Title: Contrasting organic aerosol molecular composition between the urban and agricultural environment of the Po Valley

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Response to referee #2

Comment 1: "*L37-L39: This needs more description about the study referenced. What method did they use?"*

Reply to Comment 1:

Thank you for the request of clarification. We have changed the text to take into account your request as well the one of the Referee #1, as follows (now lines 37-42):

"*Recently, Thoma et al., 2025 have investigated the OA fraction at the Taunus Observatory, a rural background station located at about 800 m a.s.l. in central Germany. By means of a multivariate analysis on an extensive dataset generated by a high-resolution mass spectrometer, the authors observed that even at a rural site, OA system is composed of several thousands of compounds affected by seasonality and short- and long-range transport, with biogenic secondary OA (BSOA) peaking during summertime and representing about 70 % of the total number of compounds, and 30 % attributed to anthropogenic SOA (ASOA), discerned because of the presence of combustion tracers, such as nitrophenols and aromatic species."*

Comment 2: "*L64: "away" should replace "far""*

Reply to Comment 2:

Thank you for the correction. We have entirely revised that section (now lines now 59-92) of the Introduction.

Comment 3: "*L45-L70: The summary of previous studies in the region is good, but it feels like it is missing some context as to why this region is a hot spot for air pollution. Is it geographical? Or solely from large emissions?"*

Reply to Comment 3:

Thank you for letting our paper more complete. We have modified the text at the current lines 50-56 as follows:

"*Another well-studied pollution hot-spot is the Po Valley, in the Northern part of Italy. A number of papers* (Bigi et al., 2023; Ferrero et al., 2012, 2014; Neuberger et al., 2025) *reported*

that this area is severely affected by its orography, which often prevents incoming air masses coming from North, West, and East able to disperse and abate the anthropogenic emission of the densely-populated valley in the lower layers of the troposphere. This leads to the accumulation of primary emitted compounds, especially during the cold season, when vertical mixing is limited to a shallow layer (Ferrero et al., 2011). In addition, Colombi et al. *(2024) have shown that aerosol homogeneously affects the basin with very similar values in both concentration and chemical composition.*"

Comment 4: "*L93: A map would be beneficial to show the relationship of the two sites to one another."*

Reply to Comment 4:

Thank you for your suggestion. We have added in Supplement (and here attached with the caption) the map (Figure S1) and highlight the position of the sampling sites.

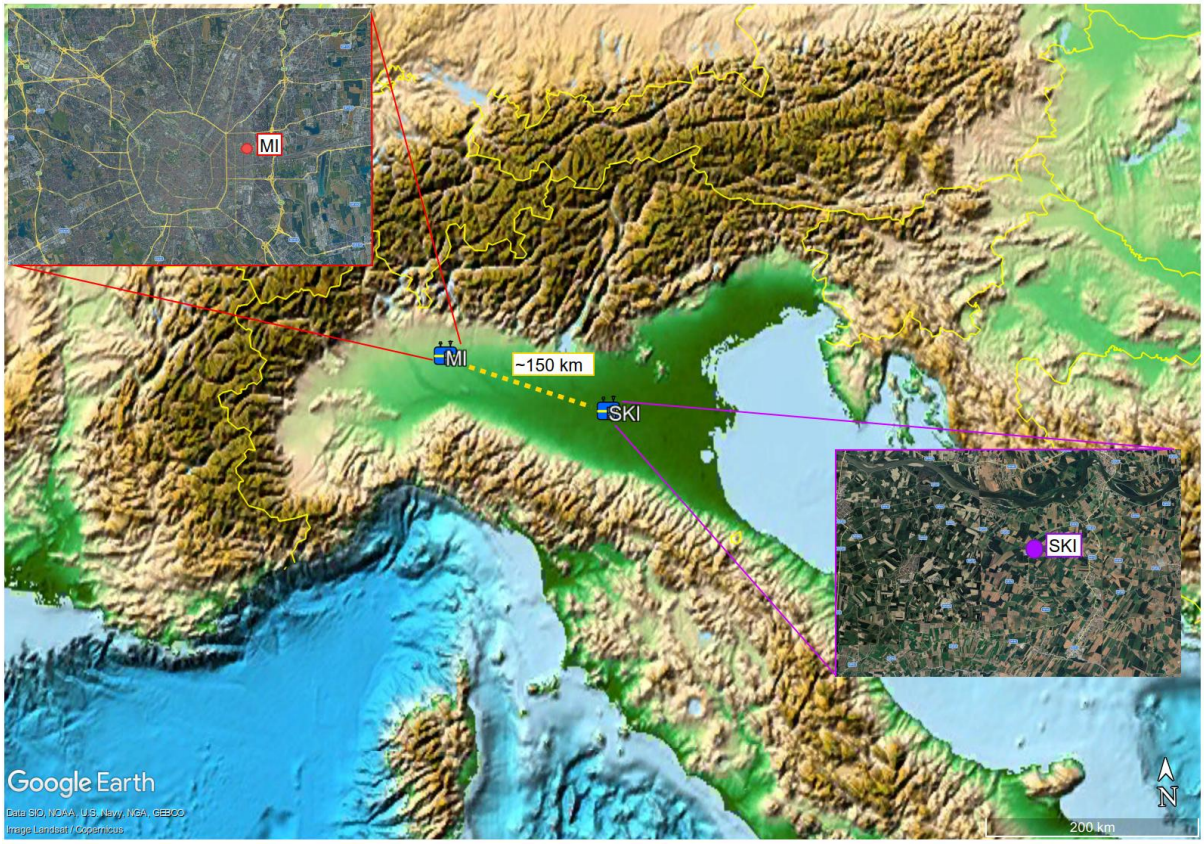

Figure S1: Map of Northern Italy. The Po Valley area is clearly visible, including the orography that often prevent incoming air masses able to abate the high aerosol concentrations that affect the basin. In the map the location of the two sampling sites considered in this work are also shown: MI (the urban background site) and SKI (the rural–agricultural background site).

We also changed the labels of each figures in the Supplement and in the main text to adapt the numbering. At now lines 130-131 we explicit the presence of the map in the Supplement as follows:

"*A map of Northern Italy showing the sampling sites is provided in the Supplement (Figure S1).*"

Comment 5 "*L99-105: Were the filters treated or baked before use? How were blanks collected and how often? These details are important and should be included."*

Reply to Comment 5:

$PM_{2.5}$ samples were collected on quartz fiber filters on a daily basis. Due to the large number of samples, the standard operating procedure of the Environmental Protection Agency of Lombardy Region (ARPA Lombardia) does not include filter pre-treatment (e.g., pre-baking). However, at the Schivenoglia site, quartz fiber field blanks were placed in the sampling lines of the sequential samplers on a weekly basis, following the same handling protocol as the collected samples, resulting in a total of 44 field blank filters analyzed in this study. At the urban site (Milan), only three field blanks, obtained using the same procedure, were available for analysis. To account for potential contamination, a data-filtering approach was applied, excluding signals with a sample-to-blank ratio ≤ 5 (current line 192) and compounds detected in fewer than 10% of the samples (current line 232). This approach allowed us to minimize false positives arising from sporadic contamination and to assess the temporal variability of the dataset.

To highlight that the filters were not pre-treated, we modified the manuscript as follows (now line 122):

"*At both sites, low volume samplers (SKYpost PM, TCR-Tecora, or Lifetek PMS, Megasystem, 16.67 Lpm) were used to collect the $PM_{2.5}$ samples on not pre-treated quartz fiber filters (Pall TissueQuartz, Ø=47 mm) for 24 hours since 2014.*"

Comment 6: "*L107: Please provide details or a reference for the IC method used."*

Reply to Comment 6:

We have changed the text as follows (now line 140-145):

"*Water-soluble inorganic compounds and levoglucosan were quantified by high-performance anion-exchange chromatography with pulsed amperometric detection by extracting 1.5 cm^2 quartz filter punches in ultrapure water (10 mL volume) for 20 min in an ultrasonic bath. After filtration (Nylon or PTFE Syringe Filter, pore size 0.45 µm), the resulting solution was injected in the analytical system and for the determination of anions (Metrohm 930), cations, and levoglucosan (Metrohm 881). A second punch was used to quantify EC and OC through thermo-optical analysis (Sunset Laboratory Inc., Tigard, OR, USA) based on the EUSAAR2 protocol. Both analytical procedures are described in Colombi et al. (2024)."*

Comment 7: "*L228-233: The discussion focuses heavily on CHN species, please expand on why that is and why other species are not discussed as in depth or at all."*

Reply to Comment 7:

These lines intend to focus to the main differences in molecular-families' contributions to the BrC fraction. Comparing the sampling sites, Figure S2 shows that three main families are involved: CHO, CHNO and CHN, whereas the remaining account for less than 2 %. To highlight this concept, we have modified the manuscript as follows (now lines 265-271):

"*Seasonally averaged BrC compound intensities were aggregated by molecular-family and normalized to the total BrC intensity (Figure S2), revealing that the relative contributions of these families differ between the two sites across seasons. During them (summer and winter) the urban site exhibits higher contributions of the CHN family compared to the agricultural site (8.8 % vs. 3.7 % at MI and SKI, respectively, in summer; 17.1 % vs. 7.9 % in winter), whereas CHO family contributes to the higher nTSI values (Fig. 2) in respect to SKI during summer only. In contrast, CHNO species contribute more at the agricultural site in both seasons (23.9 % vs. 33.9 % in summer and 46.2 % vs. 51.5 % in winter, respectively). Contributions from the other families are marginal, accounting for less than 2 % at both sites.*"

Comment 8: "*L263-264: This sentence sounds as if the authors did not identify a second and third highest signal at SKI and instead are reporting what other studies found. The authors should clarify what their data shows.*"

Reply to Comment 8:

In this section we list the compounds showing the highest signal intensities, acknowledging – despite the different ionization efficiencies of the compounds – that a relationship may exist between signal intensity and atmospheric concentration. In the part for which an explanation is requested, we report the highest CHO signals detected in positive mode. While the two most intense signals observed at the urban site have been tentatively associated in the literature (albeit at identification level L4) with oxidation products of n-dodecane, we found no corresponding evidence in the literature for the third most intense signal – which also corresponds to the highest detected at SKI – so at this stage of the paper we cannot provide a suitable explanation. Using the data analysis approach applied and described in this paper, namely NTA and HCA, we will nevertheless be able to attribute this compound to a combustion-related source at both sites. In fact, it will be prevalent in the MI-Other anthr-OA cluster at the urban site and in the SKI-BBOA/TrOA cluster at the rural site.

Comment 9: "*L296-298: Please expand here. The author is discussing wintertime increases but offering summertime photochemical degradation as a possible reason.*"

Reply to Comment 9:

The sentence intends to propose a possible explanation for a such temporal pattern. Higher intensity values during wintertime in respect to summertime suggest higher anthropogenic emission amplified by meteorological conditions or a higher depletion during summertime due to stronger photoxidation, causing a suppression of the atmospheric abundance of specific compounds. Since here we are introducing the general pattern of three different clusters we preferred to postpone a specific explanation later in the paper, where each cluster is discussed separately. To clarify better this concept, we modified the manuscript as follows(now lines 336-344):

"*According to the temporal patterns, three clusters at both sites showed a clear increase in intensity during the colder season. The higher signals observed during winter may arise from multiple contributing factors, acting either independently or in combination. Seasonal variations in emissions may lead to the presence of sources that are active or more intense in winter than in other periods of the year. In addition, meteorological conditions typical of winter, such as reduced atmospheric mixing and dispersion, can enhance aerosol concentrations. Partitioning processes may also play a role, with gas–particle equilibrium shifting toward the particulate phase under colder conditions. Furthermore, the absence or low abundance of certain compounds in summer does not necessarily imply a lack of emissions; rather, enhanced photochemical degradation may lead to their rapid transformation into other species. As a result, compounds that are prevalent in winter may be replaced in summer by secondary products that are only present at low levels during the colder season.*"

Comment 10: "*L450-457: This section is confusing as written. The authors should clarify why they believe those fractions indicate tractor emissions.*"

Reply to Comment 10:

Thank you for letting us to clarify this point. Blair et al. (2017) demonstrated that biodiesel and diesel fuel mixture emission, in presence of sulphur dioxide, can lead to organosulfur compounds. In addition, the authors state that organosulfates attributed to biogenic origin might be instead due to photoxidation of emission from biodiesel and diesel fuel. Formulae matches (identification confidence L4 based on Schymanski et al. (2014) were obtained between S-containing compounds belonging to the "SKI-Agricultural Activities". CHOS compounds populating this cluster are 123: among these, 22% are not detected at the urban site and about 15% of the molecular formulae matches with findings of Blair and co-authors. The presence of these compounds at the agricultural site and the absence at Milan one suggests a site-specific source. For these reason we hypothesize that these compounds are due to agricultural tractor emissions or sources that uses diesel or biodiesel. On the other hand, since the identification level is L4, we cannot provide any additional confirmation of our hypothesis and this is the reason why we declare in the manuscript that is a speculation. To improve clarity and explicitly state that we are proposing a hypothesis that requires further investigation for confirmation, we have revised the manuscript as follows (now lines 508-516):

"*In addition, the cluster fingerprint (Figure S19) is enriched in S-containing compounds (approximately 14%, of the number of compounds populating SKI-Agricultural activities), of which 34% are not detected at the urban site. Comparison of the chemical formulas of these S-containing compounds with the results reported by Blair et al. (2017) indicates that approximately 55% yield a match (L4). Given that Blair et al. (2017) showed that organosulfates can form through the photooxidation of hydrocarbons emitted from diesel and biodiesel in the presence of* SO_2*, the occurrence of organosulfates, such as* $C_8H_{16}O_8S$*,* $C_{16}H_{26}O_3S$*,* $C_7H_{12}O_7S$ *(L4), exhibiting temporal trends consistent with those of pesticides and other agricultural activities may suggest a contribution from emissions associated with agricultural machinery (e.g., tractors). However, alternative sources and formation pathways cannot be excluded, highlighting the need to expand available libraries, such as the Aerosolomics database, in order to more confidently link compounds to specific sources.*"

Comment 11: "*L506: "unpolar" should be "nonpolar"*

Reply to Comment 11:

We have corrected the manuscript based on your suggestion.

Comment 12 "*L528: Why were samples from June and December excluded? Did no samples meet the criteria? If so that seems worth a small discussion."*

Reply to Comment 12:

Thank you for requesting this clarification. Considering the entire year, the conditions we take into account to consider a pair of samples as "similar", i.e. $|\Delta OC| < 2$ μg m^{-3} and $|\Delta$ OC/$PM_{2.5}| < 5$ %, results in 116 pair of samples, distributed all along the year with the lowest occurrences during June, September and December. On the other hand, only a subset of the samples was extracted and analyzed via our HPLC-HRMS system. Hence, the absence of samples that not match with the chosen condition was noticed during the data analysis processes and not planned. We attach here and in the Supplement (Figure S22) a histogram showing the difference between the entire dataset and the sample set used in this work.

In addition, we modified the manuscript as follows (now lines 588-592):

"*Considering the full year, 116 sample pairs meet this criterion, although they are unevenly distributed over time. In particular, the number of pairs is the lowest in June (#5), September (#4), and December (#1). When restricting the analysis to the subset of filters used in this study, the number of valid pairs decreases to 54, and no pairs meet the above criterion in June and December. Consequently, these months are not represented in the figures showing similar sample pairs (Figures 6 and 8).*"

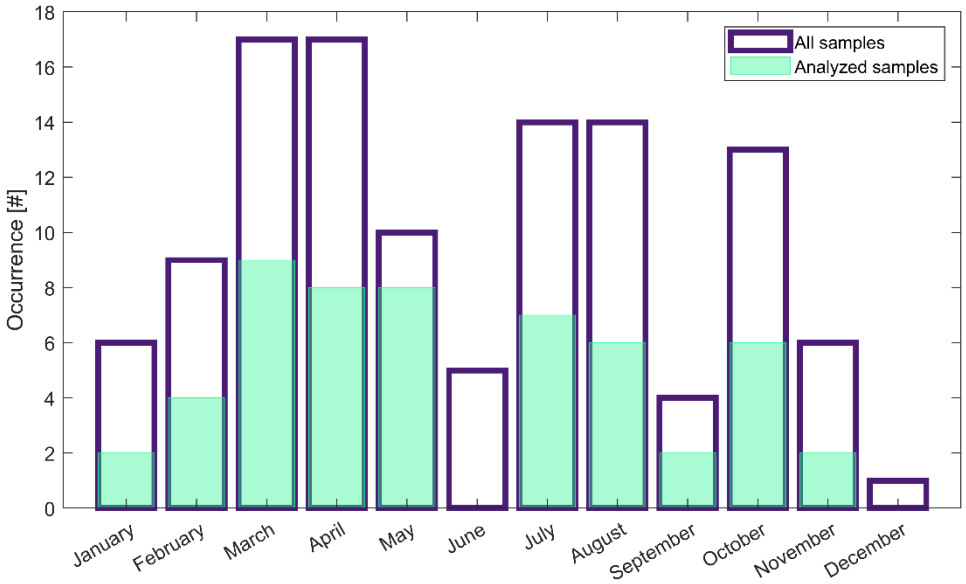

Figure 2: *Frequency histogram of samples (collected on the same day) that meet the criteria to be defined as 'similar samples,' grouped by month. The blue bars represent the entire*

dataset of samples collected throughout the year, whereas the green bars indicate the pairs of samples that were actually extracted and analyzed in this study.

References

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