Response to Reviewers

Referee #1

The manuscript "Seasonal variation of oxygenated organic molecules in urban Beijing and their contribution to secondary organic aerosol" addresses the seasonality of oxygenated organic molecules (OOM) in urban Beijing measured by a nitrate-CIMS over one year. And their potential contributions to secondary organic aerosol (SOA) via vapor condensation were estimated using an aerosol dynamic model. OOM concentrations were found to be highest in summer and generally followed the trend of radiation and temperature. OOM were classified into IP-OOM, MT-OOM, aromatic and aliphatic OOM. IP-OOM concentration vary strongly among seasons with lowest concentration in winter. Isoprene-OOM accounted for a large fraction in summer while in other seasons aromatic and aliphatic-OOM were the two major components. MS Profile of MT-OOM, aromatic and aliphatic OOM were similar among different seasons. Condensation of aromatic- and aliphatic-OOM contributed most to SOA throughout the year. Observation OOMs in urban environment are important to elucidate the SOA formation and particle growth but are scare as most field observations of OOMs were conducted in forested regions. Especially long time observation regarding seasonality of OOM is lacking. This study investigated one-year OOM compositions and concentrations systematically, which provides very valuable information of OOM seasonality and potential contribution to SOA. The manuscript is well written and fits well with the scope of ACP. I recommend its publication after addressing the following comments, which mainly work to clarify some important details and improve the readability and discussion of the manuscript.

We thank the reviewer for the constructive comments and suggestions. And as suggested, we added more details and modified corresponding descriptions to make our analysis easier to follow. The point-to-point response to the comments is given below. And the comments, our replies, and the corresponding changes in the revised manuscript and supplementary information are marked in black, blue, and green texts, respectively.

Specific comments

1. L60, I suggest explicitly mentioning the definition of OOM.

Response: Thanks a lot and this is really necessary.

The terminology OOMs comes from the term HOMs (Highly Oxygenated Organic Molecules), which is defined based on three criteria (Bianchi et al., 2019): a. HOMs are formed via autoxidation involving peroxy radicals, b. HOMs are formed in the gas phase under atmospherically relevant conditions, and c. HOMs typically contain six or more oxygen atoms. However, when looking into the oxygenated organic molecules measured at urban Beijing, the criteria of a. and c. are not always met. For example, in the oxidation processes, precursor VOCs may undergo multi-generation oxidation (Zaytsev et al., 2019;Garmash et al., 2020) and the autoxidation is sometimes suppressed by high NO_x level. This leads to the fact that not all organic molecules measured by the nitrate CIMS contain six or more oxygen atoms (see Fig. S7). This is the reason why we don't use the term HOMs.

OOMs is a more general terminology that refers to the gas phase organic compounds which are formed via oxidation process under atmospheric conditions. Thus, the guidelines for the classification of OOMs should be:

a. OOMs are the gas-phase oxygen-containing organic molecules detected under atmospherically relevant conditions.

b. OOMs can be formed via oxidations in the gas phase, heterogeneous reactions on aerosol surface, or evaporated processes from aerosols.

The definition of OOMs has been explicitly explained in a recent work by Nie et al. (Nie et al., 2022). Therefore, we added this paper as a reference of this sentence and explain the definition in more details in Sect. S2 (Line 22 – 35, Page 2).

"oxygenated organic molecules (OOMs, see the definition in Sect. S2 the work of Nie et al. (Nie et al., 2022)) have been acknowledged as an important contributor" (Line 59 – 60, Page 3)

2. In this study only m/z 200-400 was analyzed. Why other m/z, such as higher m/z were not included? What about their contributions? Are they too low to be important? It would be worth clarifying and noting the m/z range in the conclusion.

Response: We didn't report OOMs with higher m/z primarily because peaks in this range are very weak. Please note that those weak signals are not due to the transmission of the instrument, which remain roughly 94 % for m/z 400-680 range relative to that in the m/z 200-400 range. Rather, the low signal at higher m/z suggests that compounds of these masses are in very low concentrations. According to previous studies, the peaks with m/z larger than 400 are usually C_{15}-C_{20} compounds. They can either be the products from the dimeric reactions of monoterpenes (Ehn et al., 2012;Jokinen et al., 2014;Yan et al., 2016), or the oxidations of larger VOCs, such as sesquiterpene and diterpenes (Richters et al., 2016;Luo et al., 2022). However, in our studied urban environment, the concentrations of sesquiterpene and diterpenes are very low, and the formation of dimeric compounds is greatly suppressed by high-level NO_x. Therefore, the low signal at m/z > 400 can be well expected.

Meanwhile, we do observe some peaks at m/z > 400 range, but they are likely fluorine-containing contaminants and irrelevant to ambient processes. For example, the signal at m/z = 427 is mainly contributed by $(C_3F_7COO)_2H^-$ and the isotope of $C_6H_{13}COOH{\bullet}NO_3^-$, and remaining OOM signals are quite low (Fig. R1). The weak OOM signals together with the prominent contaminant signals make accurate peak identification difficult. Therefore, we decided not to focus too much on the higher m/z range, which nevertheless, has little influence on the conclusion of this study.

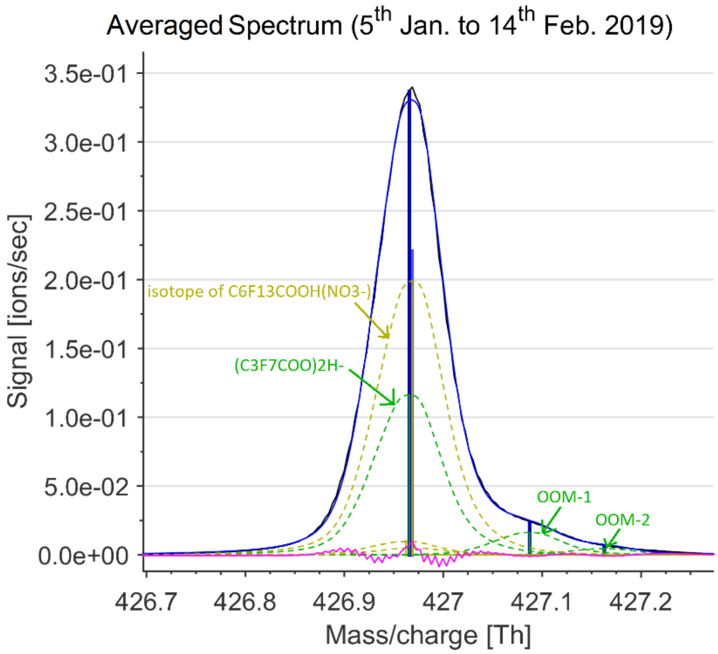


Figure R1. Fitted peaks at m/z = 427 Th of averaged winter spectrum (5th Jan. to 14th Feb., 2019).

For OOMs with m/z lower than 200 Th, their real molar weight after subtracting reagent ions should be low. Thus, they are generally more volatile and are not important to the condensational growth of SOA. One of the aim of this study is to investigate the SOA growth caused by OOM condensation, and this is the main reason why “light OOMs” are not included.

To clarify this consideration, we added the mass range of OOMs in the revised conclusion part as follows:

“A long-term measurement of OOMs based on nitrate CIMS was conducted in urban Beijing. OOMs in the mass range of 200-400 Th were systematically investigated.” (Line 494 – 495, Page 21)

3. In the method part (L173, Fig. 1), it seems that the authors used a IP-OOM list to differentiate whether a compound belongs to IP-OOM. It may be helpful to include the list and describe what experiments/observations the list is based on.

Response: Thanks a lot for your suggestion. This isoprene OOM list is taken from the work of Xu et al. (Xu et al., 2021), where multifunctional products of isoprene oxidation were observed in both Nanjing and Shanghai. In this study, based on the molecular composition of precursor isoprene as well as current knowledge of atmospheric isoprene oxidation, the authors were able to constrain the double bond equivalence, numbers of hydrogen and number of effective oxygen of isoprene oxidation products. And according to those constrains, isoprene OOM molecules were selected.

We also added the isoprene OOM list in the revised supplement as Table S6.

Table S6. Peak list of isoprene OOMs in this study based on the work of Xu et al. (Xu et al., 2021)

Molecular Formula	**Exact Mass**
CHO	
$C_4H_6O_4(NO_3^-)$	180.0150
$C_5H_8O_4(NO_3^-)$	194.0306
$C_5H_8O_5(NO_3^-)$	210.0255
$C_4H_6O_6(NO_3^-)$	212.0048
$C_5H_{10}O_5(NO_3^-)$	212.0412
$C_4H_8O_6(NO_3^-)$	214.0205
$C_5H_{12}O_5(NO_3^-)$	214.0568
$C_5H_8O_6(NO_3^-)$	226.0205
$C_5H_{10}O_6(NO_3^-)$	228.0361
$C_4H_8O_7(NO_3^-)$	230.0154
$C_5H_{12}O_6(NO_3^-)$	230.0518
$C_5H_8O_7(NO_3^-)$	242.0154
CHON	
$C_5H_9O_4N(NO_3^-)$	209.0415
$C_4H_7O_5N(NO_3^-)$	211.0208
$C_5H_9O_5N(NO_3^-)$	225.0364
$C_4H_7O_6N(NO_3^-)$	227.0157
$C_5H_9O_6N(NO_3^-)$	241.0314
$C_4H_7O_7N(NO_3^-)$	243.0106
$C_5H_{11}O_6N(NO_3^-)$	243.0470
$C_5H_9O_7N(NO_3^-)$	257.0263
$C_5H_{11}O_7N(NO_3^-)$	259.0419
$C_5H_9O_8N(NO_3^-)$	273.0212
$C_4H_7O_9N(NO_3^-)$	275.0004
$C_5H_{11}O_8N(NO_3^-)$	275.0368
$C_5H_{11}O_9N(NO_3^-)$	291.0317
$C_5H_9O_{10}N(NO_3^-)$	305.0110
$CHON_{2,3}$	

$C_5H_{10}O_6N_2(NO_3-)$	256.0423
$C_4H_8O_7N_2$ (NO_3-)	258.0215
$C_5H_{10}O_7N_2(NO_3-)$	272.0372
$C_5H_{10}O_8N_2(NO_3-)$	288.0321
$C_5H_{10}O_9N_2(NO_3-)$	304.0270
$C_4H_8O_{10}N_2(NO_3-)$	306.0063
$C_5H_{10}O_{10}N_2$ (NO_3-)	320.0219
$C_5H_9O_{10}N_3(NO_3-)$	333.0172

4. Also in this part and Fig. 3, have the authors considered the possible contribution of isoprene to C10-OOM via accretion reactions and contribution of monoterpene to C5-OOM via fragmentation?

Response: We didn't incorporate the C5 OOMs formed from monoterpene (MT) fragmentation, nor the C10 OOMs formed from isoprene (IP) accretion in the workflow. This can result in some uncertainties, which however, are expected to be quite low.

As aforementioned, the list of IP oxidation products was taken from the work of Xu et al. (Xu et al., 2021), where all the IP OOMs are either C_4 or C_5 compounds. It has shown in chamber studies that via RO_2 cross reactions, isoprene oxidation can lead to the formation of C10 dimeric products (Bernhammer et al., 2018;Wu et al., 2021), yet such RO_2 cross reaction is severely suppressed by the high-level NO_x (up to 9.5 – 38.3 ppb) in Beijing, limiting the formation of C10 isoprene products. Therefore, the C10 OOMs generated from isoprene are neglected in the workflow.

In previous experiments conducted in the CLOUD chamber, monoterpene oxidation by OH radical together with O_3 in the presence of a few ppb NO_x have been investigated by Yan et al. (Yan et al., 2020). We revisited the data of one 4.5 ppb NO_x experiment and found that $C_{4,5}$ fragmented peaks only accounted for ~ 4.5 % of total products (Fig. R2). In addition, the DBE values of most $C_{4,5}$ fragments are larger than 2, whereas the highest DBE values of IP OOMs in this study is only 2 (Fig. 3). Thus, these fragments almost have no interference with the classification of IP OOMs. Furthermore, the total concentration of MT OOMs in this study is also much lower than IP OOMs. Therefore, a negligible fraction of IP OOMs could raise from fragmented MT OOMs by misclassification.

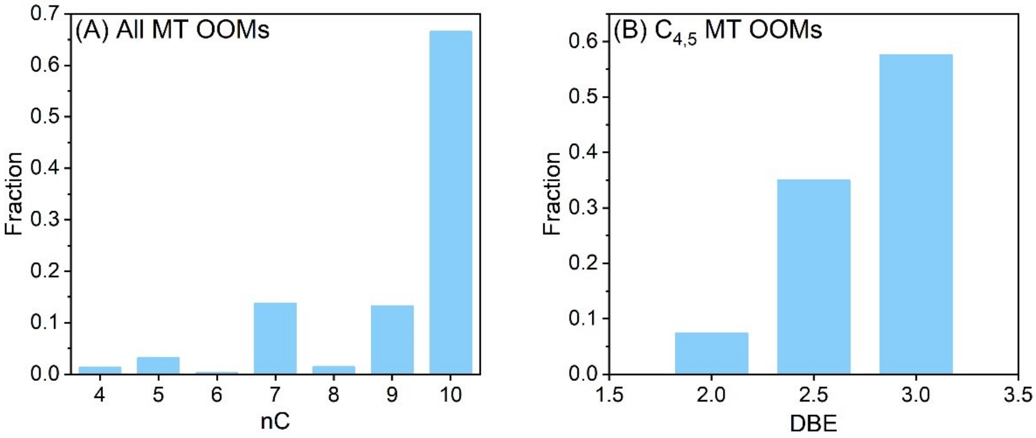


Figure R2. (A) Carbon distribution of all monoterpene oxidation products, and (B) DBE distribution of $C_{4,5}$ monoterpene oxidation products formed by OH radical oxidation together with ozonolyis in previous experiment (Yan et al., 2020). The experiment was conducted under 278 K and the NO_x level was 4.5 ppb.

5. Fig. 3, considering nitrate-CIMS does not detect OOM with low O number, are the OOM with nO_{eff}<=4 mostly organic nitrates?

Response: Yes. Most of $nO_{eff} \leq 4$ OOMs are organic nitrates.

The nitrogen number distributions of OOMs with $nO_{eff} \leq 4$ in four seasons are shown in Fig. R3 (A). It can be found that most OOM molecules contain one or more nitrogen atoms, and they are most likely organic nitrates. Besides, around 11 – 17 % of $nO_{eff} \leq 4$ OOMs contain no nitrogen atom, and most $nO_{eff} \leq 4$ and nN = 0 OOMs possess 4 oxygen atoms (Fig. R3 (B)).

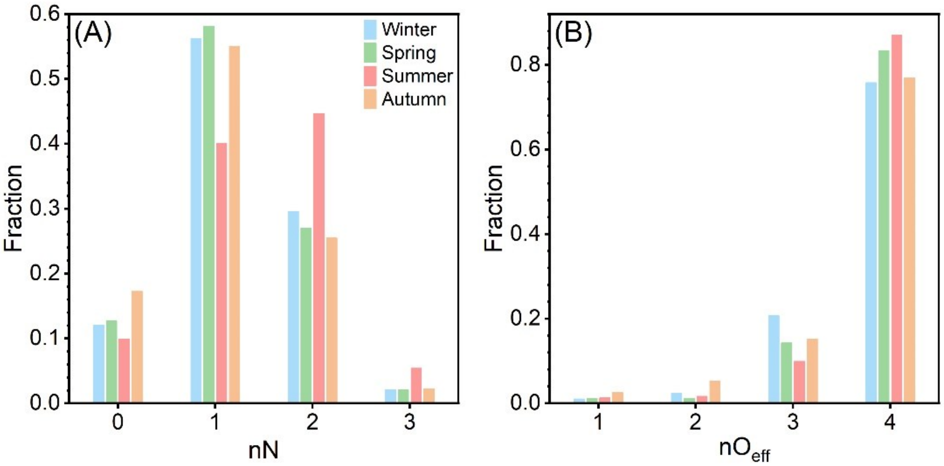


Figure R3. (A) Distribution of nitrogen number (nN) for OOMs with number of effective oxygen no larger than 4 ($nO_{eff} \leq 4$). (B) Distribution of effective oxygen number (nO_{eff}) for OOMs with $nO_{eff} \leq 4$ and nN = 0. The light blue, green, red and orange bars denote winter, spring, summer and autumn, respectively.

6. Fig. 5, it is not completely clear how the spectral profiles are obtained.

Response: In each subplot of Fig. 5, Fig. 7 and Fig. 9, the fraction of each compound is calculated via dividing its concertation by the corresponding total concentration of isoprene OOMs, monoterpene OOMs, aromatic OOMs or aliphatic OOMs.

To clarify this consideration, the captions of Fig. 5, Fig. 7 and Fig. 9 have been modified as follows:

"The fraction of each compound is calculated as the ratio of its concentration to the total concentration of IP OOMs." (Line 344 – 345, Page 13 for Fig. 5)

"The fraction of each compound is calculated as the ratio of its concentration to the total concentration of MT OOMs." (Line 372 – 373, Page 15 for Fig. 7)

"The fraction of each compound is calculated as the ratio of its concentration to the total concentration of aromatic OOMs ((A) to (D)) or aliphatic OOMs ((E) to (H))." (Line 432 – 433, Page 18 for Fig. 9)

7. L262-264, Fig. 5, and Fig.7, analyzing day and night MS spectra separately and plotting the diurnal variation for IP-OOM and MT-OOM may be helpful to estimate the relative contribution of nitrate OOM from NO_x termination and NO_3 radical.

Response: Thank you very much for your suggestions.

The high resolution mass spectra of measured OOMs during day and night are plotted in Fig. R4. It can be found that although the concentrations of OOMs during the night are typically lower than during the day, the overall distributions and patterns of the mass spectra are very similar. Besides, there is almost no peak that is unique for day or night. Therefore, the it is not easy to determine the contribution of NO_3 radical and NO_x termination to nitrate OOM formation based on mass spectra.

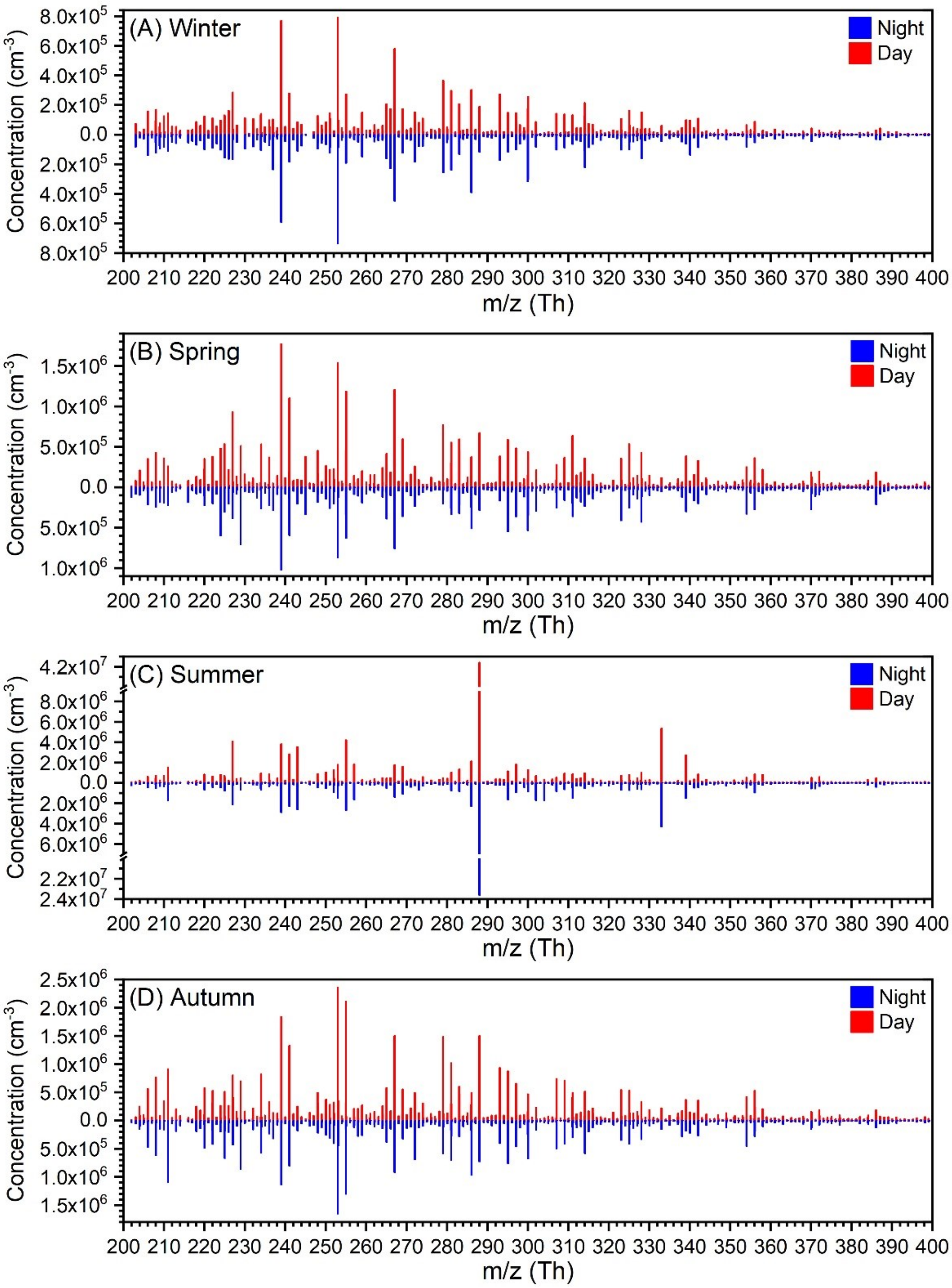


Figure R4. High resolution mass spectrum of measured OOM species during daytime (08:00 – 16:00) and nighttime (20:00 – 04:00 next day) for **(A)** winter, **(B)** spring, **(C)** summer and **(D)** autumn. Red and blue sticks denote datasets from day and night respectively.

As suggested, we further turn to the diurnal variation analysis of IP and MT OOMs. During summertime, each IP or MT OOM can be classified into one of the three types: a. the one with distinct daytime peak; b. the one with day and night dual peaks, and c. the one with elevated concentration at night. Fig. R5 shows the diurnal variations of typical IP and MT OOMs belonging to the above three groups, and **Table R1** summarizes the OOM formulae in each group.

For OOMs with only daytime peaks, they are primarily formed during the day. Some CHON and $CHON_2$ IP-OOMs belong to this group (Table R1), suggesting that they are likely produced from OH initiation followed by NO_x termination. For OOMs with only nighttime peaks, the nighttime chemistry should be their main sources. Only a few IP and MT OOMs containing nitrogen atoms are in this category ($C_5H_9O_4N$, $C_5H_9O_5N$, $C_5H_9O_8N$, $C_5H_{10}O_9N_2$ and $C_{10}H_{15}O_{10}N$). And they should be primarily formed via NO_3 radical oxidation. Besides, their concentration during the day are not zero, suggesting that OH initiation also have contribution to their daytime formation. For OOMs with day and night dual peaks, they have both daytime and nighttime sources. Those OOMs are CHON IP-OOMs, CHON MT-OOMs and $CHON_2$ MT-OOMs. They could be formed from both NO_3 radical oxidation and OH initiation followed by NO_x termination. It should be noted that the diurnal variations of OOMs are also influenced by the boundary layer dynamics and precursor levels. During the night, precursor VOCs, oxidants as well as OOMs should be concentrated by the low boundary layer height and the weak atmospheric diffusion capacity. Therefore, detailed analysis of OOM formation pathway should include the information of boundary layer dynamics and precursor VOCs, but this is out of the scope of current study and we will get into more details in future work.

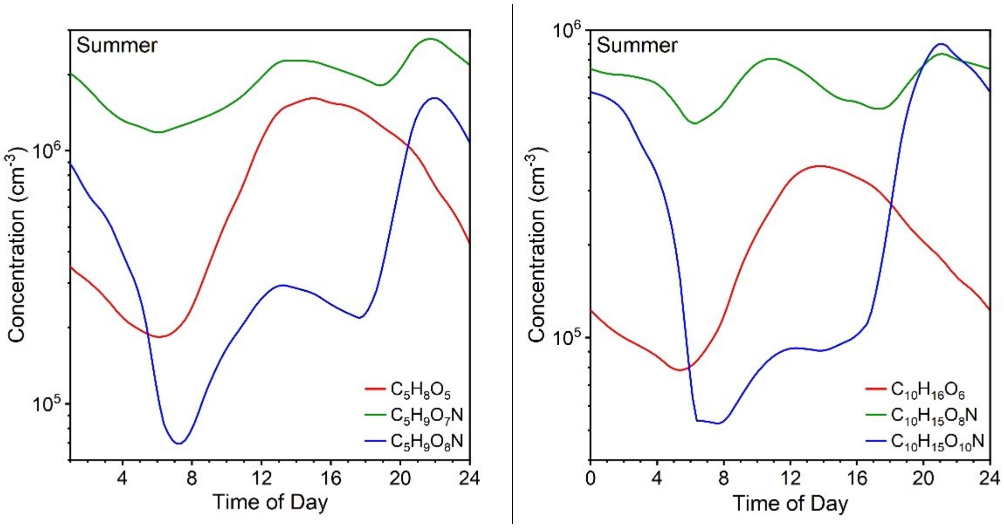


Figure R5. Diurnal variations of typical IP and MT OOMs during summertime. $C_5H_8O_5$ and $C_{10}H_{16}O_6$ only have daytime peak. $C_5H_9O_7N$ and $C_{10}H_{15}O_8N$ possess day and night dual peaks. $C_5H_9O_8N$ and $C_{10}H_{16}O_{10}N$ only have nighttime peak.

Table R1. Formulae of IP and MT OOMs with daytime peak, day-night dual peaks and nighttime peaks in summer.

Daytime Peak		Day-Night Dual Peaks		Nighttime Peak	
IP OOMs	MT OOMs	IP OOMs	MT OOMs	IP OOMs	MT OOMs
$C_4H_8O_6$	$C_{10}H_{14}O_5$	**$C_5H_9O_7N$**	$C_{10}H_{13}O_7N$	$C_5H_9O_4N$	**$C_{10}H_{15}O10N$**
$C_5H_8O_4$	**$C_{10}H_{14}O_6$**	$C_5H_{11}O_7N$	$C_{10}H_{13}O_8N$	$C_5H_9O_5N$	
$C_5H_8O_5$	$C_{10}H_{14}O_7$		$C10H_{13}O_9N$	**$C_5H_9O_8N$**	
$C_5H_8O_6$	$C_{10}H_{16}O_5$		$C_{10}H_{13}O_{10}N$	$C_5H_{10}O_9N_2$	
$C_5H_{10}O_3$	$C_{10}H_{16}O_6$		$C_{10}H_{15}O_7N$		
$C_5H_{10}O_5$	$C_{10}H_{16}O_7$		**$C_{10}H_{15}O_8N$**		
$C_4H_7O_6N$	$C_{10}H_{18}O_5$		$C_{10}H_{15}O_9N$		
$C_5H_9O_6N$	$C_{10}H_{18}O_6$		$C_{10}H_{17}O_7N$		
$C_5H_9O_{10}N$			$C_{10}H_{17}O_8N$		
$C_5H_{11}O_9N$			$C_{10}H_{17}O_9N$		
$C_4H_8O_{10}N_2$			$C_{10}H_{12}O_9N_2$		
$C_5H_{10}O_6N_2$			$C_{10}H_{14}O_{10}N_2$		
$C_5H_{10}O_8N_2$			$C_{10}H_{16}O_{10}N_2$		
$C_5H_9O_{10}N_3$					

Furthermore, for one specific OOM, its diurnal variation may also change in different seasons (Fig. R6). For example, $C_5H_9O_7N$ and $C_{10}H_{15}O_8N$ have day and night dual peaks in summer and spring, while only possess distinct daytime peaks in winter and autumn, suggesting that the their NO_3 radical chemistry plays more important role in summer and spring. Similarly, $C_5H_9O_8N$ and $C_{10}H_{16}O_{10}N$ have higher concentration at night in summer, while this is not all the case for other three seasons.

In summary, the relative contribution of NO_3 radical oxidation and NO_x termination to nitrate OOM formation varies for different OOMs and changes with seasons. Further binPMF analysis, as the work done by Liu et al. (Liu et al., 2021) where nighttime factors take ~ 30 % of total OOM concentration, may help to de-convolute a more accurate contribution.

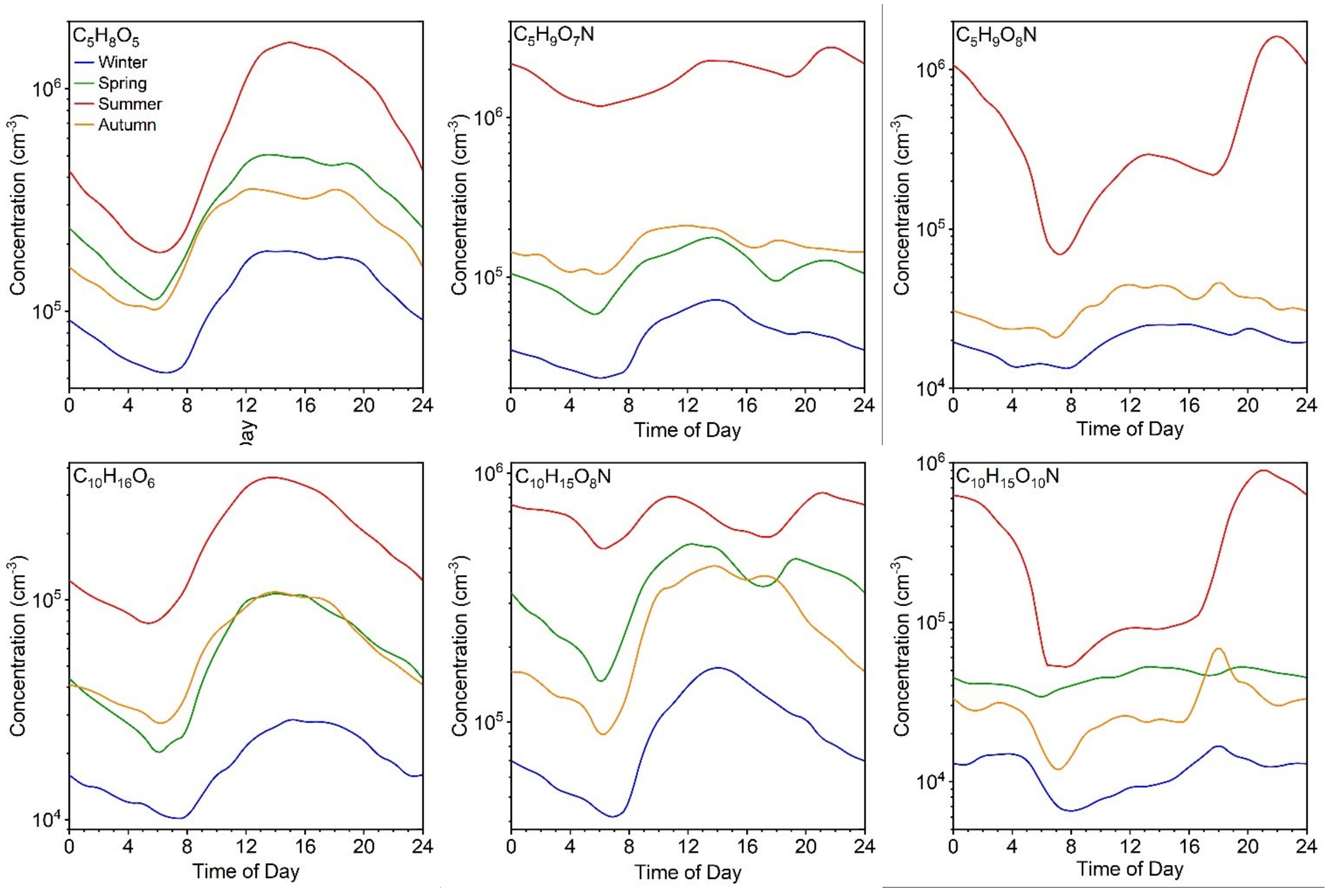


Figure R6. Diurnal variations of typical IP ($C_5H_8O_5$, $C_5H_9O_7N$ and $C_5H_9O_8N$) and MT OOMs ($C_{10}H_{16}O_6$, $C_{10}H_{15}O_8N$ and $C_{10}H_{16}O_{10}N$) in four seasons.

8. L403-405, why CHO accounts for so low fraction compared to other OOM classes?

Response: The reason is not fully understood. The lowest fraction of CHO aliphatic OOMs compared with other OOM classes is probably caused by the highest branching ratio of aliphatic RO_2 - NO_x reaction forming $CHON_x$ species. However, as there the RO_2 + NO_x branching ratios of many OOM molecules are lacking, this hypothesis needs further validation by well controlled chamber experiments.

9. Fig. 11, how the volatility was calculated? As volatility highly depends on the method to derive it, it would be helpful to clarify and maybe add a short discussion on the influence of the methods adopted.

Response: Thanks a lot for pointing out that. The method for estimating OOM volatility was provided in Sect. S2 as follows:

"Detailed structure information of OOMs in real atmosphere is still unknown, therefore, the volatility of each OOM molecule was estimated based on a parameterization using numbers of different atoms (Donahue et al., 2011). For the oxidation products from monoterpenes, previous studies show that except from hydroxyl (-OH), carbonyl (=O) and carboxyl (-O(=O)H) groups, hydroperoxide (-OOH) also takes a large portion (Tröstl et al., 2016;Stolzenburg et al., 2018). Then by assuming that all nitrogen atoms exist as organonitrate groups ($-ONO_2$), the saturation mass concentration of OOM molecule at 300 K can be given as follows (Mohr et al., 2019):

$$\log_{10}C^*(300\mathrm{K}) = (25-\mathrm{nC})\cdot\mathrm{bC} - (\mathrm{nO}-3\mathrm{nN})\cdot\mathrm{bO} - 2*\left[\frac{(\mathrm{nO}-3\mathrm{nN})\cdot\mathrm{nC}}{\mathrm{nC}+\mathrm{nO}-3\mathrm{nN}}\right]\cdot\mathrm{bCO} - \mathrm{nN}\cdot\mathrm{bN} \quad (1)$$

where nC, nO and nN are the numbers of carbon, oxygen, and nitrogen in each molecule respectively, and bC=0.475, bO=0.2, bCO=0.9, and bN=2.5. For oxidation products from aromatics, the work of Wang et al. shows that they possess more hydroxyl and carbonyl groups as well as less hydroperoxides, and that their estimated saturation concentrations suggested by Donahue et al. (Donahue et al., 2011) match well with the experiment ones (Wang et al., 2020). Therefore, for those non-monoterpene OOMs, the estimation from Donahue et al. was applied:

$$\log_{10}C^*(300\mathrm{K}) = (25-\mathrm{nC})\cdot\mathrm{bC} - \mathrm{nO_{eff}}\cdot\mathrm{bO} - 2*\left(\frac{\mathrm{nC}\cdot\mathrm{nO_{eff}}}{\mathrm{nC}+\mathrm{nO_{eff}}}\right)\cdot\mathrm{bCO} \quad (2)$$

where nC, $\mathrm{nO_{eff}}$ and nN are the numbers of carbon, effective oxygen and nitrogen in each molecule separately, and bC=0.475, bO=2.3, and bCO=-0.3.

The temperature dependence of C^* is given by the Clausius-Clapeyron equation (Epstein et al., 2010;Donahue et al., 2012), which we can be approximated as:

$$\log_{10}C^*(T) = \log_{10}C^*(300\mathrm{K}) + \frac{\Delta H_{vap}}{R\ln(10)}\left(\frac{1}{300}-\frac{1}{T}\right) \quad (3)$$

where the evaporation enthalpy ΔH_{vap} can be linked with $\log_{10}C^*(300\mathrm{K})$ according to the following equation:

$$\Delta H_{vap}[\mathrm{kJ\ mol^{-1}}] = -5.7\cdot\log_{10}C^*(300\mathrm{K}) + 129 \quad (4)$$

After the temperature related saturation concentrations were calculated, OOMs were then grouped into different bins based on the volatility basis set (VBS) (Donahue et al., 2006), and further classified as ELVOCs (extremely low volatility organic compounds), LVOCs (low volatility organic compounds), SVOCs (semi-volatile organic compounds), IVOCs (intermediate volatility organic compounds) and VOCs (volatile organic compounds) according to their volatilities (Donahue et al., 2012)."

We also modified one sentence in the revised manuscript to refer to this volatility calculation.

"Therefore, we estimate the volatility of source-classified OOMs (detailed method can be found in Sect. S3) and summarize the results in Fig. 10." (Line 445 – 446, Page 19)

As for the volatility calculation method, it is true that the derived OOM volatility may vary among different methods. Volatility parameterization based on numbers of different atoms originated from the work of Donahue (Donahue et al., 2011). This study gave a good volatility estimation for OOMs which only contain carbon, hydrogen and nitrogen atoms, and meet the requirements of containing mostly hydroxyl, carbonyl and carboxyl groups and possessing equal fraction of hydroxyl and carbonyl.

With deeper understanding of monoterpene oxidation mechanism during the past decade, many studies have found that hydroperoxide is also a key functional group of monoterpene oxidation products (Ehn et al., 2014;Jokinen et al., 2014;Praplan et al., 2015;Berndt et al., 2016). Based on the proposed structures of those products, the group-contribution method SIMPOL could be applied to calculate the volatilities of monoterpene-derived OOMs. And the results were further used for revising the original volatility parameterization (Tröstl et al., 2016;Stolzenburg et al., 2018;Mohr et al., 2019;Bianchi et al., 2019). And therefore, the volatility estimation of monoterpene OOMs based on Eq. 1 should be pretty robust and has the least uncertainty compared with other types of OOMs.

For aromatic OOMs, the volatility estimation according to Eq. 2 was also evaluated by Wang et al. (Wang et al., 2020). In this work, the oxidation experiments of toluene and naphthalene by OH radical were performed under conditions similar to typical urban environments. Results showed that this equation works well for toluene dimers, naphthalene monomers and naphthalene dimers, while overestimates the volatility a little bit for toluene monomers. In our study, it is likely that most aromatic OOMs are in the form of monomers. And thus, the values of $\log_{10}\mathrm{C}^*$ for aromatic OOMs derived from Eq. (2) might be overestimated slightly.

The chemical pathways of atmospheric isoprene oxidation have been investigated for years. Early studies showed that carbonyl, hydroxyl and organonitrate groups are the main functional groups of isoprene OOMs (Lee et al., 2014;Schwantes et al., 2015). In recent years, some studies found that hydroperoxide could also be formed through the process of intramolecular H-shift (Wang et al., 2018;Zhao et al., 2021;Wu et al., 2021). However, different from the stable hydroperoxides on monoterpene OOMs, some hydroperoxides on isoprene OOMs are unstable and may undergo fragmentation (Teng et al., 2017). Besides, this formation of hydroperoxides tend to occur under low-NO_x or experimentally design conditions (D’Ambro et al., 2017;Zhao et al., 2021;Wu et al., 2021). Therefore, the fraction of hydroperoxide groups on isoprene OOMs could not be taken directly from experimental results. Fortunately, the work of Xu et al. (Xu et al., 2021) provided us valuable information of observed isoprene OOMs in Nanjing, one of the Chinese megacities. Results showed that there is large fraction of organonitrate groups and probably small fraction of hydroperoxide groups for isoprene OOMs formed under megacity atmosphere. And this is the reason why we didn’t apply the volatility parameterization from monoterpene OOMs, which contain large fraction of hydroperoxides, to isoprene OOMs. In addition, the work of Wu et al. (Wu et al., 2021) estimated the volatility of isoprene nitrates by comparing the difference between two sets of experiments with and without seed aerosol addition. But as seed aerosols inevitably brought in heterogeneous reactions on the surface and liquid phase reactions in the particle phase, this method seems not suitable for volatility acquisition. Future thermal desorption experiments like the one conducted by Wang et al. (Wang et al., 2020) may give better estimation.

For aliphatic OOMs, direct volatility parameterization has been lacking, and only few studies proposed its formation pathways. Conventional knowledge suggests that the oxidation products from alkanes as well as alkenes mainly contain carbonyl, hydroxyl and organonitrate groups (Ziemann, 2011), while possibilities still remain for the formation of hydroperoxides (Rissanen et al., 2014;Rissanen, 2018;Wang et al., 2021). Yet, the lack of mechanism on aliphatic OOM formation under urban-related atmospheric conditions hampers the understanding of aliphatic OOM structures. Thus, we are not able to decide whether Eq. (1) or Eq. (2) is more suitable for them.

To solve this problem, we calculated aliphatic OOM volatility with both methods the results were summarized in Fig. S2. Although some difference appears for detailed volatility distribution, the concentrations of condensable aliphatic OOMs (ELVOCs and LVOCs) based on Eq. (1) and Eq. (2) are very consistent. And therefore, the contribution of aliphatic OOMs to SOA condensation growth will not be influenced too much by the method chosen. In this study, we finally use Eq. (2) to calculate the volatility of aliphatic OOMs.

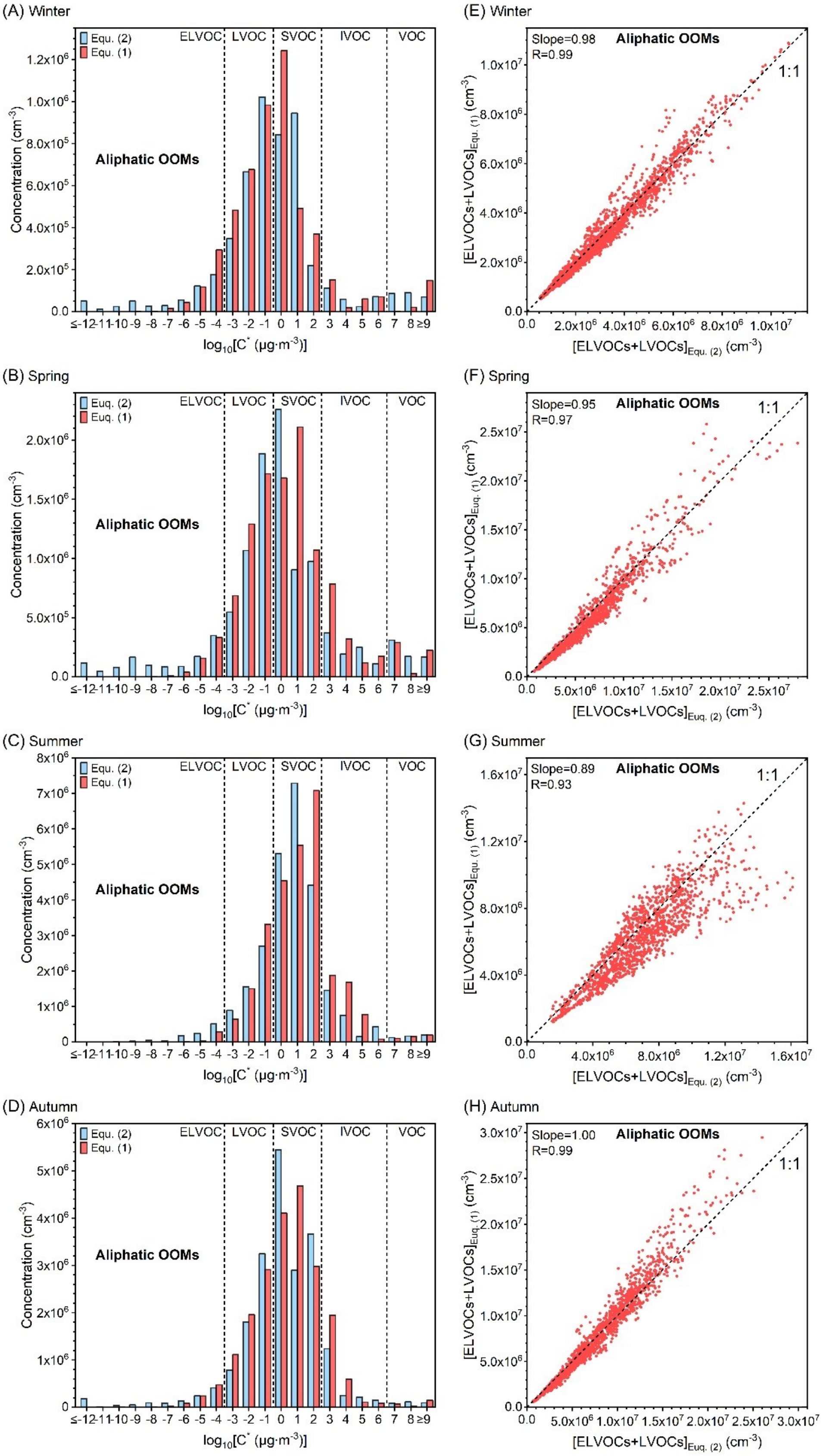

(A) Winter
(B) Spring
(C) Summer
(D) Autumn
Equ. (2)
Equ. (1)
ELVOC
LVOC
SVOC
IVOC
VOC
Aliphatic OOMs
Concentration (cm^{-3})
$\log_{10}[C^*$ (μg·m^{-3})]
≤-12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7 8 ≥9
0.0
2.0x10^5
4.0x10^5
6.0x10^5
8.0x10^5
1.0x10^6
1.2x10^6
5.0x10^5
1.5x10^6
2.0x10^6
0
1x10^6
2x10^6
3x10^6
4x10^6
5x10^6
6x10^6
7x10^6
8x10^6
(E) Winter
(F) Spring
(G) Summer
(H) Autumn
Slope=0.98
R=0.99
Slope=0.95
R=0.97
Slope=0.89
R=0.93
Slope=1.00
R=0.99
1:1
[ELVOCs+LVOCs]$_{\text{Equ. (1)}}$ (cm^{-3})
[ELVOCs+LVOCs]$_{\text{Equ. (2)}}$ (cm^{-3})
[ELVOCs+LVOCs]$_{\text{Euq. (1)}}$ (cm^{-3})
[ELVOCs+LVOCs]$_{\text{Euq. (2)}}$ (cm^{-3})
0.0
2.0x10^6
4.0x10^6
6.0x10^6
8.0x10^6
1.0x10^7
5.0x10^6
1.5x10^7
2.0x10^7
2.5x10^7
3.0x10^7
1.2x10^7
1.6x10^7

Figure S2. (A) - (D) Estimated aliphatic OOM volatility distribution derived from two parameterization methods for four season. **(E) - (F)** Comparison of aliphatic OOM concentrations belonging to ELVOCs and LVOCs between two parameterization methods for four seasons. In Fig. (E) to (F), the slopes of least-square linear fit and Pearson coefficients are also listed.

And to clarify this consideration, we added Fig. S2 and the above discussion in the revised supplement as Sect. S4 (Line 62 – 107, Page 3 – 4).

10. L493, "the dominant formation pathways of OOMs stay the same during the year", it might be easier to follow to add "…each OOM stay constant during the year", otherwise it would sound that all OOM are formed in the same pathways.

Response: Thanks a lot for your suggestions and we rewrote this sentence as follows:

"indicating that the dominant formation pathways of each source-classified OOMs stay constant during the year". (Line 503, Page 21)

Technical comments:

1. L173, in Fig. 1, "nO=10" or "nC=10?

Response: Yes, thank a lot. We have corrected this error in Fig. 1.

2. Fig. 3, the order of the legend is not consistent with the order of appearance. It might be easier to follow by keeping it consistent. And there is no legend for light blue.

Response: Yes, thank you very much for your suggestion. We have modified the sequence of the legend in Fig. 3, making it consistent with the appearance order of four seasons.

What do you mean "light blue"? There are only blue bars with diagonal lines and filled colors, and no light blue ones.

3. L443, a space is missing before "94 %".

Response: Thank a lot. We modified this in the revised manuscript. (now Line 455, Page 19)

Referee #2

This manuscript presents the results of a field study of oxygenated organic molecules (OOMs) and their contribution to secondary organic aerosol (SOA) in urban Beijing. The measurements of OOMs were conducted over the four seasons of the year 2019 using a nitrate-CIMS. The measured OOMs mainly contained 5-10 carbon atoms, 3-7 effective oxygen atoms and 0-2 nitrogen atoms and had 0-6 DBE values. The OOM concentration exhibited an obvious seasonal variation, ranging from ~1 ppt in winter to ~7 ppt in summer. Such seasonality was thought to be mainly driven by the seasonal variation of the intensity of photochemistry. According to the DBE value and the number of carbon, oxygen and nitrogen atoms in the molecules, ~1000 OOMs were classified into four groups, that is, isoprene, monoterpene, aliphatic and aromatic OOMs. Among them, aromatic (29-41%) and aliphatic (26-41%) OOMs were found to be the major contributors to OOMs in all seasons. The vapor condensation flux calculations further showed that these two classes of OOMs had largest contributions (46-62% and 14-32%, respectively) to SOA in urban Beijing throughout the year. Up to date, field measurements of OOMs in urban areas are rare. This study provides valuable data on the concentration, chemical composition and seasonal variation of OOMs, as well as their potential contributions to SOA in polluted urban areas. Overall, the measurements and data analysis in this study are well performed, the results are appropriately discussed, and the manuscript is nicely written. I would recommend the publication of this manuscript in ACP after the following comments are fully addressed.

We thank the reviewer for the constructive comments and suggestions. We have carefully revised our manuscript and supplement accordingly. The point-to-point response to the comments is given below. And the comments, our replies, and the corresponding changes in the manuscript and supplementary information are in black, blue, and green, respectively.

1. Line 63-65: It is described here that API-TOF provided the first direct measurements of OOMs. That is true for semi-volatile and low-volatility OOMs. However, OOMs literally mean organic compounds with oxygenated functional groups and also include the family of oxygenated volatile organic compounds, which had been measured, e.g., by GC-MS and PTR-MS before API-ToF or ToF-CIMS have been developed. The authors should provide a clear definition or specify the range of OOMs discussed in this study.

Response: Thank you very much for your suggestion. Our description is not that rigorous and should be modified.

Here the OOMs mainly refer to the more oxygenated ones measured by Chemical Ionization-APi-ToF mass spectrometers, such as nitrate CIMS, iodide CIMS, and bromide CIMS. Therefore, we modified this sentence in the revised manuscript as follows:

"… the first direct measurement of highly oxygenated organic molecules (HOMs), a subgroup of OOMs with the most oxygen content, …" (Line 64 – 65, Page 3)

For the terminology OOMs, it is a more general one that refers to the gas phase organic compounds which are formed via oxidation process under atmospheric conditions. We didn't use the term HOMs (Highly Oxygenated Organic Molecules) proposed by Bianchi (Bianchi et al., 2019) because a. not all OOMs are formed through autoxidation, and precursor VOCs may undergo multi-generation oxidation (Zaytsev et al., 2019;Garmash et al., 2020) , and b. not all OOMs contain six or more oxygen atoms (see Fig. S7). Thus, the guidelines for the classification of OOMs in this study should be:

a. OOMs are the gas-phase oxygen-containing organic molecules detected under atmospherically relevant conditions.

b. OOMs can be formed via oxidations in the gas phase, heterogeneous reactions on aerosol surface, or evaporated processes from aerosols.

The definition of OOMs has been explicitly explained in a recent work by Nie et al. (Nie et al., 2022). Therefore, we added this paper as a reference of this sentence and explain the definition in more details in Sect. S2 (Line 22 – 35, Page 2).

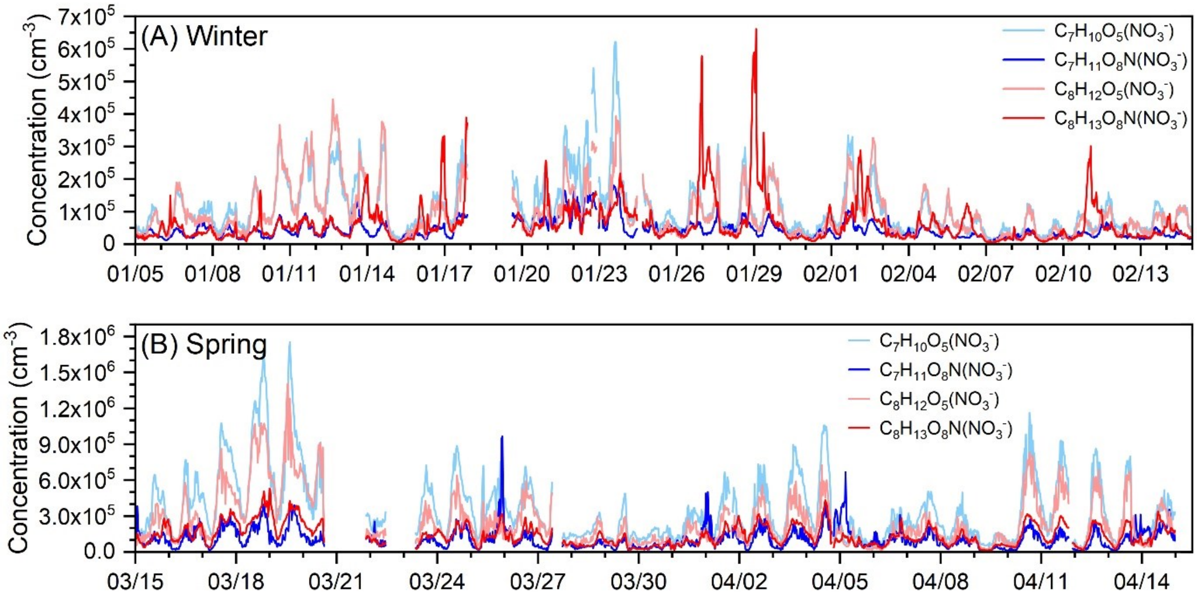
"oxygenated organic molecules (OOMs, see the definition in Sect. S2 the work of Nie et al. (Nie et al., 2022)) have been acknowledged as an important contributor" (Line 59 – 60, Page 3)

2. Line 119-121: Since OOMs can be detected either as a nitrate ion cluster (i.e., [M+NO3-] or [M+HNO3•NO3-]) or as a deprotonated ion by nitrate-CIMS, additional information as to how the product ions [CHON+NO3-] vs. [CHO+ HNO3•NO3-] and [CHON-] vs. [CHO•NO3-] were differentiated in this study should be provided in the manuscript.

Response: Thanks a lot. This is indeed a piece of important information that needs to be provided.

The acidity of OOM molecules is not very strong so that they hardly exist in de-protonated ions. In Ehn et al., by using isotopically labeled nitric acid ($H^{15}NO_3$) as the reagent, it was found that OOMs mainly existed as adducts with NO_3^-, and to a lesser extent with $HNO_3NO_3^-$ (Ehn et al., 2014). This is because the binding energy of OOMs with NO_3^- is smaller than with $HNO_3NO_3^-$ (Hyttinen et al., 2015).

Besides, the evidence that most OOMs cluster with NO_3^- could also be found from the time variations of corresponding OOMs. As shown in Fig. S1, the time variations of $C_7H_{10}O_5NO_3^-$ and $C_7H_{11}O_8NNO_3^-$ are not consistent, indicating that they are different OOMs charged both by NO_3^-, instead of the same OOM charged by NO_3^- and $HNO_3NO_3^-$, respectively. This is also the same for other OOMs, such as $C_8H_{12}O_5NO_3^-$ and $C_8H_{13}O_8NNO_3^-$.



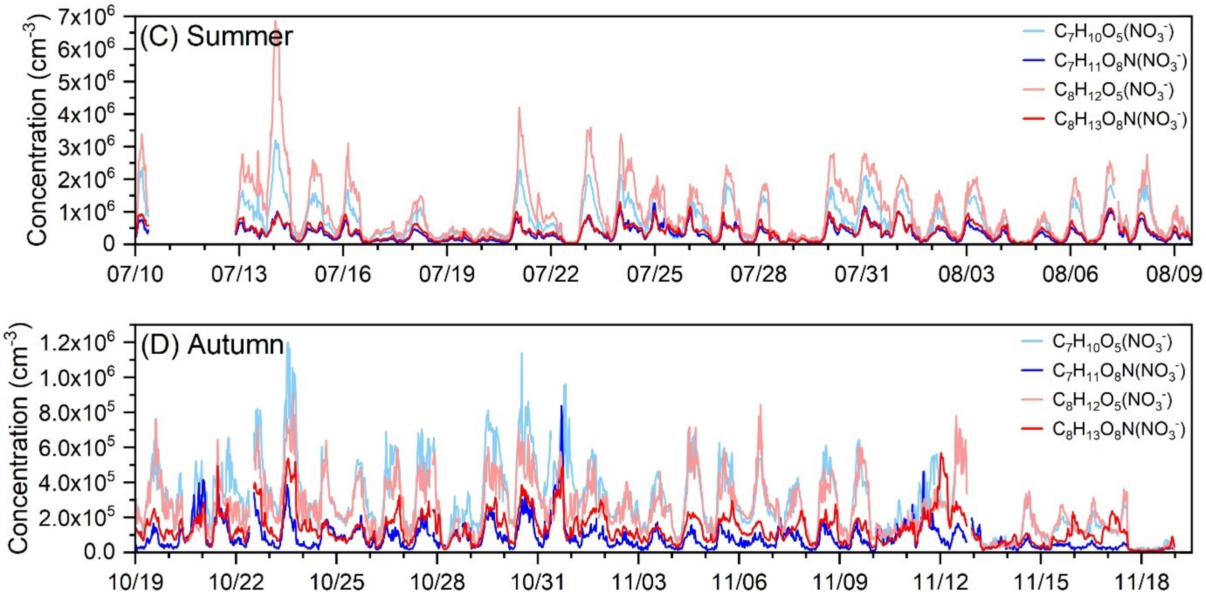


Figure S1. The time variations of $C_7H_{10}O_5(NO_3^-)$, $C_7H_{11}O_8N(NO_3^-)$, $C_8H_{12}O_5(NO_3^-)$ and $C_8H_{13}O_8N(NO_3^-)$ during four seasons.

From the above discussion, we believe that OOMs (X) are primarily detected as clusters with NO_3^-. ($X \bullet NO_3^-$). Therefore, the original formula of a detected ion Y could be obtained based on the following criteria:

a. If there is no nitrogen atom in Y, it is treated as a deprotonated species.

b. If there is at least one nitrogen atom in Y, it is treated as an adduct with NO_3^-.

To clarify this consideration, we added Fig. S1 and the above discussion in the revised supplement as Sect. S1 (Line 8 – 21, Page 2) and modified the following sentence in the revised manuscript:

"It should be pointed out that in the nitrate CIMS, most OOMs were detected as the cluster form of $(OOM)NO_3^-$, and detailed information can be found in Sect. S1." (Line 121 – 122, Page 5)

3. Line 143-144: The selection of monoterpene OOMs excluded < C10 compounds, which have been shown to account for a considerable fraction of monoterpene oxidation products in laboratory studies. To what extent would this assignment affect the accuracy of the results regarding the contributions of monoterpene OOMs to total OOMs and SOA? If applying the binPMF results of Nie et al, 2022 to this study, what signal ratios of C10 compounds vs. < C10 compounds would be obtained in the monoterpene OOM factor?

Response: The contribution of nC < 10 monoterpene (MT) OOMs was investigated by analyzing the results from a. one monoterpene oxidation chamber experiment (Yan et al., 2020) and b. the binPMF workflow proposed by Nie et al. (Nie et al., 2022).

The chamber experiment was conducted under 278 K. The NO_x level was 4.5 ppb, and both OH radical and O_3 were used as oxidants. The distributions of nC, nO_{eff}, nN and DBE of MT OOMs in this experiment as well as in our observation are shown in Fig. R1 (E) – (H) and Fig. R1 (A) – (D), respectively. It should be noted that for consistency with target OOMs in this study, only the ones with masses between 200 and 400 Th are investigated. There are four main differences between observational and experimental MT OOMs. First, the nC = 10 compounds contribute ~ 67 % of total MT OOMs in experiment. If this is the case in real atmosphere, the concentration of MT OOMs might be underestimated by ~ 30 % through applying the workflow in this study. But some nC = 10 species may also come from the oxidation of C10 aromatics. Therefore, the exact uncertainty of this nC = 10 constrain is hard to evaluate. Second, for nO_{eff} distribution, our observation shows that there is a general decreasing trend with the increase of nO_{eff}, while in experiment, the trend is opposite. Third, observational organonitrates take ~ 80 % of total MT OOMs during the year, while in experiment, this fraction reduces to only ~ 43 %. The lower oxygen and higher nitrogen content of observational MT OOMs is probably caused by high NO_x level in urban Beijing (9.5 – 38.3 ppb) compared with that in experiment (4.5 ppb). Fourth, based on our measurement, few MT OOMs possess non-integer DBE values. In experiment, however, there exist large fraction of DBE = 3.5 MT OOMs (17 %). Those molecules with non-integer DBE values are considered as radicals, and this suggests that the lifetime of MT radicals in experiment are probably longer than that in Beijing atmosphere. Despite the above differences, the upper and lower limits of DBE and nO_{eff} for observational and experimental MT OOMs are quite similar. Therefore, the constrains of $2 \leq DBE \leq 4$ and $nO_{eff} \geq 4$ of MT OOMs are reasonable.

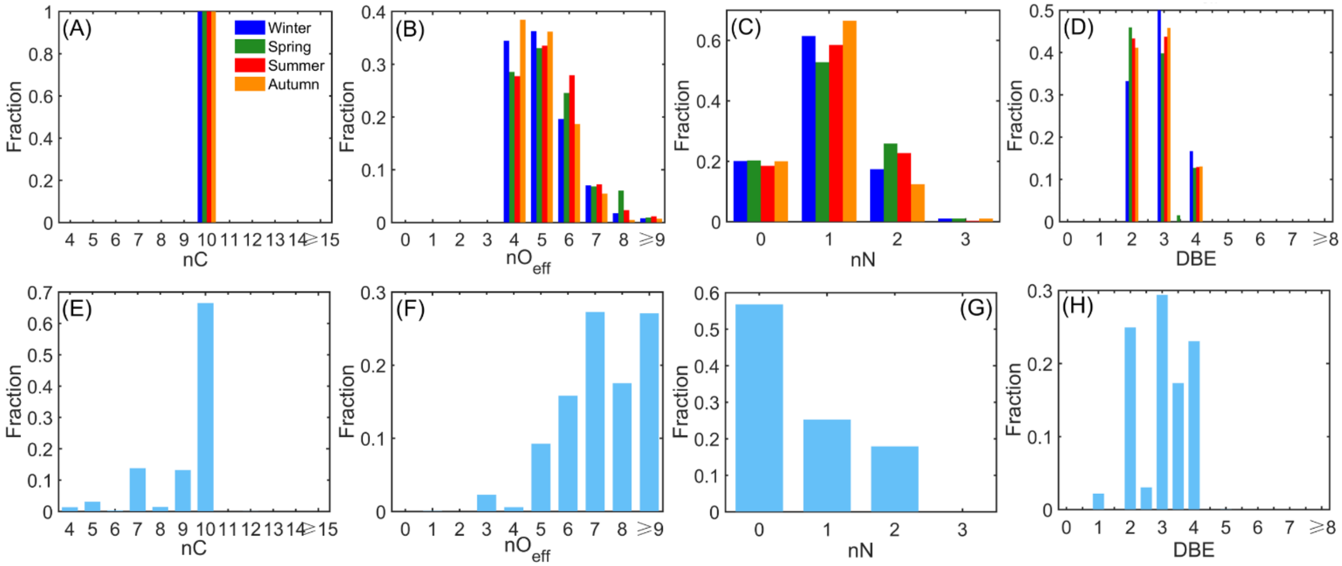


Figure R1. (A) – (D) Distribution of number of carbon (nC), effective oxygen (nO_{eff}), nitrogen (nN), and double bond equivalence (DBE) of monoterpene OOMs observed in this study. Blue, green, red and orange bars denote winter, spring, summer and autumn, respectively. (E) – (F) Distribution of nC, nO_{eff}, nN and DBE of monoterpene OOMs formed by OH radical oxidation together with ozonolyis in previous experiments (Yan et al., 2020). The experiment was conducted under 278 K and the NO_x level was 4.5 ppb.

The binPMF had been performed for the datasets between 26th December 2018 and 26th January 2019. The nC, nO_{eff}, nN and DBE distributions of MT OOMs derived from the workflow in this study and binPMF method are shown in Fig. R2. For nC distribution, binPMF MT OOMs have small fraction of nC = 10 compounds (~ 32 %). Besides, the distributions of nO_{eff} and nN between the two methods also vary a lot. Here are some possible reasons which may cause the above difference. First, as the diurnal variations of MT OOMs have daytime peaks (Fig. R3, corresponding winter period), they should have daytime sources. However, binPMF was only able to resolve a nighttime MT OOM factor. Thus, daytime MT OOMs were not included in the binPMF results. Second, many aromatic OOMs have the same DBE values as MT OOMs. Even though their formation pathway is dominated by OH-initiated oxidation, they may show elevated concentration at night due to the shallow boundary layer. Therefore, it is not avoidable that some aromatic OOMs are dragged into the nighttime MT OOM factor.

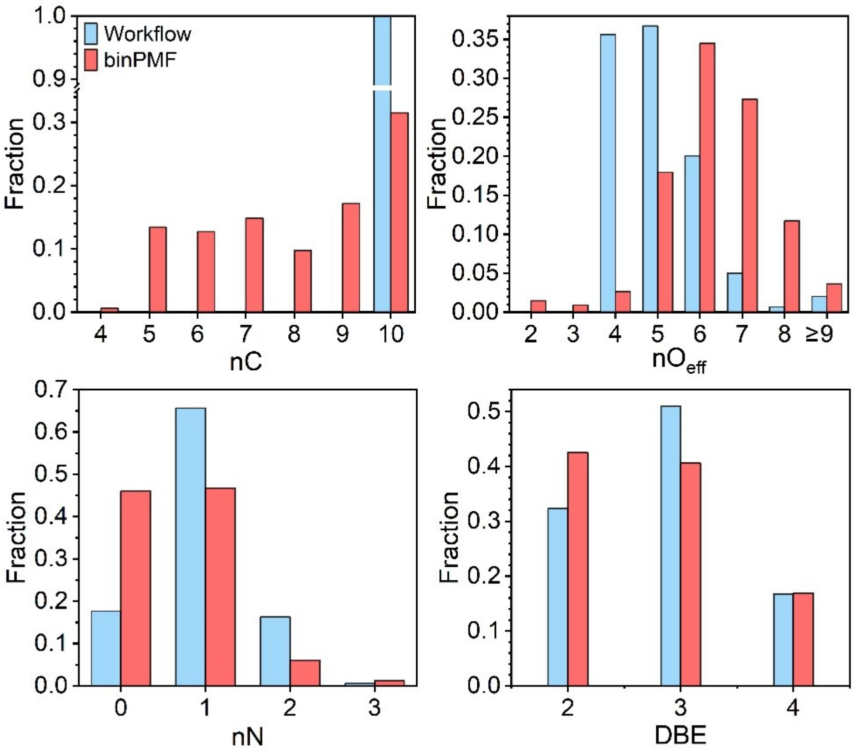


Figure R2. Distribution of number of carbon (nC), effective oxygen (nO_{eff}), nitrogen (nN), and double bond equivalence (DBE) of monoterpene OOMs derived from the workflow in this study and binPMF method in Nie et al. (Nie et al., 2022). The datasets are from 26th December 2018 to 26th January 2019.

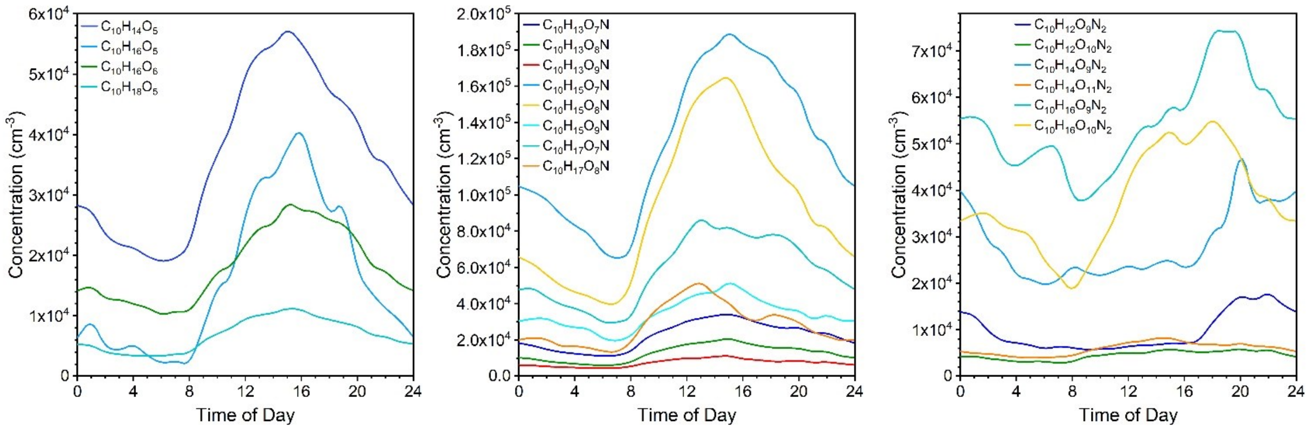


Figure R3. Diurnal variation of representative monoterpene OOMs of days from 26th December 2018 to 26th January 2019.

Based on the above discussion, binPMF method may remain larger uncertainty than chamber experiment. Therefore, we prefer to use the experiment result to evaluate the contribution of nC < 10 MT OOMs. If assuming a 30 % underestimation of MT OOM concentration caused by nC = 10 constrain, the contribution of MT OOMs to total OOM concentration would increase to 6.5, 7.9, 6.8 and 8.0 % in the seasons of winter, spring, summer and autumn, respectively (Table R1).

To further evaluate the change of MT OOM contribution to SOA caused by the nC = 10 constrain, we first analyzed the volatility distributions of observational and experimental MT OOMs (Fig. R4). Since temperatures in different seasons vary a lot and the volatility of OOMs is sensitive to temperature, the comparison is only made between winter observation (274 K) and the experiment (278 K). For observed winter MT OOMs, all of them lie in the ELVOC and LVOC regions. For experimental ones, despite small fraction of MT OOMs fall on ULVOC and SVOC regions, most of them also belong to either ELVOCs or LVOCs. In our study, it is found that the condensation flux and [Condensable OOMs] × Area$_{aero}$ have perfect linear correlation (Fig. S4). Therefore, the change of MT OOM contribution to SOA should be similar to the change of MT OOM concentration. That is, the contribution of MT OOMs to SOA condensational growth might also be underestimated by ~ 30 % if applying the nC = 10 constrain. And after this 30 % correction, the SOA contribution of MT OOMs would increase to 9.9, 14.2, 13.9 and 15.6 % for winter, spring, summer and autumn, respectively (Table R1). Still, this will not change our current conclusion that MT OOMs are not as important as aromatic and aliphatic OOMs in SOA formation.

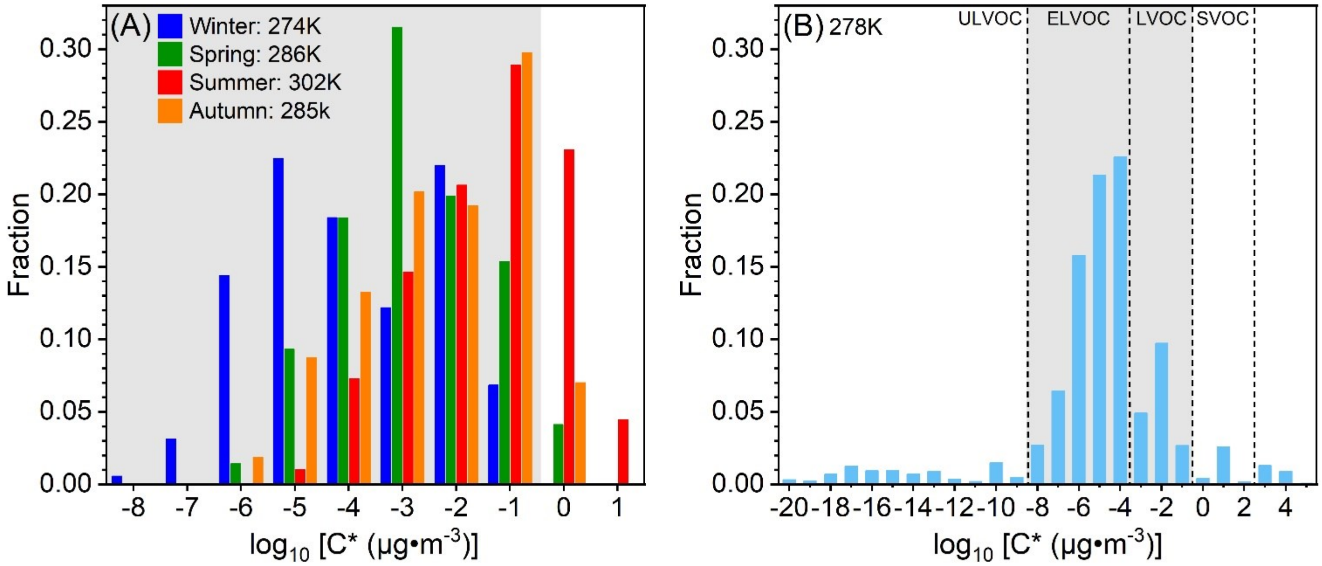


Figure R4. (A) Volatility distribution of monoterpene OOMs observed in this study. Blue, green, red and orange bars denote winter, spring, summer and autumn, respectively. The temperatures in the legend are median values of each season. (B) Volatility distribution of monoterpene OOMs formed by OH radical oxidation together with ozonolyis in previous experiments (Yan et al., 2020). The experiment was conducted under 278 K and the NO$_x$ level was 4.5 ppb. ULVOC, ELVOC, LVOC and SVOC denote ultra-low volatility organic compound, extremely low volatility organic compound, low volatility organic compound, and semi-volatile organic compounds, respectively.

Table R1. The contribution of monoterpene OOMs to total OOM concentration and SOA condensational growth.

	Contribution to OOM Concentration		Contribution to SOA Growth	
	This Study	With 30 % increase	This Study	With 30 % increase
Winter	5.0 %	6.5 %	7.6 %	9.9 %
Spring	6.1 %	7.9 %	10.9 %	14.2 %
Summer	5.2 %	6.8 %	10.7 %	13.9 %
Autumn	6.2 %	8.0 %	12.0 %	15.6 %

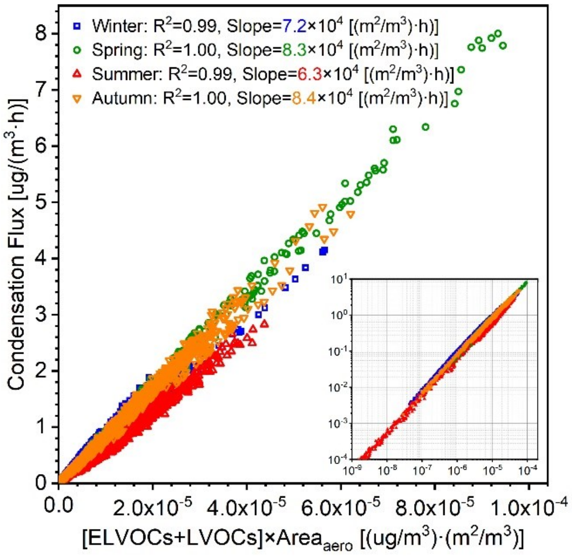
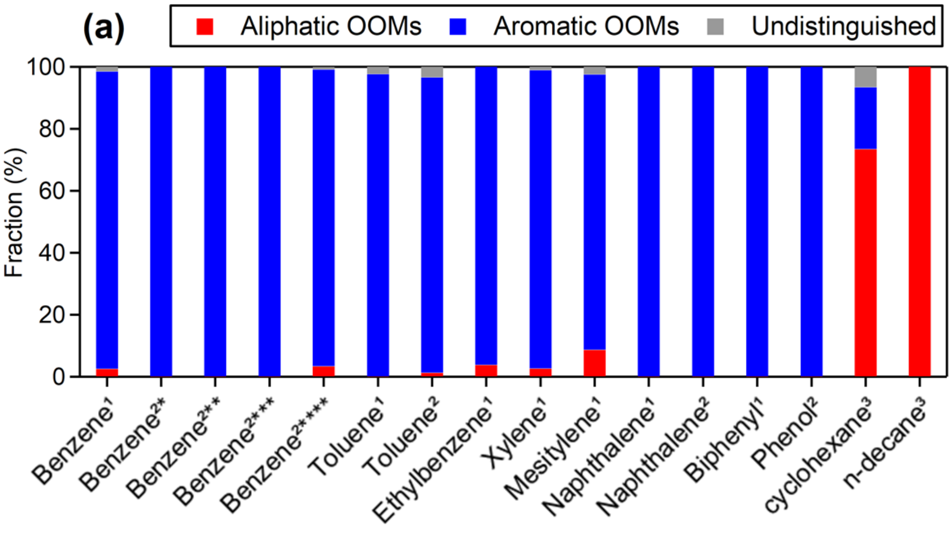


Figure S4. Relationship between OOM condensation flux and concentration of ELVOCs and LVOCs ([ELVOCs+LVOCs]) times aerosol surface area ($\text{Area}_{\text{aero}}$). The figure inserted is in log scale.

4. Line 174: According to the workflow shown in Figure 1, the species with DBE = 2-3 and $nO_{\text{eff}} \geqslant 6$ were considered as aromatic OOMs. However, recent laboratory studies (e.g., Wang et al., Commun Chem, 2021) have shown that alkanes (and oxygenated alkanes) can undergo efficient autoxidation to form highly oxygenated molecules with DBE = 1-3 and $nO_{\text{eff}} > 6$, even at high concentrations of NO_x. The authors should include a discussion about the uncertainty of this assignment in the manuscript.

Response: Thanks a lot for providing this valuable information. Some uncertainties do exist for the classification of aromatic and aliphatic OOMs.

In Nie et al. 2022 (Nie et al., 2022), where the workflow method was first proposed, its performance was tested by known peak lists of aromatic and aliphatic OOMs from laboratory experiments (Molteni et al., 2018;Garmash et al., 2020;Wang et al., 2021), including the one of Wang et al. 2021. The figure below shows the results from Nie et al. 2022. For tested aromatic OOMs, the accuracy is more than 95 %. For aliphatic OOMs, the accuracy is almost 100 % for *n*-decane and ~ 70 % for cyclohexane. Therefore, the workflow should work well for aromatic VOCs and linear alkanes, but indeed have larger uncertainty for cycloalkanes.



Extended Data Figure 5. (a) The accuracy of workflow tested by known OOM peak lists of nitrate-CIMS from laboratory experiments. Number of 1, 2, 3 in panel refer to Molteni et al., 2018, Garmash et al., 2020, and Wang et al., 2021. There are 4 different experiments for the oxidation of benzene: * Exp. in the flow reactor, ** Exp. with low OH/VOC ratio in the JPAC chamber, *** Exp. with high OH/VOC ratio in the JPAC chamber, and **** Exp. effected by NO_x in the JPAC chamber. (Nie et al., 2022)

It should also be noted that the atmospheric conditions, such as VOC concentration and VOC to NO_x ratio, in Wang et al. 2021 and urban Beijing are quite different. In the Helsinki flow reactor experiments, where linear alkanes, cycloalkanes and aliphatic oxygenated compounds were used as precursors, no NO_x was added so that autoxidation was highly favored. But this is different from the case in Beijing where the level of NO_x during the year is always high (Table R5). Besides, the VOC concentration during the experiment was also too high (~ 10 ppm) compared with the values measured in urban Beijing (tens of ppb, Table R2 and Table R3). Therefore, the Helsinki flow reactor experiment is not a good representative of atmospheric oxidation of aliphatic VOCs for this study.

In the Leipzig free-jet flow reactor experiments, *n*-decane, cyclohexane and decalin were chosen as precursors, and their initial concentration were 130, 558 and 74 ppb, respectively. The NO concentration was varied to be 0.17, 3.10, 1.15, 2.27, 3.42, 4.46, 7.00 and 8.93 ppb, respectively. OH radicals were formed through the photolysis of isopropyl with an initial nitrate concentration of 2.7×10^{11} molecules/cm^3, but the exact OH radical concentration was not provided. From those information, the VOC to NO (NO_x) ratio can be obtained and the results are summarized in Table R4. Generally, the level of VOC is much higher than NO, and VOC concentration is around tens to hundreds times of NO. For real atmosphere in Beijing, however, the average NO_x concentration is comparable with average VOC concentration, and the VOC to NO_x ratio (VOC / NO_x) is around 0.36 – 1.20 (Table R5). Compared with the Leipzig free-jet flow reactor experiments, the VOC / NO_x ratios in Beijing atmosphere are much lower, and thus the $RO_2 + NO_x$ reaction likely dominate the fate of RO_2 radicals. That is, the high-level NO_x in our study might terminate the autoxidation more efficiently than in the experiments by Wang et al., leading to comparatively lower nO_{eff}. Therefore, we prefer not to directly take the conclusion from the work of Wang et al. Further oxidation experiments of cycloalkanes and linear alkanes / alkenes / oxygenated VOCs under atmospheric condition of urban Beijing is needed for the determination of aliphatic OOM composition.

Table R2. Daily average of ambient VOC concentrations in urban Beijing from the work of Zhang et al. (Zhang et al., 2017). Time period covers 120 days from April 2014 to January 2015. The concentrations of VOCs have been converted from μg·cm^{-3} to ppb.

Species	Winter	Spring	Summer	Autumn
Total aromatics	6.15	8.78	3.13	7.93
Total alkanes	19.09	10.49	10.21	19.55
Total alkenes	15.58	4.49	5.04	9.04
Acetylene	6.90	1.87	1.71	2.73
Total hydrocarbons	47.72	25.63	20.09	39.25

Table R3. Average ambient VOC concentrations in urban Beijing from the work of Zhang et al. (Zhang et al., 2020). Time period covers 120 days from November 2016 to August 2017. The concentrations of VOCs have been converted from μg·cm^{-3} to ppb.

Species	Winter	Spring	Summer	Autumn
Total aromatics	3.23	2.28	3.16	3.07
Total alkanes	9.66	5.29	6.15	6.31
Total alkenes	3.26	0.99	1.53	2.98
Acetylene	0.22	0.44	0.77	0.59
Total hydrocarbons	16.37	9.0	11.61	12.95

Table R4. Concentrations of NO, *n*-decane, cyclohexane and decalin as well as corresponding VOC to NO ratios in the Leipzig free-jet flow reactor experiments.

NO (ppb)	0.17	1.15	2.27	3.42	4.46	7.0	8.93
n-decane (ppb)				130			
***n*-decane / NO**	**745**	**113**	**57**	**38**	**29**	**19**	**15**
cyclohexane (ppb)				558			
cyclohexane / NO	**3192**	**484**	**246**	**163**	**125**	**83**	**63**
decalin (ppb)				74			
decalin / NO	**426**	**65**	**33**	**22**	**17**	**11**	**8**

Table R5. NO_x, total hydrocarbons (HCs) and hydrocarbon to NO_x ratios (HCs / NO_x) for urban Beijing. The NO_x concentration are the measured ones (mean values) in this study. Hydrocarbon concentrations are taken from literatures (Zhang et al., 2017;Zhang et al., 2020).

	Winter	**Spring**	**Summer**	**Autumn**
NO (ppb)	15.7	6.7	1.6	24.7
NO_2 (ppb)	23.8	18.6	10.9	27.1
NO_x (ppb)	39.9	25.2	12.0	51.6
2017, Hao Zhang et al.				
Total HCs (ppb)	47.72	25.63	20.09	39.25
HCs / NO_x	**1.20**	**1.02**	**1.67**	**0.76**
2020, Lihui Zhang et al.				
Total HCs (ppb)	16.37	9.0	11.61	12.95
HCs / NO_x	**0.41**	**0.36**	**0.97**	**0.25**

To clarify the uncertainty of aliphatic and aromatic OOM assignment, we added Table R4 (Table S17) and Table R5 (Table S18) in the revised supplement and the following discussion in the revised manuscript:

"Due to the complexity of atmosphere, there indeed remain some uncertainties in the workflow. For example, a recent study found that some aliphatic VOCs were able to produce OOMs with DBE values of 2 – 3 and nO_{eff} no smaller than 6 (Wang et al., 2021), which however, are classified as aromatic OOMs in the workflow. Nie et al. (Nie et al., 2022) has tested the performance of the workflow on OOMs from Wang et al. 2021. Results show that the accuracy is almost 100 % for OOMs from *n*-decane and ~ 75 % for OOMs from cyclohexane (Nie et al., 2022). Thus, the workflow is generally reliable in classifying aliphatic OOMs. In addition, the VOC to NO_x ratios in the experiments of Wang et al. (Table S17) is much higher than in urban Beijing (Table S18). This high-level NO_x might suppress the autoxidation as the RO_2 + NO termination reaction likely dominates the fate of RO_2 radicals, leading to comparatively lower nO_{eff}. In this way, aliphatic OOMs is difficult to reach nO_{eff} of 6." (Line 171 – 179, Page 6)

5. Line 219-221 and 245-248: What was the influence of the seasonal variation of the NO_x level on the seasonality of the oxygen content of OOMs?

Response: The seasonality of NO_x causes changes in both the atmospheric oxidation capacity and the RO_2 termination reactions, both of which influence the oxygen content of OOMs. We then plotted the average number of effective oxygen ($nO_{eff\text{-}ave}$) vs. NO_x mixing ratio for four seasons in Fig. R5.

It can be found that $nO_{eff\text{-}ave}$ shows a general decreasing trend with the increase of NO_x. This decreasing trend is consistent with our understanding that high-level NO_x is prone to terminate RO_2 autoxidation. In addition, at the same NO_x level, $nO_{eff\text{-}ave}$ is the highest in summer, followed by spring, and decreases to the lowest in winter and autumn. Therefore, we can conclude that in urban Beijing, high oxidation capacity and low NO_x levels favor the increase of OOM oxygen content.

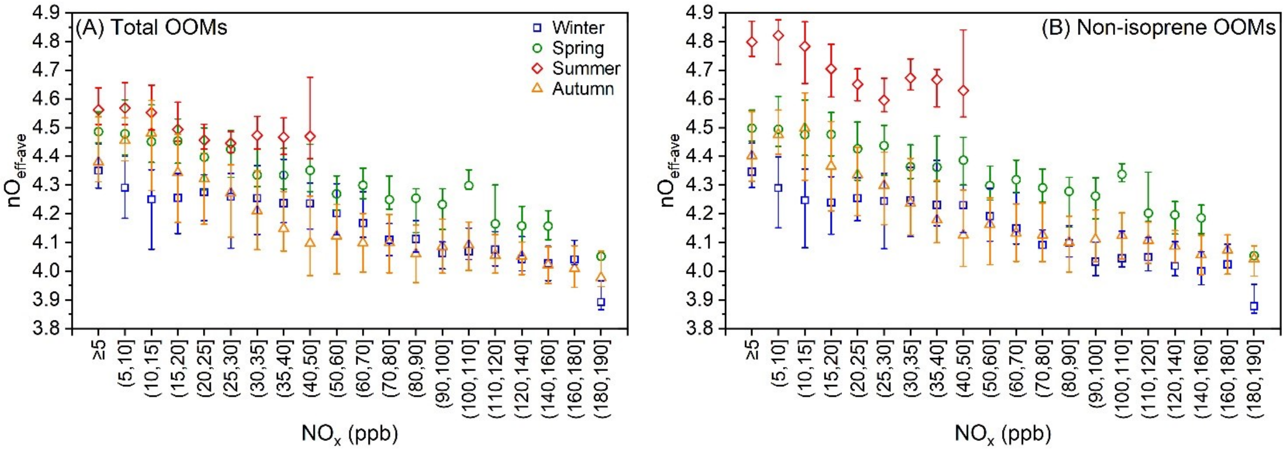


Figure R5. Concentration weighted average number of effective oxygen ($nO_{eff-ave}$) vs. NO_x mixing ratio in four seasons for (A) total OOMs, and (B) non-isoprene OOMs. The markers are median values, and the bottom and up ranges of the error bars denote 25th and 75th percentiles respectively.

6. Line 272-277: The authors concluded that the formation of epoxide group during isoprene oxidation was not favored based on their observations that most of isoprene OOMs had 0 or 1 DBE. This conclusion should be made with caution for two reasons: First, nitrate-CIMS is generally more sensitive to organic species containing -OOH and -OH groups than to epoxides and aldehydes/ketones, which might make isoprene OOMs with 0 or 1 DBE as the most abundantly detected species; Second, the epoxide species formed from isoprene photooxidation might undergo fast heterogeneous ring-opening reactions to form products with 0 to 1 DBE, resulting in low gas-phase epoxide concentrations.

Response: Thank you very much for your valuable comments. The above deduction of isoprene OOM formation pathways based on the only measurement of nitrate CIMS is not so rigorous. And we modified the discussion as follows:

"This indicates that hydroxyl or hydroperoxyl are the major functional groups of these products, whereas products with higher DBE values are not prominent. It could mean that compounds containing carbonyl or epoxide groups are either not efficiently formed under the urban environment, or fast lost via heterogeneous reactions (Riedel et al., 2015;Zhang et al., 2022). Meanwhile, the instrumental detection bias, i.e., nitrate CIMS is less sensitive to carbonyl and epoxide groups, cannot be excluded. Therefore, further combination of CIMS instruments with different chemical ionization methods are highly desirable in the future." (Line 279 – 285, Page 10 – 11)

7. Line 405-406: The two sentences here seem to convey the same information, that is, RO_2 termination reactions with NO_x are more important for aliphatic species than for aromatics. Did the authors mean to say in the second sentence that the branching ratio of the aliphatic RO_2+NO_x to form CHON species is higher than that of the aromatics?

Response: Yes. That is the message we expect to convey, but it seems that the current expression is not very clear. So we modified the description in the revised manuscript as follows:

"For nitrogen content, CHO aliphatic OOMs only take a small fraction of 8-11 %, implying that NO_x termination may dominate the formation of aliphatic close-shell molecules. Meanwhile, this CHO OOM fraction of aliphatic OOMs is much smaller than that of aromatic OOMs (42-52 %), suggesting that the branching ratio of aliphatic RO_2 - NO_x reaction forming $CHON_x$ species is higher than that of the aromatic one." (Line 410 – 414, Page 17)

8. Line 408-411: It is not clear how the correlation between $CHON_2$ species and $PM_{2.5}$ could lead to the conclusion that $CHON_2$ species or their precursor VOCs originated from long-distance transport. Please clarify this.

Response: In winter Beijing, the regional transportation of air masses from the south and southeast areas is a large source of $PM_{2.5}$ (Wang et al., 2015;Chen et al., 2021;Chen et al., 2022;Tan et al., 2022). As shown in Fig. S14, $PM_{2.5}$ seldom had diurnal variations, rather, it could accumulate for a couple of days, indicating that it not only can be formed locally, but also can be transported from other regions. Thus, the $PM_{2.5}$ in winter Beijing is correlated with regional transportation, although local production of $PM_{2.5}$ cannot be entirely ruled out. In that case, the good correlation between $CHON_2$ species and $PM_{2.5}$ suggests that those compounds might also have regional sources, i.e., they could either be transported directly, or generated within the polluted air masses.

To clarify whether $C_{6-14}H_{12-28}O_7N_2$ could be directly transported, the volatilities of them had been calculated and summarized in Table S12. $C_{6-10}H_{12-20}O_7N_2$ are relatively volatile and are classified as semi-volatile organic compounds, thus they could originate from long-distance transport. Whereas $C_{11-14}H_{22-28}O_7N_2$ are less volatile and lie in the range of low-volatility organic compounds, hence, they can hardly be transported and are more likely produced during the air mass transportation.

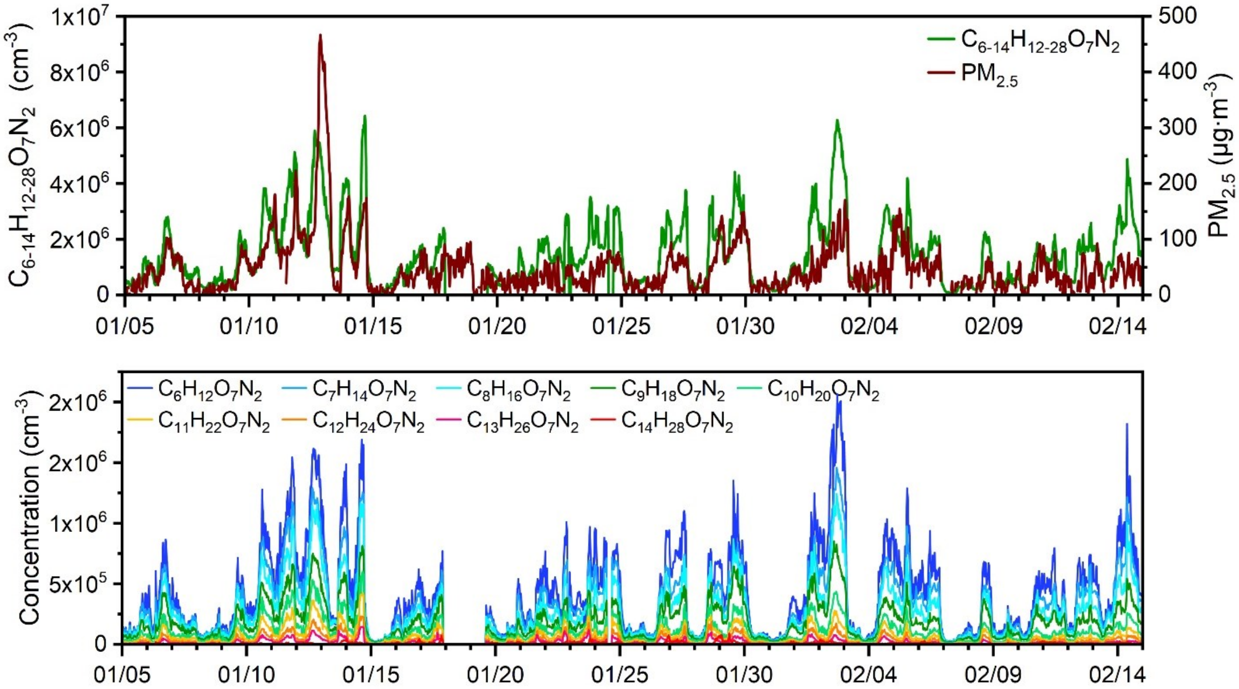


Figure S14. Time variation of $C_{6-14}H_{12-28}O_7N_2$ OOMs and $PM_{2.5}$ in winter.

Table S12. The median volatility ($\log_{10}$ [C^* (μg·cm$_{-3}$)]) of $C_{6-14}H_{12-28}O_7N_2$ compounds during the winter period (5th January to 14th February, 2019).

Compound	$\log_{10}$ [C^*(μg·cm^{-3})]	Volatility Type
$C_6H_{12}O_7N_2$	1.47	SVOCs
$C_7H_{14}O_7N_2$	1.02	
$C_8H_{16}O_7N_2$	0.55	
$C_9H_{18}O_7N_2$	0.07	
$C_{10}H_{20}O_7N_2$	-0.41	
$C_{11}H_{22}O_7N_2$	-0.90	LVOCs
$C_{12}H_{24}O_7N_2$	-1.39	
$C_{13}H_{26}O_7N_2$	-1.88	
$C_{14}H_{28}O_7N_2$	-2.38	

To make the discussion on the transported sources of $C_{6-14}H_{12-28}O_7N_2$ more clear, we added part of the above explanation in the revised manuscript as follows:

"In winter Beijing, the regional transportation of air masses from the south and southeast areas is a large source of $PM_{2.5}$ (Wang et al., 2015;Chen et al., 2021;Chen et al., 2022;Tan et al., 2022), therefore, the good correlation between $CHON_2$ species and $PM_{2.5}$ suggests that those compounds might also have regional sources. Table S12 shows that $C_{6-10}H_{12-20}O_7N_2$ are relatively volatile and are classified as semi-volatile organic compounds, thus they could originate from long-distance transport." (Line 417 – 421, Page 17)

"Whereas for $C_{11-14}H_{22-28}O_7N_2$, they are less volatile and lie in the range of low-volatility organic compounds, hence, they can hardly be transported and are more likely produced during the air mass transportation.". (Line 422 – 424, Page 17)

9. Line 448-449: The authors stated that the condensation of isoprene OOMs had little contribution to SOA growth regardless of the season. However, Figure 11 shows that isoprene OOMs had a contribution of up to 5% to SOA, which is obviously non-negligible. Therefore, this statement needs to be rephrased.

Response: Thanks you very much for your comments.

Fig. 11 really tells us that the pure condensation of IP OOMs has small contribution to SOA growth (2.7 – 5.0 %). But the description in Line 448 – 449 in the original manuscript (Line 461– 462 in the revised manuscript) is written before the aerosol growth model was performed, so it is a hypothesis based on the fraction of IP OOMs in ELVOCs, LVOCs and SVOCs in Fig. 10 (B). Even so, we agreed that the description is kind of misleading, and we modified this sentence in the revised manuscript as follows:

"… Consequently, it is likely that the pure condensation of IP OOMs has a minor contribution to SOA growth regardless of the season." (Line 460 – 461, Page 19)

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