Response to reviewer comments for manuscript ‘Influence of anthropogenic emissions on the composition of highly oxygenated organic molecules in Helsinki: a street canyon and urban background station comparison’

We thank the reviewers for their valuable comments and suggestions that have helped to improve our manuscript. Here, we present answers to each of their comments in blue. Reviewers’ comments are quoted as black text, while the text from the manuscript is marked with grey italics and the changes in the text are marked in red italics.

Reviewer 1

Okuljar et al. present measurements of HOMs and other condensable vapors from measurements at two sites in 1 km distance from another in Helsinki. The manuscript is well written and uses state-of-the-art scientific methods.

Given that there is still a lot that the atmospheric chemistry community does not know about the formation of HOMs/SOA, these observations in a suburban area provide an important addition to the literature. What I find the most interesting and striking point of this study is the strong difference between the composition and diurnal behavior of observed compounds during the same time, although the two sites are spatially so close to each other. This points to an important lesson for the atmospheric chemistry community regarding the (non-)representativeness of a single observation site for a whole metropolitan area, and generally to a very localized inhomogeneity of emissions, reaction processes and products. Therefore, I wish this point would be brought across more strongly, perhaps graphically. Thus see my comments below.

We thank the reviewer for all their useful input. Concerning the emphasis on inhomogeneities, we now added the following sentence to the end of the abstract to make this point clearer:

*This further suggests that studies should be careful when extrapolating single-point measurements in an urban setting to be representative for district or city scales.*

I recommend this article for publication in ACP after the following comments have been addressed:

**General comments:**

1. Did you see any evidence for cooking emissions contributing to any of the observed PMF factors? E.g. Zotter et al. (2014, https://doi.org/10.1002/2013JD021114, 2014) mention that at least 25% of the non-fossil SOA is from cooking.

We do not observe cooking emissions contributing to PMF factors. Although, cooking emission can have important contribution to non-fossil SOA (Zotter et al., 2014), previous studies in Helsinki have not identified any factor of SOA associated with cooking (Timonen et al., 2013). It is likely due to smaller population density and sparser restaurant distribution in measurement area of Helsinki than in Los Angeles basin. Since the cooking contribution was not observed for particles, it is also not surprising that we do not expect to find its contribution to such signatures in the condensable vapors measured in this study.

The contribution of emissions from a near-by coffee roastery to SOA has previously been observed at the urban background station (Timonen et al., 2013), and we tried to investigate whether we can see any contribution to condensable vapors. We did not find any factor influenced by the coffee
roastery but were also not able to detect any contribution to SOA during our campaign (based on AMS measurement from corresponding time). The absence of coffee roastery factor in our data is likely due to the very low contribution (1%) and high variance of this factor (Timonen et al., 2013).

2. You report that only few PMF factors correlated with each other between the two sites. I wonder if some of the reason may be that the air transported from one place to the other by prevailing winds takes some time, so that the correlation would be shifted in time, and would require a method like time-warping to find correlations? Also, was the PMF conducted separately for the time where there is overlapping data between the two sites? I wonder if there could be a bias if the latter is not the case, since both sites were measured for a longer time separately than simultaneously.

We agree that there could be a time shift between factors which we are not accounting for, thus we had calculated cross-correlation for our factors. The Pearson’s coefficient increased only by a few hundredths while using cross-correlations, which is a negligible difference, and thus we have not discussed it in the manuscript. Time warping methods could be suitable to account for differences in the speed of processes influencing condensable vapor formation and transport, but we find time-warping methods risky to use for calculating correlations as it may greatly overestimate them. We tried dynamic-time warping with the time constrained, and it improves correlations of factors that should not correlate with each other as they originate from different sources on different stations (for example Fig. R1). We think that dynamic time warping should be only used when we are sure that measured condensable vapors at both sites were formed from VOCs emitted from the same source. Unfortunately, we cannot make this assumption for our data.

Another aspect to keep in mind is that condensable vapors are very short-lived species; for average condensation sink equal to 0.005 s\(^{-1}\) (Okuljar et al., 2021) the estimated lifetime of HOM is no longer than 2 min (Bianchi et al., 2019). With a 900 m distance between the stations and median wind speed of approximately 3 m/s, during most measurement time we do not expect to observe exactly the same molecules at both stations. The similarities of condensable vapors composition come rather from the same processes of HOM formation. Additionally, based on previous study on the dispersion mechanisms for particles and trace gases from a highway in Helsinki (Pirjola et al., 2006), we can estimate that compounds that could survive the transportation, would most likely have too small concentration to detect them on the downwind station. Lastly, we would like to point out that the time resolution of the data used for PMF is 30 minutes, thus any species transported with wind should largely end up in the same data point. Since we do not expect to be able to measure the same molecules at both stations, we did not run the PMF for the time when we had simultaneous measurement but rather focused on describing each station separately.

While looking at correlations between PMF factors, we noticed that one and half day of data was removed from the correlation analysis by accident. After adding the missing data, the Pearson coefficients for correlations between PMF factors did not change or changed negligibly. Nevertheless, the Pearson coefficient for correlation between factor SC2-1 and UB1-6 decreased from 0.7 to 0.66, thus we removed the time-series of these factors from Fig 5. We also applied changes to Fig. S12.
Inspired by this question, we decided to add an estimation of the ceiling correlation, the highest correlation expected between stations calculated from sulfuric acid time-series, for times series of condensable vapors between stations:

Tables 1 and S3 present the most plausible interpretation of selected and not selected factors, respectively. For each factor, we propose VOC precursors, oxidants, and terminators, which were most likely to influence the formation of species in this factor. We also specify an hour of the day when factor’s signal reached its maximum as well as the contribution of this factor to the total signal both within its own m/Q sub-range and within the full analyzed range (200-650 Th). See Table 1 caption for a more detailed description of how to read the table. The findings and implications are discussed below. While discussing time series correlations between factors from both stations, it is important to keep in mind that they cannot be ideal. We estimated that the highest correlation between stations for condensable vapors is approx. 0.88 which is a correlation between concentrations of a compound that is mostly produced in the same pathway on both sites: sulfuric acid (SA) (Fig. S15).
3. How deep is the “street canyon”, i.e., how high are the surrounding buildings? If they are high: Do you see any evidence that the street canyon site has more stagnant air, i.e., that emissions spend more time there so that local emissions reach higher oxidation states, vs. a more well-ventilated suburban site, where observed HOMs may stem from longer range transport? I think the discussion lacks a little bit of consideration that local emissions and reactants may not be the only reason for the differences observed between the two sites. Please discuss meteorology/transport.

We added a short description of the street canyon and a paragraph discussing pollution transport at the stations:

Station for Measuring Ecosystem-Atmosphere Relations (SMEAR III, 60°12′10.4″ N, 24°57′40.2″ E) (Fig. 1). The HSY supersite is located at a street canyon, less than a meter from Mäkelänkatu street (around 28 000 vehicles/weekday) (Kuuluvainen et al., 2018). The street canyon is 42 m wide and the height of buildings on both sides of the supersite is 19 and 16 m, leading to the average height-to-width ratio of 0.45 (Järvi et al., 2023). It contains a pavement and three lines of road for both directions separated by the two tram lines and trees.

The detailed meteorological description of the transport of pollutants at both stations with the emphasis on the mechanism affecting this transport at the street canyon is presented by Järvi et al. (2023). In summer the atmosphere is very stable during nighttime and very unstable during daytime at the urban background station. The meteorological conditions at the urban background station (Fig. 2) resemble the one described by Järvi et al. (2023) for summer, which suggests limited vertical mixing of the atmosphere during nighttime and very well-mixed lower atmosphere during daytime during our measurement. At both stations, during the warm period the mechanical and thermal mixing is stronger than during cold periods resulting in conditions more favorable for pollution dispersion (Järvi et al., 2023). At the street canyon, not only mean wind but also the turbulent mixing is important for the transport of pollutants. This may suggest that even though the air is not stagnant, the pollutants are not efficiently transported from the street canyon.

4. I suggest adding a graphical depiction of the amount of overlap between the observed signals between the two sites since this is such an important message. Maybe a pie chart showing the fraction of total ions (sum of both sites) only observed at SC, fraction only observed at UB, fraction observed at both sites? E.g. similar to Fig. 2 of https://doi.org/10.1021/acs.est.2c07260.

We agree that it would be beneficial for the paper to make a visual comparison between stations. Nevertheless, we cannot think of a way to present it without the risk of being misleading. We were not able to identify all peaks in our mass spectra, sometimes due to low signals, sometimes due to overlapping ions. As such, the choice of whether a given ion was in fact detected or not becomes ambiguous for a large number of peaks. The current comparison in the paper reflects all relations between the two stations that we were confident to interpret from our data. The inability of comparing the results from both stations in a broader sense is one of the reasons why we recommend a follow-up study that uses a mass spectrometer with a higher mass resolution than the one used in this study.

Specific comments:

1.44: apart from the listed sources, I suggest to mention cooking since it is also a strong source of anthropogenic VOCs/condensable vapors.
We added cooking as a source of VOC:

The sources of anthropogenic emissions consist of traffic, cooking, industrial processes and production of customer goods, and volatile chemical products (VCP) (Li et al., 2022; Koppmann, 2007; Watson et al., 2001).

Fig. 1: It would be helpful to add a wind rose to see which of the two stations is up-/downwind of each other.

This is a good suggestion and we think that a wind rose could also help understanding the atmospheric conditions at our stations in general, thus we added it to the Fig. 2:

Figure 2 presents diurnal variations of measured variables that can influence HOM formation pathways: global radiation, ambient temperature (T), and concentrations of O₃, NO, and NO₂ as well as the wind direction measured during this campaign.

Figure 2. Diurnal variations of (a,b) global radiation and ambient temperature, and (d,e) NO, NO₂, and O₃ concentrations at the street canyon (left) and urban background station (middle). The median diurnal variations are shown as solid lines with markers; 25th to 75th percentile ranges are presented as shaded areas. Time is local. The right panel (c) shows a wind rose for the overlapping time at both stations as well as outline of wind rose for the period when data was collected from the street canyon (SC, dark red) and the urban background station (UB, dark blue). Arrow in panel (c) shows the direction of the urban background station (UB) in relation to the street canyon (SC). Presented data contain both workdays and weekends.

Diurnal variation of global radiation is similar between the two stations (Figure 2 a,b), though with slightly more cloudy periods at the street canyon. Global radiation initiates photolysis reactions and, as a result, enhances the formation of OH and O₃ as well as the decomposition of NO₃. During the overlapping time of measurements, the urban background station was more likely to be the downwind station, however the wind was mostly coming from North (Fig. 2c), meaning that neither station would receive emissions from the other.
Sect. 2.5 regarding transmission: I assume the signals are corrected for transmission/normalized to transmission - I think this should be mentioned for clarity that the signal strength is not impacted by the transmission issue between the two instruments.

Unfortunately, we were not able to correct our measurement for transmissions, hence we are limited in our interpretation of data and cannot compare concentrations between stations. We added information about it to the article:

Transmission is a result of voltage settings in CI-APi-TOF, which are optimized for each instrument separately. **We could not correct our data for transmission.**

Fig. 2: I think it would be helpful to add two panels showing the same data just for the time when there were simultaneous measurements at both sites. Otherwise, it is impossible to see how comparable the conditions (temperature etc.) are between both sites during this relevant time.

In order to not overcrowd Fig. 2, we added a figure comparing meteorological variables and trace gases for overlapping time of measurement as Fig. S2 to SI:

![Figure S2](image)

**Figure S2.** Diurnal variations of (a,b) global radiation and ambient temperature, and (c,d) NO, NO$_2$, and O$_3$ concentrations at the street canyon (left) and urban background station (middle) for the overlapping time of measurements (11 May 2018 13:00:00 – 23 May 2018 15:30:00). The right panels represent the difference between (c) ambient temperature and (f) NO, NO$_2$, and O$_3$ concentrations measured at the street canyon and the urban background station. Presented data contain both workdays and weekends. The median diurnal variations are shown as solid lines with markers; 25th to 75th percentile ranges are presented as shaded areas. Time is local.

We also refer to it in the manuscript:

As mentioned earlier, the measurement periods overlapped but were not identical between the two stations. Therefore, differences in campaign averages between sites are partly driven by differences in location and partly by differences in time. **The difference in methodological parameters (ambient**
temperature, global radiation, wind direction) are driven mostly by changes in the measurement period (Fig. 2, S2), while the trace gases (NO, NO₂, O₃) vary largely also during overlapping times of measurements (11 May 2018 – 24 May 2018) (Fig. S2).

1.313: Since you mention monoterpene monomer factors with different diel variabilities – was there any diel variability in the monoterpene composition measured with sorbent tubes that could help to find out which monomer stems from which monoterpene or which part of the monoterpenes is anthropogenic/biogenic?

For a given site, we have not observed any correlation between the time-series of VOCs and condensable vapors, which we expect is greatly due to the large effect of oxidative conditions on the products formed from VOC oxidation. We have also looked at diel behaviors of VOCs; however, the time resolution of VOCs measurement is 4 hours, thus there is not much variability between diurnal trends of the different VOCs. Almost all of the main BVOCs measured at street canyon reach the highest concentrations in the morning (4 or 8 a.m.) (Fig. R2). There is therefore not enough variability to make any clear separation between different monoterpenes, suggesting also that they were mostly from biogenic sources based on their diurnal behaviors.

Figure R2. Diurnal variations of main BVOCs measured at street canyon. The median diurnal variations are shown as solid lines with markers; 25th to 75th percentile ranges are presented as shaded areas. Time is local.
1.316-369: I think it would be interesting to mention the most important compounds/chemical formulas observed in each factor as you do for some, but not all that factors you describe here.

We added chemical formulas of key compounds for all factors that had not had description of their chemical composition. All key compounds are also listed in Table S2.

1.495: “This is clearly different from Helsinki” – I am not sure you can make that statement in the way you are making it, since you have only a few weeks of observations in one season and for China you are mentioning variability between seasons. It would be more appropriate to compare concrete cases with concrete numbers (which percentage of condensable vapors in Helsinki is biogenic, vs. which percentage is biogenic in the same season in a Chinese city?).

We agree that we should make this comparison for the same season thus we added information about contribution of AVOC to condensable vapors during spring in Beijing. Since we were not able to identify all compounds in our mass spectrum, we cannot calculate the exact percentage of condensable vapors originating from AVOC. Nevertheless, the higher abundancy of BVOC-derived condensable vapors observed in our data agrees with the estimation that the majority of oxidation products come from BVOC at the street canyon in Helsinki (Saarikoski et al., 2023). Hence, even though we are not able to identify all peaks, and thus calculate fraction of compounds originating from AVOC, we remain confident in the conclusion.

However, depending on the time of the year, the main precursors for condensable vapors in cities in China are either AVOCs or a mix of AVOCs and BVOCs (Guo et al., 2022b; Liu et al., 2021; Nie et al., 2022). During spring, 77% of all measured condensable vapors originate from AVOC in Beijing (Guo et al., 2022b). This is different compared to Helsinki, where BVOC-derived vapors were more abundant.

Technical comments:

1.145: “only we can narrow it usage” – this phrase is unclear to me.

We clarified this sentence:

Therefore, most of our analysis is based on unit mass resolution (UMR) data and **we apply HR analysis at times where PMF indicated low interference to this factor as described in section 2.4.**

1.195: missing “the” before “identified”

Corrected.

Fig. 3 caption: It was not initially clear to me that “SC-1” stands for street canyon, factor 1. Please make the meaning of the numbering clearer in the caption.

We added explanation to every figure caption containing short names for factors: ‘SC’ or ‘UB’.

1.412-413: This sentence is not clear to me, it seems as if both grammatically and content-wise something is mixed up in there?

We clarified it:
This suggests that the local emissions from traffic at these sites did not oxidize fast enough, and with high enough yields of detectable compounds, to considerably contribute to our measured signals. This is in line with conclusions presented by Brean et al. (2019) and Saarikoski et al. (2023).

1.482: lower resemblance than what?

We modified that sentence:

Still, a comparison of our results with other studies done in rural environments (Massoli et al., 2018; Kürten et al., 2016) showed clearly lower resemblance between MT-derived dimers than one described in preceding sentences, which is likely a result of different biome types in their studies (isoprene-dominated south east US and rural agricultural site in Germany respectively) compared the ones conducted in Finland.

1.490: “influenced” should be “influence”.

Corrected.

1.507: “particular” should be “particulate”.

Corrected.

Reviewer 2

General comment:

The authors present an interesting data set, focusing on the factors governing HOM/SOA formation in biogenically influenced urban areas. In general, the manuscript is well structured, and the authors clearly communicate their approach and goals, as well as the limits of their analysis. Therefore, I would recommend this manuscript for publication with the minor re-works and additions outlined below.

Specific comments:

- As the transmission is one differing factor between the two employed CIMS instruments, I suggest to include details about the instrument transmission curve determination as well as the transmission curves themselves in the supplement.

  We refer to our response to Reviewer 1 concerning the transmission.

- One aspect that intrigued me and that I would like to have seen discussed further is the possibility of NO3 oxidation with subsequent termination by NO (see lines 347-352). Was this observed before or are there any model calculations estimating the likelihood?

  Condensable vapors formed through the monoterpene oxidation with NO3 and subsequent termination by NO were previously observed in chamber experiments on NOx influenced VOC oxidation (Nie et al., 2023; Yan et al., 2020). Furthermore, Nie et al. (2023, Supplementary, Fig. 4) linked ‘NO3 + NO’ factor identified from the chamber experiment to a factor measured previously in Hyytiälä, Finland. Guo et al. (2022) suggested this mechanism as a possible explanation for the high nitrogen content in the condensable vapors during nighttime in Beijing. However, in that work
the NO$_3$ oxidation was not considered during daytime due to the photolysis of NO$_3$. Saarakoski et al. (2023) showed that at the street canyon in Helsinki NO$_3$ is expected to not only have slightly elevated concentration during noon but also react with monoterpenes.

We added a short explanation of this mechanism to the manuscript:

Range 2 contains various daytime and nighttime factors (Fig. 4). Factor UB2-1 reaches the highest concentrations at 5 am. and 10 pm., which corresponds to the time of sunrise and sunset during our measurement period. As this factor consists of MT-derived ONCs, possibly with at least two N-atoms (C$_{9}$H$_{14}$O$_{9}$,N$_{2}$ or C$_{10}$H$_{16}$O$_{9}$,N$_{2}$ and C$_{10}$H$_{17}$O$_{12}$N$_{3}$), we can speculate that they are formed from NO$_3$ oxidation of MT and terminated by NO. Chamber experiments have shown that formation of condensable vapors through NO$_3$ oxidation and NO termination is a possible mechanism during NO$_x$-influenced oxidation of monoterpenes (Yan et al., 2020; Nie et al., 2023). It is typically assumed that NO$_3$ and NO would not co-exist in the atmosphere. However, in urban areas NO concentration is not negligible during the night and this pathway was previously suggested as possible mechanism of ONC formation in Beijing (Guo et al., 2022). Simultaneous presence of NO$_3$ and NO when photolysis is just high enough to form NO but not to fully deplete NO$_3$ is a plausible explanation for the diurnal pattern of UB2-1.

-In Section 3.3 the implications for air quality are discussed, and though the section gives a good quick overview over the general present understanding of SOA toxicity if it is intended as it’s own section I would like to see the actual results from this study included more. I.e. how could the major contribution of ONC affect toxicity or how does the change in SOA yields due to NOx termination impact the exposition to SOA?

We agree that it would be very interesting to be able to quantify how much the pathways discussed in our study influence toxicity and the impact of exposure to SOA. Nevertheless, we can only provide qualitative insights to the impact on the condensable vapors, and are therefore not comfortable in speculating on these impacts.

-Line 151: What reagent ions were used for normalization? (NO3- / HNO3*NO3- / (HNO3)2*NO3-? Inclusion of water clusters of NO3-?)

Information about reagent ions used for normalization was added to paper:

Here, we discuss quantitative changes in condensable vapors based on their measured signal in counts per second (cps) normalized by the cps of the reagent ions (NO$_3$-, HNO$_3$NO$_3$-, and (HNO$_3$)$_2$NO$_3$-), using the unit ncps (normalized cps).

-I would cut back on the description of what will be shown in Section 3.2. Lines 278-285 give information that is partially repeated later and I think the section would profit from shortening this description.

We removed this paragraph and added the most important information to the next one:

In this subsection, we summarize the key characteristics give an interpretation of factors. The more detail description of the PMF analysis can be found in the supplementary information (SI) (S2. PMF inputs and validation, S4. Factor interpretation). Only “selected” factors are described here, while characteristics of “not selected” factors are presented and described in the SI (Sect. S4, Fig. S6-7, Table S3).
-For Fig. 3 and 4 I recommend shifting the full timeseries to the supplement. In my opinion the diurnal trend plots give a much better impression of the important influences in one PMF factor. Furthermore, the full timeseries are not extensively discussed in the manuscript itself.

The time-series from Fig. 3-4 were moved to the SI.

-On a minor note, I would also be interested what the gaps in the timeseries of the factors mean, since sometimes it seems that days with missing data (for example Fig. 4 May 14) just linearly interpolated over the missing period. Furthermore, I would mention the scaling of the temperature axis as the non-linear scaling can be a bit misleading.

Thank you for noticing it. We do not use linear interpolation for missing data. The straight line in our timeseries was an artifact of plotting time series with missing data. We removed this artifact in the new figures S3-4 and S9-10.

-For Table 1: I would be interested to understand why the importance of species was judged by different methods (factor time series, or factor mass spectrum or both) and which criteria were used to determine the chosen method.

We used all information that we deemed useful, and this varied between factors. In some the temporal trends were clear, but species identification was limited, or vice versa. We have described determination of each factor potential formation pathway in the SI. Description of factors contains detailed information about their time evolution and mass spectrum, i.e. the information on which of these were important and used to determine formation reagents.

**Technical corrections:**

-Lines 65-67: “Additionally, NO2 can terminate oxidation chain in reaction leading in most cases, which decompose back to substrates (Atkinson and Arey, 2003).“ This sentence needs to be reworked.

This sentence was removed as the meaning of this sentence was conveyed in different part of this paragraph:

[… while RO2 termination by NO2 can form relatively unstable peroxy nitrates.

-Line 72: “attach” instead of “attached”

Corrected.

-Line 229: remove “of”

Corrected.

-Line 484: include to in “compared to the”

Corrected.

-Line 490: “influence” instead of “influenced”

Corrected.
References:


