

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2022-181

Anonymous Referee #2

Referee comment on "Seasonal variation in oxygenated organic molecules in urban Beijing and their contribution to secondary organic aerosol" by Yishuo Guo et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-181-RC2>, 2022

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.

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.

Line 119-121: Since OOMs can be detected either as a nitrate ion cluster (i.e., $[M+NO_3^-]$ or $[M+HNO_3\bullet NO_3^-]$) or as a deprotonated ion by nitrate-CIMS, additional information as to how the product ions $[CHON+NO_3^-]$ vs. $[CHO+HNO_3\bullet NO_3^-]$ and $[CHON^-]$ vs. $[CHO\bullet NO_3^-]$ were differentiated in this study should be provided in the manuscript.

Line 143-144: The selection of monoterpene OOMs excluded $< C_{10}$ 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 C_{10} compounds vs. $< C_{10}$ compounds would be obtained in the monoterpene OOM factor?

Line 174: According to the workflow shown in Figure 1, the species with $DBE = 2-3$ and $O_{eff} \geq 6$ were considered as aromatics 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 $O_{eff} > 6$, even at high concentrations of NO_x . The authors should include a discussion about the uncertainty of this assignment in the manuscript.

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?

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.

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?

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.

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.