Dear reviewer 1,

Thank you for the constructive feedback and helpful comments. We think that the suggested additions and changes significantly improve the general readability of the manuscript and help the reader to better understand the key points. In the following, we address the individual comments point-by-point.

The reviewers´ comments are highlighted in **black**, our answers in **blue**, and corrections in the text are shown in **red**.

Reviewer 1

The manuscript presents an interesting non-target LC-Orbitrap dataset and a potentially useful approach for distinguishing anthropogenic and biogenic molecular fingerprints using reduced dataset number. However, the interpretation would benefit from further clarification of the role of seasonality and meteorological conditions.

See our answer to line comment 296 further below.

Line 61: Should the original ACROSS overview paper be cited here, e.g. Cantrell and Michoud (2022)?

Good addition. This gives the reader the possibility to look up general information about the campaign, as well as further acknowledge the two co-organizers of the campaign.

"The ACROSS project (Atmospheric Chemistry of the Suburban Forest), coordinated by Christopher Cantrell and Vincent Michoud (from LISA Créteil), was designed to quantify how urban emissions from a major European megacity (Paris, France) interact with biogenic emissions from surrounding vegetated areas and how this mixing modifies oxidation chemistry, secondary pollutant formation, and aerosol properties (Cantrell and Michoud, 2022)."

Line 169: Please clarify the basis for classifying air masses as "biogenic." If this classification is mainly based on air masses not passing over Paris, there may still be possible anthropogenic influence from other urban/industrial areas, for example Lille, Ghent, or Rouen, depending on trajectory direction and residence time.

This is a good comment. In accordance with reviewer 2, we have clarified the naming convention. In the scope of this manuscript, an anthropogenically influenced air mass was an air mass whose trajectory was passing over the greater Paris area. The greater Paris area is certainly the largest city / industrial area in France, and is therefore likely having one of the highest anthropogenic activities compared to the other regions in France. As was stated, the former classification of the other air masses as "biogenic" can be misleading, as there might still be some anthropogenic activity along its trajectory path. However, compared to the anthropogenically influenced "greater Paris area" samples, those samples show significantly less anthropogenic influence, which was why we initially chose the name biogenic.

To improve the manuscript, we have substituted the name "biogenic" for "regional background", a name that should better describe the content of this cluster. We have further added a section (chapter 2.5.1 Clustering naming conventions) that clarifies the classification naming convention. The changes should make it easier for the reader to understand the contents of the clusters.

"The wind data, determined as described in chapter 2.4, is used to assign sources to individual compounds, where compounds whose intensity peaks during N-NE (red shaded areas) influenced wind conditions likely originate from the greater Paris area and are therefore likely to be more *anthropogenically influenced, whereas samples taken when the airmass was coming from the other directions are,* in this study considered to be less anthropogenically influenced (green shaded areas). As Paris is the largest anthropogenic accumulation in France, the air masses that were passing over Paris are considered to be more anthropogenically influenced than samples not passing over Paris, creating two types of samples: one type of sample that experienced a higher anthropogenic activity along its trajectory and one that experienced lower anthropogenic activity. For the sake of this paper, the two types are called anthropogenic influenced and regional background air mass. ...

…

Clustering naming conventions

For the sake of this work, time periods where the air masses have passed over the greater Paris area are called anthropogenically influenced, and consequently, compounds that show the highest concentration during those time periods are called anthropogenic compounds. The other time periods, where the air did not pass over the greater Paris area are called regional background time periods. The term regional background was chosen, as for those time periods, the air did not experience the strong anthropogenic influence of Paris, but some anthropogenic influence cannot be excluded, as other cities and anthropogenic agglomerations can be found along the trajectories of those air masses. Those time periods represent a mixture of biogenic and anthropogenic influences. Compounds that do show a higher concentration during those time periods are called regional background compounds."

Line 264: When stating that the results yielded similar findings to the larger dataset of Thoma et al. (2025), please clarify whether this comparison refers specifically to their summer results or to the full dataset. Could you include a comparison in SI?

We were comparing the results to the full dataset as shown in Fig. 3 of Thoma et al. (2025). The basis for this similarity comparison is solely on the basis of the two Van-Krevelen plots in Thoma et al. (top, green bordered (biogenic cluster) and bottom, magenta bordered (anthropogenic cluster)), and the Van-Krevelen plots for the anthropogenic (Fig. 5 (bottom)) and biogenic cluster (Fig. 5 (top)) shown in this manuscript. The Van-Krevelen plots of both works show the same distinct accumulations of compounds within their respective clusters, as mentioned in chapter 3.3 (Clustering) of this work.

To clarify this for the reader, we have added a short description in the manuscript at the corresponding section.

"Upon comparison with a recent study, our results show similar clustering results, despite having significantly fewer samples (352 filter samples in Thoma et al. (2025), only 37 filter samples in this study). This observed similarity is solely on the basis of a visual comparison of the Van Krevelen plots of the two studies, where in both cases, the distinct accumulations described in chapter 3.3 can be seen. *This* similarity *can be achieved through rigorous filtering of compounds that do not show a strong wind correlation, and excluding them from the clustering results. A larger* dataset, as was used in Thoma et al. (2025), *would increase the number of compounds that are assigned to each cluster as small anomalies in the compounds concentration profiles would be averaged out."*

We have also added a chapter in the SI where this similarity is shown in more detail.

"Comparison of the clustering results with Thoma et al. (2025)

Comparison of the clustering results presented in Thoma et al. (2025) with the results presented in this work reveals that a significant portion of the identified compounds within the "biogenic" (see Thoma et al. (2025); Fig. 3, top, green bordered) or regional background (our work; Fig. 5, top part) fall within $1.2 \leq H/C \leq 1.7$ and $0.15 \leq O/C \leq 0.5$. Most of the compounds there are in the CHO subset, As explained by Thoma et al. (2025) and in our work, this area corresponds to oxidation products of terpenes/isoprenoids ($H/C = 1.6$), further verifying the biogenic origin of the compounds.

In the anthropogenic cluster on the other hand, two accumulations of compounds within other subsets can be found. The first, most prominent accumulation of compounds within the anthropogenic subset is located at $1.5 \leq H/C \leq 2.2$; $0.2 \leq O/C \leq 1.0$ and mostly consists of compounds within the CHOS subset. This accumulation can again be seen in both works (see Thoma et al. (2025); Fig. 3, bottom, magenta bordered; and our work; Fig. 5, bottom part). Due to the high H/C ratio, those compounds are likely aliphatic alkanes with a sulfur containing functional group, as might originate from fossil fuel combustion. The second accumulation of compounds within the anthropogenic cluster is located at $0.4 \leq H/C \leq 0.8$; $0.2 \leq O/C \leq 0.8$. This accumulation is not as pronounced as the CHOS accumulation, however it is still present in both works. Compounds within this accumulation are likely to be nitrogenated aromatic compounds, explaining the low H/C ratio."

Line 250: Is there a basis for determining how many clusters were used? The use of two and three clusters shows that the anthropogenic signature was consistent, but was there an original rationale for choosing two and three clusters?

Initially, we wanted to have an easy metric to determine the anthropogenic influence in a given sample, hence the need for at least two clusters (one where the anthropogenic compounds group, and one for the other compounds). However, after some initial testing, we found, that to give compounds that do not show a strong directionality a unique cluster and not “contaminate” the other two clusters, a third cluster was added to capture the compounds without strong wind directionality. This gave us the current three clusters.

Regional-background cluster 1: Strong wind directionality (not passing over the greater Paris area; regional background cluster 1)
Regional-background cluster 2: Low wind directionality (more or less constant signal intensities throughout the whole sampling period; regional background cluster 2)
Anthropogenic cluster 3: Strong wind directionality (passing over the greater Paris area, therefore being the strongest anthropogenically influenced)

We have added a section in the text that describes this process in more details.

“After initial testing with only two clusters, it was found that in order to improve robustness, allowing a third cluster for compounds without a strong wind directionality improved results. Cluster membership was interpreted as source related groups with cluster 1 and 2 being the regional background, and cluster 3 being the anthropogenic cluster. Compounds within the regional background clusters with weak wind directionality were assigned to cluster 2 and compounds with strong wind directionality were assigned to cluster 1. This can be seen in the results in Figure 7.”

Line 296: The different biogenic signature is attributed to directional dominance, but it is not clear whether this reflects a difference in wind-direction strength only or a difference in back-trajectory origin.

The directional dominance is calculated by calculating the contribution of the most dominant wind direction bin (45°; plus its two neighboring bins) to the total summed concentration of the compound across all wind direction bins. The contribution of each wind direction bin is normalized to the number of samples contained in each wind direction bin. The wind directionality can be expressed as a percentage. E.g. if a compound has a wind directionality of 0.8, and the most dominant wind direction is N-NE, it means that the N-NE wind bin makes up 80 % of the total summed concentration across the whole campaign duration. The other wind direction bins add the remaining 20% of the compounds contribution at the sampling site. This shows that the different cluster assignments are not coming from the differences in wind-direction strengths, but are rather attributed to the difference in back-trajectory origin. Furthermore, due to the normalization step during the calculation of the directional dominance, the amount of samples in each wind direction bin does not affect the outcome.

“2.5 Determining the wind directionality of individual compounds

In order to perform filtering on the compounds that undergo clustering, a wind directionality is calculated. The wind directionality is the fraction of the total concentration of a given compound found within the dominant 45° direction bin and its two neighboring bins. A value near 1 means most of the compound originates from only one specific wind direction, while a value < 0.4 means the concentration is widely spread across different directions. Wind directionality measures directional consistency. During the ACROSS campaign, the wind direction measured at the sampling site, at the time of sampling usually agrees with the back trajectory as determined by the HYSPLIT model for the sampled air mass. In order to reduce complexity of the analysis, the wind direction as was measured at the sampling site, during the sampling period was used to determine the wind directionality."

Are the dominant wind directions associated with distinct source regions, or are the back-trajectory origins broadly similar?

The dominant wind directions represent mostly different back-trajectory paths, as very rarely, the path of an air parcel has changed significantly during the 24 h before sampling. One example of such an exception is shown in the supplemental information in the HYSPLIT backwards trajectory for sample S8. Here, the air parcel that was sampled has traversed from SW over W to NW before reaching the sampling site. The wind direction bin was therefore assigned NW, whereas the actual back-trajectory path of the air parcel was starting in SW then going over W to NW. We have added this to chapter 2.5 – Determining the wind directionality of individual compounds:

"… During the ACROSS campaign, the wind direction measured at the sampling site, at the time of sampling usually agrees with the back trajectory as determined by the HYSPLIT model for the sampled air mass. In order to reduce complexity of the analysis, the wind direction as was measured at the sampling site, during the sampling period was used to determine the wind directionality."

In addition, the ACROSS period included distinct meteorological regimes, including a cleaner period and heatwave periods. Could the dataset be split into the clean period and heatwave period, following the period definitions used by Di Antonio et al. (2025), to test whether these conditions affected the clustering?

We have chosen not to include the periods defined in Di Antonio et al. (2025), specifically clean periods and heatwave periods, as we wanted to focus solely on the back-trajectory of the air mass. The periods defined in Di Antonio et al. are most likely not suitable for splitting the dataset for our $PM_{2.5}$ organic aerosol LC/HRMS analysis, as e.g. during the clean period, there are two distinct conditions described in the paper. During the first part of the clean period, the wind is coming from N-NE with $PM_{2.5}$ concentrations being nearly comparable to those during the first heatwave period, and then for the second part of the clean period, clean oceanic air with significantly reduced $PM_{2.5}$ concentrations is coming from W-SW, whereas for the last part of the clean period, the wind coming from the north again and $PM_{2.5}$ is increasing again.

However, it needs to be stressed, that this is not a shortcoming by Di Antonio et al. (2025), it rather shows that periods can be defined for various application cases. Whereas Pereira et al. (2025) have also investigated samples taken during the ACROSS campaign with LC/HRMS and have defined different “background” and “polluted” periods. Here, the time periods were defined based on the OC (organic carbon) concentration.

Line 393: Please clarify the “others” category shown in black. Does this group represent identified molecular formulas outside the CHO, CHON, and CHOS classifications, such as CHONS or halogenated species, or does it include unidentified peaks? This category appears to contribute substantially in some samples and should be more clearly defined.

Yes, in the “others” category, formulas contained in the CHONS subset and halogenated species are contained. It does not include unidentified peaks. However, to reduce complexity, we have chosen to leave it as “others”.

We have defined more clearly in the text.

“In the CHO subset 1406 compounds could be identified. In the CHOS subset 1235, in the CHON subset 1015, and 1260 compounds in the “others” subset. The “others” subset contains all other compounds that do not fit into any of the three other subsets (CHO, CHOS, CHON). It is therefore a collection of mostly halogenated compounds, or compounds with a nitrogen and sulfur atom (CHONS subset). As not to increase complexity further, it was chosen to group these remaining compounds in the “others” group. ...”

Line 374: The wording “calculation” should be reconsidered or softened. If it says calculation, I expect numbers as was done by Thoma et al. (2025). Would it be possible in the future to such estimations with this method, given that there is a lot of auxiliary data from the ACROSS campaign?

Evaluation is probably a better word here. To evaluate the anthropogenic contribution to a given sample, the intensity of all compounds that were assigned to the anthropogenic cluster are summed. This is also done with the two other regional background clusters, after which the relative contribution of each cluster is calculated. This approach allows to evaluate the anthropogenic contribution of individual samples, which can be especially useful for analyzing time series of long term organic aerosol measurements, and easily judge and assess shifts in anthropogenic emissions over time.

Although there is a lot of auxiliary data available from the ACROSS campaign, it was not within the scope of this paper to include this additional data in the analysis, as one of the main goals was to keep analysis simple.

Changed the word “calculation” to “evaluation” in the heading:

“Evaluation *of anthropogenic influence on the chemical content of a given aerosol sample.”*

Line 381: Were the four samples removed for the reduced clustering test selected randomly, or were they chosen because they represent specific source conditions, wind directions, or concentration regimes?

The samples were not chosen randomly. In the “testing” dataset, we wanted to have samples that passed over the greater Paris area (N-NE), as well as samples with air coming from SW and SE to cover a range of different wind directions and therefore also a range of different anthropogenic contributions to the sample.

We have added this in the manuscript, along with a short description.

“The four samples were chosen primarily based on wind direction of the samples. Sample S21 and S22 showed a clear trajectory passing over the greater Paris area, whereas sample S6 approached the sampling site from the SW direction and sample S38 approached from SE. Furthermore, the samples S21 and S22 are consecutive day / night samples, choosing those consecutive samples therefore ensured, that there was no diurnal effect was accidentally contained in the clustering results.”