

where R_{obs} is the NO_X^+ ratio from the observation. The value of R_{ON} is difficult to determine because it varies between instruments and precursor volatile organic compounds (VOCs). However, R_{ON}/R_{NH4NO3} has been assumed instrument-indepennt (Fry et al., 2013). In this study, we use R_{ON}/R_{NH4NO3} estimation range (from 2.08 to 3.99) from the literature (Farmer et al., 2010; Boyd et al., 2015; Bruns et al., 2010; Sato et al., 2010) to determine R_{ON} due to the variation of precursor VOCs. It is important to note that if a large percentage of organic nitrates value are negative using this method, it is because the values of R_{obs} is smaller than R_{NH4NO3}, further indicating the inorganic nitrates contributes near all to the total nitrates.

The second method is based on the positive matrix factorization (PMF) analysis. In addition to the PMF of the organic mass spectra (Zhang et al., 2011; Ng et al., 2010; Huang et al., 2013), the same analysis of the HR organic mass spectra, combined with NO^+ and NO_2^+, ions was performed to identify the relative contributions of organic and inorganic nitrates (Hao et al., 2014; Xu et al., 2015b). In this study, the detailed PMF analysis procedure can be found in our previous publications (Huang et al., 2010; Zhu et al., 2016; He et al., 2011). For each season, three organic factors and one inorganic factor are identified: a hydrocarbon-like OA (HOA), a more-oxidized oxygenated OA (MO-OOA), a less-oxidized oxygenated OA (LO-OOA) and a nitrate inorganic aerosol (NIA). In this method, the NO^+ and NO_2^+ ions are distributed among different organic aerosol factors and NIAs; the concentration of the nitrate functionality in the organic nitrates ($NO_{3,org}$) is equal to the sum of NO^+ and NO_2^+ in the organic nitrates (i.e., NO^+_{org} and $NO^+_{2,org}$) via Eqs. (3) and (4), respectively (Xu et al., 2015b):

$$NO^+_{org} = \sum([OA\ factor]_i \times f_{NOi}) \quad (3)$$

$$NO^+_{2,org} = \sum([OA\ factor]_i \times f_{NO2,i}) \quad (4)$$

where $[OA\ factor]_i$ represents the mass concentration of the ith OA factor and f_{NOi} and $f_{NO2,i}$ represent the mass fractions of NO^+ and NO_2^+, respectively.

2.4 Nitrate radical estimation

In this section, the approach of nitrates radical estimation is similar to Xu et al. (2015a). The average concentration of VOCs and the reaction rate coefficients of NO_3 + VOCs at 25 ˚C are listed in Table S1. NO_3 is the product of NO_2+O_3, and its losses

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125 react with individual VOCs, NO and photolysis. Due to the existence of N_2O_5 in equilibrium with NO_2+ NO_3, we should first
126 estimate the sinks of N_2O_5 impacting the life of nitrate radicals. There are both heterogenous and homogeneous reactions of
127 N_2O_5 with water. The N_2O_5 lifetime, with respect to the heterogeneous uptake of aqueous particles, is (Fry et al., 2013):

128 $$\tau_{N2O5,het} = \frac{1}{K_{het}} = \frac{4SA}{\gamma v} \quad (5)$$

129 where K_{het} represents the rate of heterogeneous uptake, γ is the uptake coefficient, v represents the molecular speed, and SA
130 represents the surface area of the particles. By using the upper-limit values of $\gamma = 0.04$ (Saunders et al., 2003), $v = 240$ μm^2
131 cm^{-3} ^{1} and SA = 220 μm^2 cm^{-3}, we calculate $\tau_{N2O5,het}$ to be approximately 1760 s. In addition, the N_2O_5 lifetime, with
132 respect to the reaction with H_2O, is (Crowley et al., 2011):

133 $$\tau_{N2O5,H2O} = \frac{1}{K_{H2O}} = \frac{1}{2.5\times10^{-22}[H_2O]+1.8\times10^{-39}[H_2O]2} \quad (6)$$

134 K_{H2O} represents the reaction rate of N_2O_5 and H_2O, and $[H_2O]$ represents the water concentration (unit of molecule cm^{-3}); the
135 daily maximum $[H_2O]$ is 5.5*10^{11} molecule cm^{-3} at 6:00 during the sampling period, and the calculated value is 1.4*10^{10} s.
136 Then, we estimate the NO_3 lifetime by only considering the reaction with VOCs ($\tau_{NO3,VOCs}$):

137 $$\tau_{NO3,VOCs} = \frac{1}{\sum k_{i[VOC_i]}} \quad (7)$$

138 The average lifetime of NO_3 is approximately 14.08 s. Based on the estimation of the N_2O_5 and NO_3 lifetimes above, we can
139 conclude that the influence of N_2O_5 could be ignored when estimating the NO_3 concentration and, due to the high reactivity
140 of NO_3 (14.08 s), the steady-state NO_3 can be predicted:

141 $$[NO_3 \cdot] = \frac{k_1[O_3][NO_2]}{J_{NO3}+k_2[NO]+\sum k_i[VOC_i]} \quad (8)$$

142 where J_{NO3} is calculated from the solar zenith angles and NO_3 photolysis rates (Saunders et al., 2003) and, in this study, the
143 typical value of J_{NO3} is 0.12 s^{-1} during the daytime. k_1 is 3.52*10^{-17} cm^3 molecule^{-1} s^{-1}, and k_2 is 2.7*10^{-11} cm^3 molecule^{-1} s^{-1}
144 according to the Master Chemical Mechanism model (http://mcm.leeds.ac.uk/MCM/; under 25 ˚C). The average
145 concentrations of O_3 and NO_2 are 6.82 and 19.38 ppb, respectively.

146 **3. Results and discussion**

147 **3.1 Results of the organic nitrate estimation**

148 Table 2 shows the concentrations of nitrate functionality in organic nitrates (i.e., $NO_{3.org}$) and their contributions to the total
149 measured nitrate, which is estimated by the NO^+/NO_2^+ ratio method and PMF method. Note that the small difference between
150 the average R_{obs} and R_{NH4NO3} in winter leads to a large portion of negative data (Table 1), which suggests that a very limited
151 amount of organic nitrates contribute to the total nitrate, as discussed above; thus, we only discuss the organic nitrates in spring,
152 summer and autumn. For the NO^+/NO_2^+ ratio method, two calculated R_{ON} values for each season based on the R_{ON}/R_{NH4NO3}
153 estimation range (from 2.08 to 3.99) are applied to provide the upper and lower bounds of the estimated $NO_{3.org}$ mass

concentration. For the PMF method, the NO_X^+ ions were assigned to different PMF factors (Figure S1) due to the different physicochemical properties of the nitrate components. The NIAs are dominated by NO^+ and NO_2^+ but also contain some organic fragments, such as CO_2^+ and $C_2H_3O^+$, which agrees with the literature (Hao et al., 2014; Xu et al., 2015b; Sun et al., 2012), This indicates that the NIA factor experiences potential interference from organics. In addition, the NO^+/NO_2^+ ratio in NIAs is higher than that in pure NH_4NO_3, which supports the underestimation of $NO_{3.org}$ concentrations with this method. This also explains why the concentration of $NO_{3.org}$ estimated using the PMF method is always close to the lower estimation of $NO_{3.org}$ via the NO^+/NO_2^+ ratio method in Table 2.

Table 2. A summary of organic nitrate estimations via the NO^+/NO_2^+ ratio method and PMF method

Sampling period	NO^+/NO_2^+ ratio method				PMF method	
	$NO_{3,org}$ (μg m^{-3})[a]		$NO_{3,org}/NO_3$		$NO_{3,org}$ (μg m^{-3})[b]	$NO_{3,org}/NO_3$
	lower	upper	lower	upper		
Spring	0.12	0.19	13%	21%	0.12	12%
Summer	0.34	0.53	41%	64%	0.39	43%
Autumn	0.21	0.33	16%	25%	0.21	16%
Winter	/	/	/	/	/	/

[a] $NO_{3.org}$ for upper bounds is denoted as $NO_{3.org1\_ratio}$, and $NO_{3.org}$ for lower bounds is denoted as $NO_{3.org2\_ratio}$

[b] $NO_{3.org}$ estimated using the PMF method is denoted as $NO_{3.org\_PMF}$

To verify the reliability of the estimated results, each $NO_{3.org}$ concentration time series calculated by these two methods is shown in Figure 2, and the correlation coefficient (R) for each season is adequate (0.82 for spring, 0.82 for summer and 0.77 for autumn), indicating that similar results are achieved by using the NO^+/NO_2^+ ratio method and PMF method. To summarize, we chose a reliable estimation range of $NO_{3.org}$ for each season: 0.12 to 0.19 μg m^{-3} for spring, 0.34 to 0.53 μg m^{-3} for summer and 0.21 to 0.33 μg m^{-3} for autumn. Furthermore, we found that organic nitrates contribute 9-21% to OAs in spring, 11-25% in summer and 9-20% in autumn based on the reliable estimation range of the $NO_{3.org}$ concentration and the assumption that the average molecular weight of organic nitrates ranges from 200 g mol^{-1} to 300 g mol^{-1} (Rollins et al., 2012). The level of $NO_{3.org}$ is highest during the summer in Shenzhen, which is consistent with the seasonal variations in literatures (Ng et al., 2017). In addition, it is seen that the difference in the $NO_{3.org}$ mass concentration between South China and the southeastern USA is small, even though the levels of anthropogenic emission species (such as BC and NO_X) are much higher in South China than those in southeastern USA (Xu et al., 2015b); this implies that aerosol ONs might not be closely related to anthropogenic emissions.

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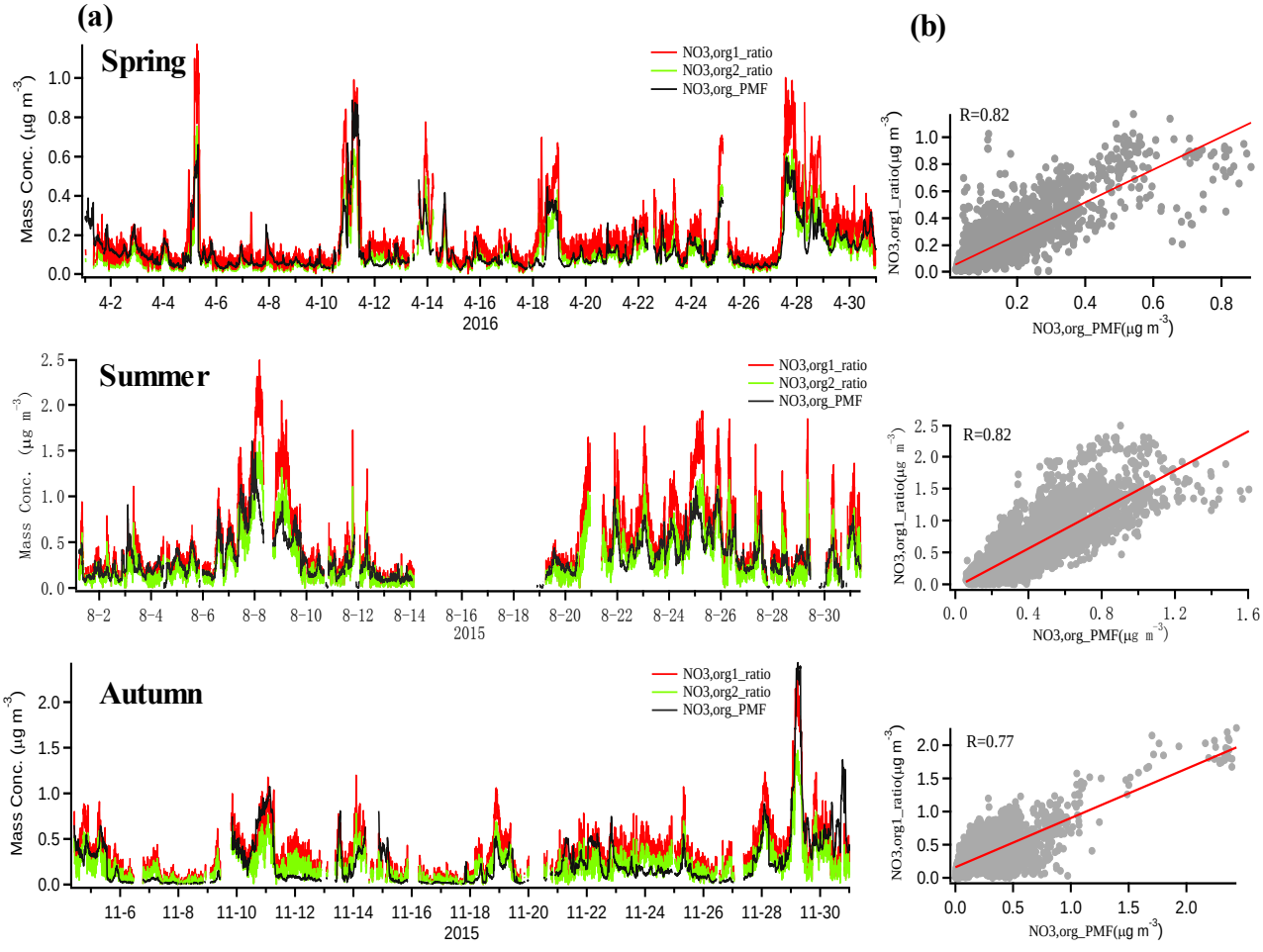

Figure 2. (a) Time series of $NO_{3.org}$ concentrations estimated by the NO^+/NO_2^+ ratio method and PMF method for each season, (b) scatter plots of $NO_{3.org1\_ratio}$ and NO_{3,org_PMF}.

3.2 Correlation between organic nitrates and LO-OOA

In this study, we also performed a PMF analysis on both organic spectra solely to investigate OA source apportionment. The same organic factors were identified as those in the PMF analysis on organics, combined with NO_X^+ ions, including HOAs, LO-OOAs and MO-OOAs. For the total daily data, organic nitrates were better-correlated with LO-OOAs than with any other factor. Then, we further found a noticeably improved correlation between the LO-OOAs and organic nitrates at night (20:00-6:00) and a decreased correlation during the daytime (7:00-19:00) in Figure 3. The biggest improvement is seen in summer, where the correlation coefficient (R) increases from 0.77 for the whole day to 0.91 at night. Considering the relatively high BVOC emissions during the summer in Shenzhen (Zhu et al., 2012), the summer LO-OOAs may be closely related to the oxidation of BVOCs, especially at nighttime.

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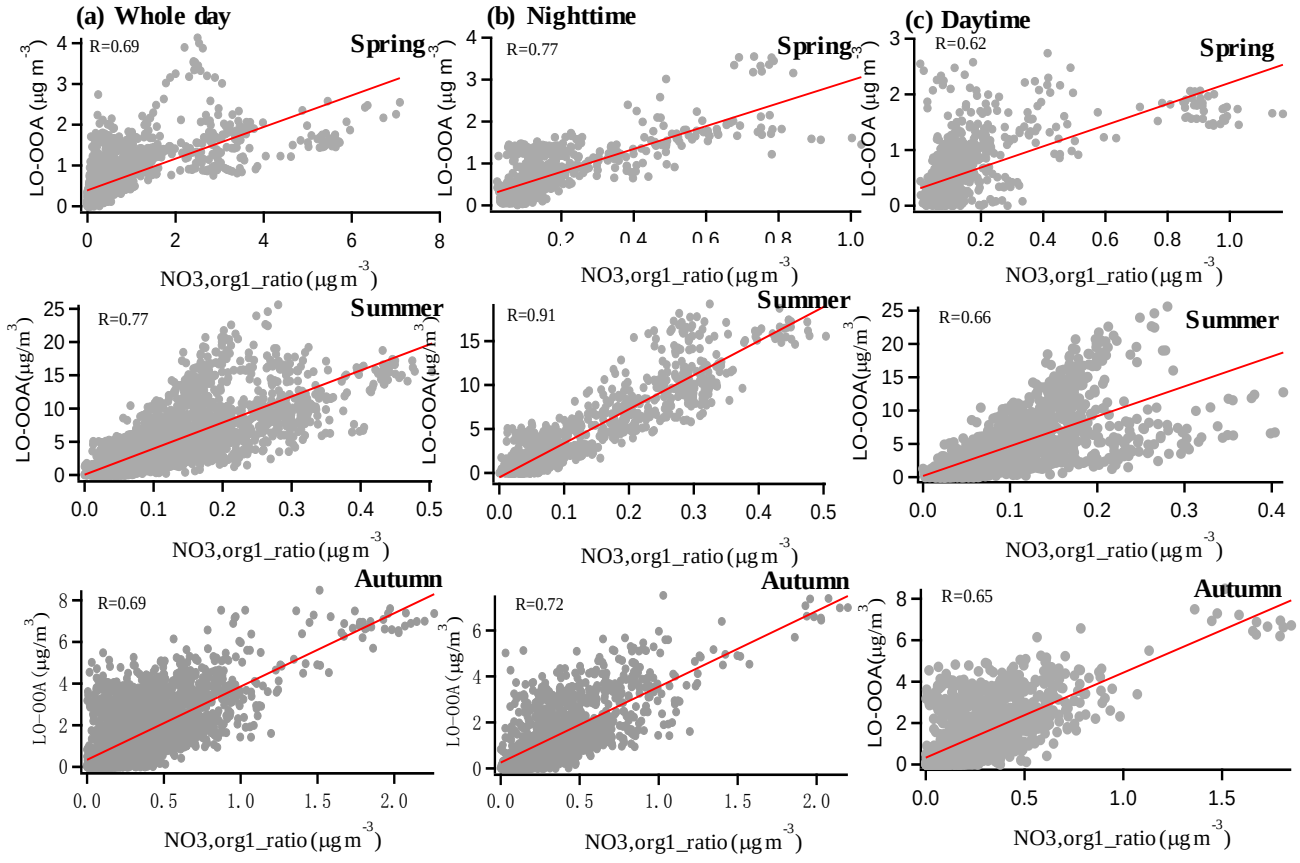

Figure 3. Scatter plots of $NO_{3.org1\_ratio}$ and LO-OOA for each season for the whole day (a), at nighttime (b) and during the day (c).

3.3 Nighttime formation of organic nitrates in particles

In this section, we will further investigate the potential formation pathway of organic nitrates at night according to the analysis of particulate organic nitrates in southeastern USA in Xu et al. (2015a). Since on-line VOCs measurement with an automated in situ gas-chromatography mass spectrometer (GC-MS) was only performed during the spring campaign, the following theoretical analysis is just applied to the dataset for the spring case. According to Figure 4, the concentrations of anthropogenic VOC species, such as propane and toluene, were dozens of times higher than those of biogenic VOCs at night. However, based on the estimation method in Section 2.3, two biogenic VOCs, i.e., limonene and α-pinene, were identified as the key VOC precursors, accounting for approximately 90% of the NO_3 lost due to the reactions with VOCs. Thus, the nighttime SOA production from limonene and α-pinene with NO_3 was further calculated (Text S1). The results showed that the estimated mass concentration range (0.15-1.29 μg m^{-3}) for SOAs agrees well with the range (0.38-0.87 μg m^{-3}) of organic nitrate concentrations at night. And noted that SOA yields from limonene + NO_3 is much higher than α-pinene + NO_3 (Hallquist et al., 1999; Fry et al., 2011, 2014; Spittler et al., 2006; Boyd et al., 2017). The diurnal patterns of the mass concentrations in the

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measured BC, SOA (LO-OOA+MO-OOA) resolved by PMF, organic nitrate functionality ($NO_{3,org1\_ratio}$) and SOAs from the BVOC+ NO_3 in the low SOA yield are shown in Figure 5. The concentration of BC is low during the daytime, with a planetary boundary layer (PBL) height that is increased, while the concentration increases in the early evening due to the effects of both the lower PBL and rush hour traffic (He et al., 2011). Compared to BC, the organic nitrate concentration shows a much more distinct variation trend, with low mass loading in the daytime and high mass loading at night, and it has two unique rapid-growth processes (19:00-22:00 and 3:00-6:00) after sunset, which cannot be explained by the PBL variation. Especially, the second increase in organic nitrates from 3:00-6:00 clearly suggests significant nighttime SOA formation. Compared to the bulk SOA, which shows an increase in the daytime related to photochemical formation while a steady level after midnight, the concentration of organic nitrates increases from 3:00-6:00 also clearly indicates different formation mechanism. However, the SOA of our theoretical calculation based on BVOCs and NO_3 indeed shows two similar increasing processes, well explaining the observed trends. Since the similar nighttime formation trend for organic nitrates from biogenic emissions was also seen in a forest environment in Finland (Yan et al., 2016), the results in this study shows that the BVOC+ NO_3 chemistry is also potentially critical for the formation of nighttime organic nitrates even in a polluted urban atmosphere.

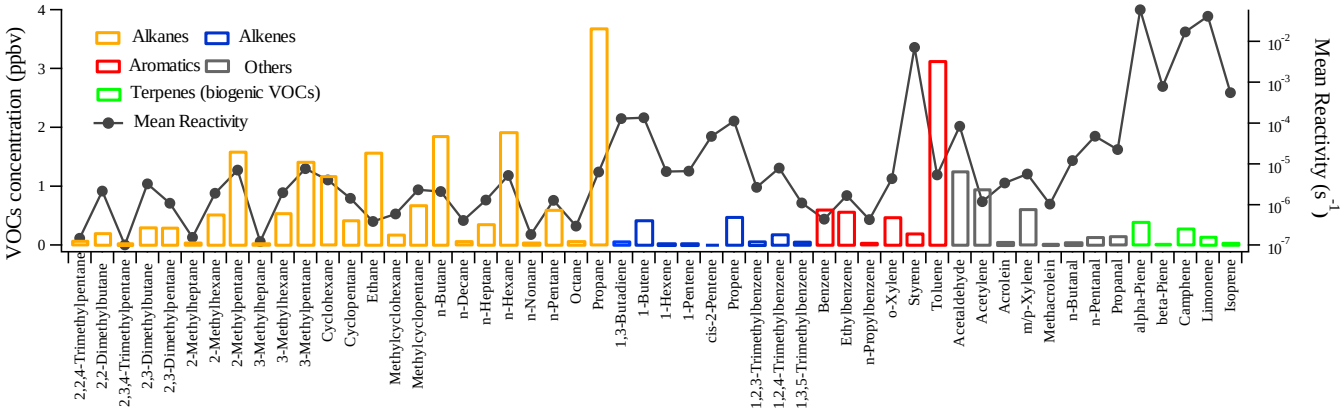

Figure 4. The mean concentrations of VOCs and the corresponding NO_3 reactivity at night during the spring campaign.

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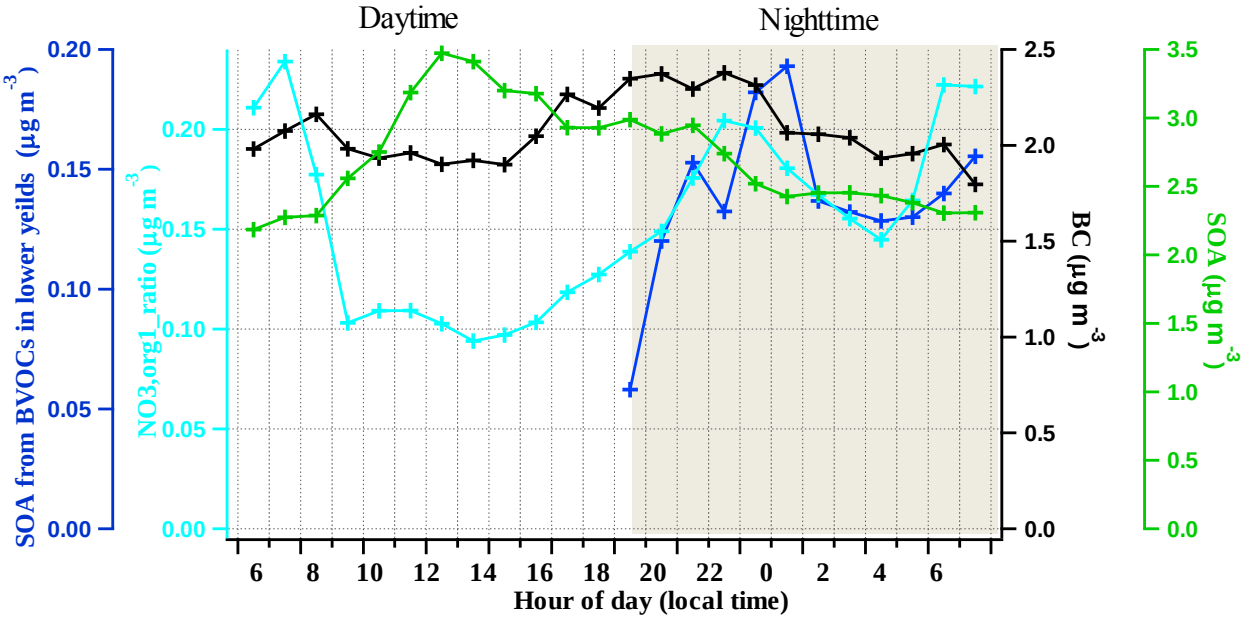

Figure 5. Diurnal trends of measured BC, SOA resolved by PMF, organic nitrate functionality ($NO_{3.org1\_ratio}$), and SOA from BVOC+ NO_3 in a low SOA yield.

4. Conclusions

An Aerodyne HR-ToF-AMS was deployed in urban Shenzhen in South China for one month per season during 2015–2016 to characterize particulate organic nitrates with high time resolution. We find that the mass fraction of organic nitrates in the total measured nitrates is substantial during warm seasons, including spring (13-21%), summer (41-64%) and autumn (16-25%), while the contribution is negligible during winter in South China. The comparison analysis between organic nitrates and each OA factor for different periods of the day shows good correlations (R=0.77 in spring, 0.91 in summer and 0.72 in autumn) between organic nitrates and the LO-OOA factor at nighttime. Based on this, we further investigate the potential pathway for the formation of nighttime organic nitrates, and the results suggest that the BVOCs+NO_3 chemistry plays a key role in the formation of nighttime organic nitrates and SOAs, and limonene is the most important precursors of VOCs for this type of reaction. Overall, we infer that, even in polluted urban atmosphere with high abundance of anthropogenic pollutants, particle-phase organic nitrates are possibly mostly derived from the formation from biogenic VOCs, and may be a good surrogate for studying the effects of biogenic emissions on air pollution and the climate.

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References

Ayres, B.R., Allen, H.M., Draper, D.C., Brown, S.S., Wild, R.J., Jimenez, J.L., Day, D.A., Campuzano-Jost, P., Hu, W., De Gouw, J.A., Koss, A., Cohen, R.C., Duffey, K.C., Romer, P., Baumann, K., Edgerton, E., Takahama, S., Thornton, J.A., Lee, B.H., Lopez-Hilfiker, F.D., Mohr, C., Wennberg, P.O., Nguyen, T.B., Teng, A.P., Goldstein, A.H., Olson, K., Fry, J.L.: Organic nitrate aerosol formation via NO3+ biogenic volatile organic compounds in the southeastern United States. Atmos. Chem. Phys. 15, 13377-13392. https://doi.org/10.5194/acp-15-13377-2015, 2015.

Boyd, C.M., Nah, T., Xu, L., Berkemeier, T., Ng, N.L.: Secondary Organic Aerosol (SOA) from Nitrate Radical Oxidation of Monoterpenes: Effects of Temperature, Dilution, and Humidity on Aerosol Formation, Mixing, and Evaporation. Environ. Sci. Technol. 51, 7831–7841. https://doi.org/10.1021/acs.est.7b01460, 2017.

Boyd, C.M., Sanchez, J., Xu, L., Eugene, A.J., Nah, T., Tuet, W.Y., Guzman, M.I., Ng, N.L.: Secondary organic aerosol formation from the β-pinene+NO3 system: effect of humidity and peroxy radical fate. Atmos. Chem. Phys. 15, 7497-7522. https://doi.org/10.5194/acp-15-7497-2015, 2015.

Bruns, E.A., Perraud, V., Zelenyuk, A., Ezell, M.J., Johnson, S.N., Yu, Y., Imre, D., Finlayson-Pitts, B.J., Alexander, M.L.: Comparison of FTIR and particle mass spectrometry for the measurement of particulate organic nitrates. Environ. Sci. Technol. 44, 1056-1061. https://doi.org/10.1021/es9029864, 2010.

Canagaratna, M.R., Jayne, J.T., Jimenez, J.L., Allan, J.D., Alfarra, M.R., Zhang, Q., Onasch, T.B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L.R., Trimborn, A.M., Northway, M.J., DeCarlo, P.F., Kolb, C.E., Davidovits, P., Worsnop, D.R.: Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. Mass Spectrom. Rev. 26, 185-222. https://doi.org/10.1002/mas.20115, 2007.

Crowley, J.N., Thieser, J., Tang, M.J., Schuster, G., Bozem, H., Beygi, Z.H., Fischer, H., Diesch, J.M., Drewnick, F., Borrmann, S., Song, W., Yassaa, N., Williams, J., Pöhler, D., Platt, U., Lelieveld, J.: Variable lifetimes and loss mechanisms for NO3and N2O5during the DOMINO campaign: Contrasts between marine, urban and continental air. Atmos. Chem. Phys. 11, 10853-10870. https://doi.org/10.5194/acp-11-10853-2011, 2011.

DeCarlo, P.F., Kimmel, J.R., Trimborn, A., Northway, M.J., Jayne, J.T., Aiken, A.C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K.S., Worsnop, D.R., Jimenez, J.L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. Anal. Chem. 78, 8281-8289. https://doi.org/10.1021/ac061249n, 2006.

Farmer, D.K., Matsunaga, A., Docherty, K.S., Surratt, J.D., Seinfeld, J.H., Ziemann, P.J., Jimenez, J.L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry. Proc. Natl. Acad. Sci. 107, 6670-6675.https://doi.org/10.1073/pnas.0912340107, 2010.

Fry, J.L., Draper, D.C., Barsanti, K.C., Smith, J.N., Ortega, J., Winkler, P.M., Lawler, M.J., Brown, S.S., Edwards, P.M., Cohen, R.C.: Secondary Organic Aerosol Formation and Organic Nitrate Yield from NO3 Oxidation of Biogenic Hydrocarbons. Environ. Sci. Technol. 48, 11944–11953. https://doi.org/10.1021/es502204x, 2014.

Fry, J.L., Draper, D.C., Zarzana, K.J., Campuzano-Jost, P., Day, D.A., Jimenez, J.L., Brown, S.S., Cohen, R.C., Kaser, L., Hansel, A., Cappellin, L., Karl, T., Hodzic Roux, A., Turnipseed, A., Cantrell, C., Lefer, B.L., Grossberg, N.: Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011. Atmos. Chem. Phys. 13, 8585-8605. https://doi.org/10.5194/acp-13-8585-2013, 2013.

Fry, J.L., Kiendler-Scharr, A., Rollins, A.W., Brauers, T., Brown, S.S., Dorn, H.P., Dubé, W.P., Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R., Wahner, A., Wooldridge, P.J., Cohen, R.C.: SOA from limonene: Role of NO3 in its generation and degradation. Atmos. Chem. Phys. 11, 3879-3894. https://doi.org/10.5194/acp-11-3879-2011, 2011.

Fry, J.L., Kiendlerscharr, A., Rollins, A.W., Wooldridge, P.J., Brown, S.S., Fuchs, H., Dube, W.P., Mensah, A., Dal Maso, M., Tillmann, R.: Organic nitrate and secondary organic aerosol yield from NO 3 oxidation of β-pinene evaluated using a gas-phase kinetics/aerosol partitioning model. Atmos. Chem. Phys. 9, 1431–1449. https://doi.org/10.5194/acp-9-1431-2009, 2008.

Hallquist, M., Wängberg, I., Ljungström, E., Barnes, I., Becker, K.H.: Aerosol and product yields from NO3radical-initiated oxidation of selected monoterpenes. Environ. Sci. Technol. 33, 553-559. https://doi.org/10.1021/es980292s, 1999.

Hao, L.Q., Kortelainen, A., Romakkaniemi, S., Portin, H., Jaatinen, A., Leskinen, A., Komppula, M., Miettinen, P., Sueper, D., Pajunoja, A., Smith, J.N., Lehtinen, K.E.J., Worsnop, D.R., Laaksonen, A., Virtanen, A.: Atmospheric submicron aerosol composition and particulate organic nitrate formation in a boreal forestland-urban mixed region. Atmos. Chem. Phys. 14, 13483-13495.https://doi.org/10.5194/acp-14-13483-2014, 2014.

He, L.Y., Huang, X.F., Xue, L., Hu, M., Lin, Y., Zheng, J., Zhang, R., Zhang, Y.H.: Submicron aerosol analysis and organic source apportionment in an urban atmosphere in Pearl River Delta of China using high-resolution aerosol mass spectrometry. J. Geophys. Res. Atmos. 116, D12. https://doi.org/10.1029/2010JD014566, 2011.

Huang, X.F., He, L.Y., Hu, M., Canagaratna, M.R., Sun, Y., Zhang, Q., Zhu, T., Xue, L., Zeng, L.W., Liu, X.G., Zhang, Y.H., Jayne, J.T., Ng, N.L., Worsnop, D.R.: Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic games using an aerodyne high-resolution aerosol mass spectrometer. Atmos. Chem. Phys. 10, 8933-8945.https://doi.org/10.5194/acp-10-8933-2010, 2010.

Huang, X.F., He, L.Y., Xue, L., Sun, T.L., Zeng, L.W., Gong, Z.H., Hu, M., Zhu, T.: Highly time-resolved chemical characterization of atmospheric fine particles during 2010 Shanghai World Expo. Atmos. Chem. Phys. 12, 4897-4907. https://doi.org/10.5194/acp-12-4897-2012, 2012.

Huang, X.F., Xue, L., Tian, X.D., Shao, W.W., Sun, T. Le, Gong, Z.H., Ju, W.W., Jiang, B., Hu, M., He, L.Y.: Highly time-resolved carbonaceous aerosol characterization in Yangtze River Delta of China: Composition, mixing state and secondary formation. Atmos. Environ. 64, 200-207.https://doi.org/10.1016/j.atmosenv.2012.09.059, 2013.

Lee, B.H., Mohr, C., Lopez-Hilfiker, F.D., Lutz, A., Hallquist, M., Lee, L., Romer, P., Cohen, R.C., Iyer, S., Kurten, T., Hu, W., Day, D.A., Campuzano-Jost, P., Jimenez, J.L., Xu, L., Ng, N.L., Guo, H., Weber, R.J., Wild, R.J., Brown, S.S., Koss, A., de Gouw, J., Olson, K., Goldstein, A.H., Seco, R., Kim, S., McAvey, K., Shepson, P.B., Starn, T., Baumann, K., Edgerton, E.S., Liu, J., Shilling, J.E., Miller, D.O., Brune, W., Schobesberger, S., D'Ambro, E.L., Thornton, J.A.: Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets. Proc. Natl. Acad. Sci. 113, 1516-1521. https://doi.org/10.1073/pnas.1508108113, 2016.

Lelieveld, J., Gromov, S., Pozzer, A., Taraborrelli, D.: Global tropospheric hydroxyl distribution, budget and reactivity. Atmos. Chem. Phys. 16, 12477-12493. https://doi.org/10.5194/acp-16-12477-2016, 2016.

Middlebrook, A.M., Bahreini, R., Jimenez, J.L., Canagaratna, M.R.: Evaluation of composition-dependent collection efficiencies for the Aerodyne aerosol mass spectrometer using field data. Aerosol Sci. Technol. 46, 258-271. https://doi.org/10.1080/02786826.2011.620041, 2012.

Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, Atmos. Chem. Phys., 17, 2103-2162, https://doi.org/10.5194/acp-17-2103-2017, 2017.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K.S., Chhabra, P.S., Bahreini, R., Murphy, S.M., Seinfeld, J.H., Hildebrandt, L., Donahue, N.M., Decarlo, P.F., Lanz, V.A., Prévôt, A.S.H., Dinar, E., Rudich, Y., Worsnop, D.R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. Atmos. Chem. Phys. 10, 4625-4641.https://doi.org/10.5194/acp-10-4625-2010, 2010.

Rollins, A.W., Browne, E.C., Min, K.-E., Pusede, S.E., Wooldridge, P.J., Gentner, D.R., Goldstein, A.H., Liu, S., Day, D.A., Russell, L.M., Cohen, R.C.: Evidence for NOx Control over Nighttime SOA Formation. Science. 337, 1210-1212. https://doi.org/10.1126/science.1221520, 2012.

Sato, K., Takami, A., Isozaki, T., Hikida, T., Shimono, A., Imamura, T.: Mass spectrometric study of secondary organic aerosol formed from the photo-oxidation of aromatic hydrocarbons. Atmos. Environ. 44, 1080-1087. https://doi.org/10.1016/j.atmosenv.2009.12.013, 2010.

Saunders, S.M., Jenkin, M.E., Derwent, R.G., Pilling, M.J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. Atmos. Chem. Phys. 3, 161–180. https://doi.org/10.5194/acp-3-161-2003, 2002.

Sobanski, N., Thieser, J., Schuladen, J., Sauvage, C., Song, W., Williams, J., Lelieveld, J., Crowley, J.N.: Day and night-time formation of organic nitrates at a forested mountain site in south-west Germany. Atmos. Chem. Phys. 17, 4115-4130.https://doi.org/10.5194/acp-17-4115-2017, 2017.

Spittler, M., Barnes, I., Bejan, I., Brockmann, K.J., Benter, T., Wirtz, K.: Reactions of NO3 radicals with limonene and α-pinene : Product and SOA formation. Atmos. Environ. 40, 116–127. https://doi.org/10.1016/j.atmosenv.2005.09.093, 2006.

Sun, Y., Zhang, Q., Schwab, J.J., Yang, T., Ng, N.L., Demerjian, K.L.: Factor analysis of combined organic and inorganic aerosol mass spectra from high resolution aerosol mass spectrometer measurements. Atmos. Chem. Phys. 12, 8537–8551. https://doi.org/10.5194/acp-12-8537-2012, 2012.

Teng, A.P., Crounse, J.D., Lee, L., St. Clair, J.M., Cohen, R.C., Wennberg, P.O.: Hydroxy nitrate production in the OH-initiated oxidation of alkenes. Atmos. Chem. Phys. 139, 5367-5377. https://doi.org/10.5194/acp-15-4297-2015, 2015.

Teng, A.P., Crounse, J.D., Wennberg, P.O.: Isoprene Peroxy Radical Dynamics. J. Am. Chem. Soc. 15, 4297-4316. https://doi.org/10.1021/jacs.6b12838, 2017.

Xu, L., Guo, H., Boyd, C.M., Klein, M., Bougiatioti, A., Cerully, K.M., Hite, J.R., Isaacman-VanWertz, G., Kreisberg, N.M., Knote, C., Olson, K., Koss, A., Goldstein, A.H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R.J., Ng, N.L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States. Proc. Natl. Acad. Sci. 112, 37-42. https://doi.org/10.1073/pnas.1417609112, 2015a.

Xu, L., Suresh, S., Guo, H., Weber, R.J., Ng, N.L.: Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: Spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates. Atmos. Chem. Phys. 15, 7307-7336. https://doi.org/10.5194/acp-15-7307-2015, 2015b.

Xu, W., Sun, Y., Wang, Q., Du, W., Zhao, J., Ge, X., Han, T., Zhang, Y., Zhou, W., Li, J., Fu, P., Wang, Z., Worsnop, D.R.: Seasonal Characterization of Organic Nitrogen in Atmospheric Aerosols Using High Resolution Aerosol Mass Spectrometry in Beijing, China. ACS Earth Sp. Chem. 1, 673–682. https://doi.org/10.1021/acsearthspacechem.7b00106, 2017.

Yan, C., Nie, W., Äijälä, M., Rissanen, M.P., Canagaratna, M.R., Massoli, P., Junninen, H., Jokinen, T., Sarnela, N., Häme, S.A.K., Schobesberger, S., Canonaco, F., Yao, L., Prévôt, A.S.H., Petäjä, T., Kulmala, M., Sipilä, M., Worsnop, D.R., Ehn, M.: Source characterization of highly oxidized multifunctional compounds in a boreal forest environment using positive matrix factorization. Atmos. Chem. Phys. 16, 12715-12731. https://doi.org/10.5194/acp-16-12715-2016, 2016.

Zhang, Q., Jimenez, J.L., Canagaratna, M.R., Ulbrich, I.M., Ng, N.L., Worsnop, D.R., Sun, Y.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: A review. Anal. Bioanal. Chem. 401, 3045-3067. https://doi.org/10.1007/s00216-011-5355-y, 2011.

Zhang, Y.H., Su, H., Zhong, L.J., Cheng, Y.F., Zeng, L.M., Wang, X.S., Xiang, Y.R., Wang, J.L., Gao, D.F., Shao, M., Fan, S.J., Liu, S.C.: Regional ozone pollution and observation-based approach for analyzing ozone-precursor relationship during the PRIDE-PRD2004 campaign. Atmos. Environ. 42, 6203-6218. https://doi.org/10.1016/j.atmosenv.2008.05.002, 2008.

364 Zhu, Q., He, L.Y., Huang, X.F., Cao, L.M., Gong, Z.H., Wang, C., Zhuang, X., Hu, M.: Atmospheric aerosol compositions
365 and sources at two national background sites in northern and southern China. Atmos. Chem. Phys. 16, 10283-10297.
366 https://doi.org/10.5194/acp-16-10283-2016, 2016.
367 Zhu, S. F.; Huang, X. F.; Ling-Yan, H. E.; Si-Hua, L. U.; Feng, N.: Variation characteristics and chemical reactivity of ambient
368 VOCs in Shenzhen. China Environmental Science. 32, 2140-2148, 2012.
369