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

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Response to referee #1

Comment 1: “*Lines 35-70: The introduction first emphasizes the importance of molecular-level characterization of OA and then lists previous studies conducted in the Po Valley, but it lacks a concise synthesis of existing knowledge. I suggest adding a short summary outlining the major OA sources identified in the Po Valley, their seasonal and spatial variability, and the main hypotheses proposed to explain these variations, which would better contextualize the novelty of this work.”*

Reply to Comment 1:

Thank you for pointing out the need of a short summary to clarify the overall findings in the Po Valley. It worth noticing that the analytical approach we used for this work about the Po Valley is unique so far. Despite this, several authors studied the aerosol organic fraction in the Po Valley mainly using the thermo-optical analysis to quantify organic, elemental and total carbon, and by means of the aerosol mass spectrometer (AMS). Therefore, we improved the introduction section by summarizing the most important figures reported in literature. Particularly, Paglione et al. (2020) investigated the submicron aerosol organic fraction (OA) by means of high-resolution AMS showing that OA can vary from 33% to 58% of the total particle mass, being due to both primary and secondary OA with the latest that accounts to a larger extent on OA due to, for example, biomass burning, aging and secondary formation in the aqueous phase. In this respect, Bressi et al. (2016) confirmed the biomass burning role for OA and found a high degree of oxygenation (especially in wintertime) due to the contribution of secondary biomass burning OA and the enhancement of aqueous-phase production of OA; this is in line with Sandrini et al. (2016), which observed that the photochemical oxidation of organic gaseous precursors was an important mechanism of secondary aerosol formation especially under stagnant conditions. At nighttime the relative humidity increase leads to peak of concentrations of secondary water-soluble organic carbon and making OA in the Po Valley region a complex mixture of components from both local and regional sources (Decesari et al., 2014; Saarikoski et al., 2012) leading to chemical tracers (e.g. aliphatic carbonyls, carboxylic acids, etc.) observed in several studies (Dall’Osto et al., 2015; Perrone et al., 2012). This phenomenon can also lead to "brown" aerosol (AAE from 2.5 to 6) within the "droplet" mode where aerosol is enriched in aged OA and nitrate (Costabile et al., 2017). Such features require a deep understanding even at molecular scale; in fact, despite AMS is a powerful instrument able to provide useful data to perform a source apportionment of the non-refractory organic aerosol via positive matrix factorization, it does not provide enough information, due to its hard ionization approach, about the molecular composition. Thus, a molecular in-depth characterization is missing for this hot-spot for air pollution. To our knowledge and to date, OA sources were identified so far via the mentioned techniques only. Such knowledge is required even to improve modelling simulation for OA with respect to photochemical/chemical activity and related parametrizations (Basla et al., 2022). With these preconditions, we added in the text the following paragraph just after the mentioned lines (now 59-92):

"*Many studies have been published on source apportionment in the Po Valley, consistently highlighting the dominant role of anthropogenic emissions. For example, Perrone et al. (2012) performed a source apportionment on $PM_{2.5}$ samples collected at urban and rural sites over a three-year period (2006-2009), identifying the local contribution of traffic (Tr), the widespread influence of biomass burning (BB), and the importance of secondary aerosols (both organic and inorganic) particularly during spring and summer. Similarly, Bernardoni et al. (2013) used ^{14}C analysis on PM_{10} samples collected in Milan during wintertime to distinguish organic carbon (OC) and elemental carbon (EC) from fossil and modern carbon sources, estimating that OC_{fossil} accounts for about 30.8% of total carbon, while primary wood burning contributes 14.8 %, with an additional 37.5 % attributed to other modern sources. Source apportionment of the organic aerosol (OA) fraction in this region has been extensively performed over the past decade using aerosol mass spectrometry (AMS). Several authors (Dall'Osto et al., 2015; Paglione et al., 2020; Saarikoski et al., 2012) conducted field campaigns at both urban and rural sites. Their results consistently showed that biomass burning organic aerosol (BBOA) significantly contributes to OA mass, especially in winter, through both primary and secondary components. Regarding the primary fraction, Decesari et al. (2014) highlighted the importance of hydrocarbon-like OA (HOA) and a cooking-related component, whereas Daellenbach et al. (2023) estimated that primary BBOA accounts for 37 % of the OA mass. Concerning the secondary fraction, secondary organic aerosol (SOA) was found to dominate summertime, especially due to low-oxygenated compounds (Daellenbach et al., (2023). Sandrini et al. (2016) demonstrated that photochemical oxidation of gaseous precursors is a key mechanism for SOA formation, particularly under stagnant conditions. In addition, nighttime increases in relative humidity promote the formation of secondary water-soluble organic carbon, further enhancing the complexity of OA composition (Decesari et al., 2014; Saarikoski et al., 2012). These processes lead to the formation of light-absorbing "brown carbon" (BrC), often associated with the droplet mode (400–700 nm), enriched in aged OA and nitrate (Costabile et al., 2017). In this regards, Kiendler-Scharr et al. (2016) showed that, in the southern Po Valley, the fraction of organic nitrates is comparable to that of inorganic nitrate and among the highest observed in Europe. Aqueous-phase reactions have been identified as a key pathway for BrC formation (Gilardoni et al., 2016), while a significant fraction of BrC has been found to be water-insoluble and associated with primary emissions from wood combustion (Gilardoni et al., 2020). Overall, the Po Valley atmosphere is strongly impacted by anthropogenic emissions, with more pronounced effects during winter, when meteorological conditions and orography favor air stagnation. Increasing dry periods throughout the year (Baronetti et al., 2020; Monteleone and Borzí, 2024) further enhance the accumulation and spatial homogenization of secondary species. Consequently, source apportionment studies have reported relatively low spatial variability across the region, identifying traffic-related fossil emissions as a persistent source throughout the year, secondary aerosols as dominant in summer, and biomass burning as prevalent in winter. Despite these extensive efforts, a detailed molecular-level characterization of OA remains limited. Although AMS-based techniques are powerful tools for apportioning non-refractory OA sources via positive matrix factorization, their hard ionization approach limits the identification of specific molecular species. As a result, a comprehensive understanding of OA composition at the molecular scale is still lacking in this major air pollution hot-spot. Such knowledge is essential to improve the representation of OA* *in atmospheric models, particularly with respect to photochemical processes and parameterizations (Basla et al., 2022).*"

Comment 2: "*Lines 37-39: "Recently, Thoma et al. (2025) have observed that even at a rural site, OA system is composed of several thousands of compounds affected by seasonality and short- and long-transport events, with biogenic secondary OA (BSOA) representing about 70 % of compounds and 30 % attributed to anthropogenic SOA (ASOA)." It is unclear whether these percentages refer to the number of detected compounds or to signal intensity. If based on signal intensity, this should be explicitly stated and discussed with caution, as ESI measurements are strongly affected by ionization efficiency and matrix effects, making direct interpretation of intensity fractions as SOA contributions uncertain.***"**

Reply to Comment 2:

Thank you for clarifying this point. In their work, Thoma et al. analysed 352 samples collected at Taunus Observatory, a rural background station located 20 km North of Frankfurt am Main, Germany. Their analytical method brought to light 6080 compounds and the consequent data analysis highlighted two main clusters of compounds: 70 % of the detected compounds were attributed to compounds transported or to biogenic origins, whereas 30 % to anthropogenic activities. Their results are based on the number of compounds. To take into account your request of clarification and as well as the Referee #2 requests, we have modified the sentence 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 3: "*Lines 81-82: "Non-targeted analysis allows for inferring the overall properties of OA and has the potential to identify relationships between groups of compounds and their sources or other endpoints." This statement requires literature support and further explanation, as non-target analysis provides comprehensive molecular fingerprints but does not inherently guarantee source attribution without additional assumptions. Please clarify why this approach is particularly suited for identifying such relationships.***"**

Reply to Comment 3:

Thank you to provide us the possibility to explicitly explain the potential of the non-targeted analysis (NTA). Without focusing on known compounds only, NTA requires assessing molecular formula-based descriptors, such as aromaticity equivalent, averaged oxidative state of carbons, oxygen-to-carbon ratio, etc. These descriptors provide insights on the properties of the analysed aerosol system as it is. Additionally, NTA applied on a time-series dataset can be supported by multivariate analysis (e.g. a cluster analysis) to infer common pattern and properties of the compounds (as shown Breuninger et al., 2026; Ma et al., 2022; Thoma et al., 2025; Wang et al., 2024). As a consequence, other than the use of analytical standards, the matches with MS/MS fragmentation spectra retrieval in available libraries (such as mzCloud or the Aerosolomic databased described in Thoma et al., 2022) or with previous findings in literature and the correlation with external data (such as levoglucosan and soluble potassium from ion chromatography, gaseous benzene and other species) enable the NTA to indicate common aerosol sources or meteorological/emissive conditions for the compounds that show the same temporal pattern. To assess this *a priori* findings, specific standards can be later tested to check their presence within a specified cluster enabling its final interpretation/source attribution. This is the approach we used and that allowed us to verify the plant protection products presence in the cluster called "SKI-Agricultural activities" and it is in keeping with Duarte et al. (2023) who pointed out that, being the OA on of the most complex environmental matrices known, targeted and untargeted profiling of OA are both required to extract chemical information from the voluminous amount of data generated using newly available analytical approaches such as the one presented in this study.

We have modified the manuscript as follows (now lines 103-115):

"Non-targeted analysis enables the characterization of the overall properties of OA and, when applied to time series of samples and supported by multivariate analysis, has the potential to identify relationships between groups of compounds, molecular markers, and their sources (e.g., Wang et al., 2024). These relationships can be further constrained using source-specific analytical standards, external datasets, or other endpoints, as recently demonstrated by Breuninger et al. (2026) for the oxidative potential of PM. As noted by Tang et al. (2026), and originally proposed by Thoma et al. (2022), the concept of "Aerosolomics" advocates the integration of controlled experiments to elucidate chemical reaction pathways with atmospheric observations, time-series analysis, and correlations with known markers, supported by multivariate analysis, to identify the sources of atmospheric molecular species. In this context, the present work provides a substantial dataset of compounds that contributes to the Aerosolomics database, focusing on the Po Valley, a region for which, to our knowledge, these mentioned analytical techniques and data analysis approaches have not previously been applied. In this respect, (Duarte et al., 2023) pointed out that, being the OA on of the most complex environmental matrices known, targeted and untargeted profiling of OA are both required to extract chemical information from the voluminous amount of data generated using newly available analytical approaches such as the one presented in this study."

Comment 4: **"***Figure 1: The distinction between aromatic and aliphatic compounds is shown in Figure 1, but the manuscript does not clearly explain how this classification is derived from Xc values. Please describe the Xc thresholds.***"**

Reply to Comment 4:

Thank you for this recommendation. First, we wrongly attributed the name "aromaticity index" (often indicated as AI) to the "aromaticity equivalent" (indicated as X_c). We have corrected this in the text (now line 204). In addition, we have added the required explanation into a sentence just after the reference paper (i.e. Yassine et al., 2014), now lines 205-206:

“*This last descriptor was validated to provide information concerning the presence of aromatic structure in a molecule ($X_c \geq 2.5000$), while aliphatic structures show lower values of the mentioned threshold.*”

Comment 5: **“***Lines 217-219: “Retrieving light-absorption information via a molecular-derived proxy, we use the DBE/#C ratio to identify compounds of light-absorbing aerosols (LAAs), setting limits for this range between 0.5 (for polyenes) and 0.9 (for fullerene-like hydrocarbons) (e.g., Lin et al., 2018; Laskin et al., 2015).” As mentioned in Lin et al., 2018, the DBE/#C proxy has mainly been validated for APPI measurements, where most detected compounds fall within the BrC domain, whereas ESI positive mode typically detects a much smaller fraction of compounds in this region. Since this study relies on ESI, please discuss the potential bias introduced by ionization selectivity and how undetected BrC compounds may affect the interpretation of light-absorbing aerosol contributions. Please consider whether complementary MS/MS structural information could support the BrC interpretation, for example by identifying characteristic functional groups or neutral losses (e.g., aromatic nitro or nitroso groups, heteroaromatic N-containing rings, conjugated carbonyl systems, or diagnostic losses such as NO2, HNO2, CO, or CO2) that have been previously associated with light-absorbing chromophores.***”**

Reply to Comment 5:

Thank you for pointing out this topic. An increasing number of papers focused on the chemical characterization of BrC compounds via the soft-ionization techniques, mainly ESI and APPI. Recently, Laskin et al., 2025 reviewed the different sensitivity of these techniques in detecting BrC compounds based on their polarity, highlighting that electrospray is more efficient regarding polar and semi-polar compounds and the polarization mode address the sensitivity to the functional groups. On the opposite, APPI is highly sensitive to nonpolar compounds, such as PAHs, and it is more efficient in ionizing compounds with high carbon content (≥25), more likely to have double conjugated or aromatic bonds. Due to this, we do expect to not observe low-polar to nonpolar molecules, therefore their contribution in the molecular characterization and the subsequent discussion is neglected. On the other hand, Lin et al. (2018) observed that on BBOA aerosol samples, 65 % of compounds detected in ESI(−) are potential BrC compounds (based on DBE/#C proxy), confirming the applicability of this ionization in detecting polar and semi-polar compounds. In this regards, Xing et al., (2023) classified BrC chromophores in atmospherically relevant samples (such as ambient, biomass burning and road tunnel aerosols) in nine groups (such as nitrophenols, benzoic acids, O-PAHs, phenols, aryl amides/amines, and others) coupling UHPLC-HESI-HRMS with a photo-diode-array detector after the chromatographic separation. Their findings confirmed the capability of the HESI source in ionizing BrC compounds.

On the other hand, the analytical approach that we have used in this work allowed focusing on the molecular characterization of polar and semi-polar BrC compounds not only by means of the ionization technique (HESI) but also by means of a polar extraction solvent, consisting of water and acetonitrile (9:1 v/v); therefore, we do not expect an efficient extraction of nonpolar compounds, such as PAHs. The solvent effects on the extractable light-absorbing organic aerosol fraction is proved in Lin et al. (2018). Thus, we consider our analytical approach suitable and reliable in describing the investigated polar and semi-polar BrC organic aerosol fraction. Moreover, about this topic, the goal of our paper focuses on the observation of the seasonal and local variability of BrC species and we are not aiming to fully characterize the entire molecular composition of BrC, from polar to nonpolar species and from low to high molecular mass.

Predicting the contribution of the less polar/nonpolar fraction of OA to the BrC compounds present in our samples is highly speculative. We can hypothesize that this is greater in the winter months due to increased biomass combustion and a lower oxidation rate than in summer. Referring to the work of Gilardoni et al. (2020) – who found that in winter 50% by mass of BrC is due to water-insoluble compounds – we can assume that we have extracted about half of the BrC, but we cannot estimate whether this also reflects the number of chemical species. A comparison of two different sampling sites of the Po Valley, Bologna (urban background) and San Pietro Capofiume (rural background), is provided in Paglione et al. (2020): by means of AMS measurements and a positive matrix factorization approach, the authors confirm that SOA dominates at both sites, ranging from about 60 % to 90 % of the OA. Moreover, Bressi et al. (2016) found a high degree of oxygenation (especially in wintertime) due to the contribution of secondary biomass burning OA and the enhancement of aqueous-phase production of OA in the Po Valley.

We appreciate the suggestion of Referee #1 in analysing the MS^2 spectra and the subsequent neutral losses to obtain additional information about likely functional groups of the detected compounds. After your hint, we consider this and we added to Table S1 and Table S2 the neutral losses we checked. Unfortunately, the MS^2 coverage in our dataset is limited: for about 83 % of the overall BrC dataset no MS^2 was carried out by the instrument or no neutral loss estimation was provided. For the remaining compounds, a number of losses were provided by the software. Overall, carboxylic, carbonyl, amino, benzene, phenolic, nitric, nitroso and cyano groups are the most represented in BrC dataset, together with fragments suggesting the possibility to have a double-bond conjugated system. On the other hand, the molecular population detected by the instrument might be such heterogeneous that a characteristic functional group is not identified. The barcharts in **Errore. L'origine riferimento non è stata trovata.** show the neutral losses abundancy in the entire dataset (upper plot), related for potential BrC compounds (centre), and the relative contribution of the neutral losses of potential BrC compounds related to the entire dataset. As clearly shown, the majority of the detected neutral fragments belong to potential BrC compounds. Nevertheless, the statistics is very limited to assess a significant difference between BrC and non-BrC compounds, and the predominance and the seasonality of specific functional groups in our dataset. On the other hand, your suggestion provides a new data analysis perspective and we will take it into account for further studies.

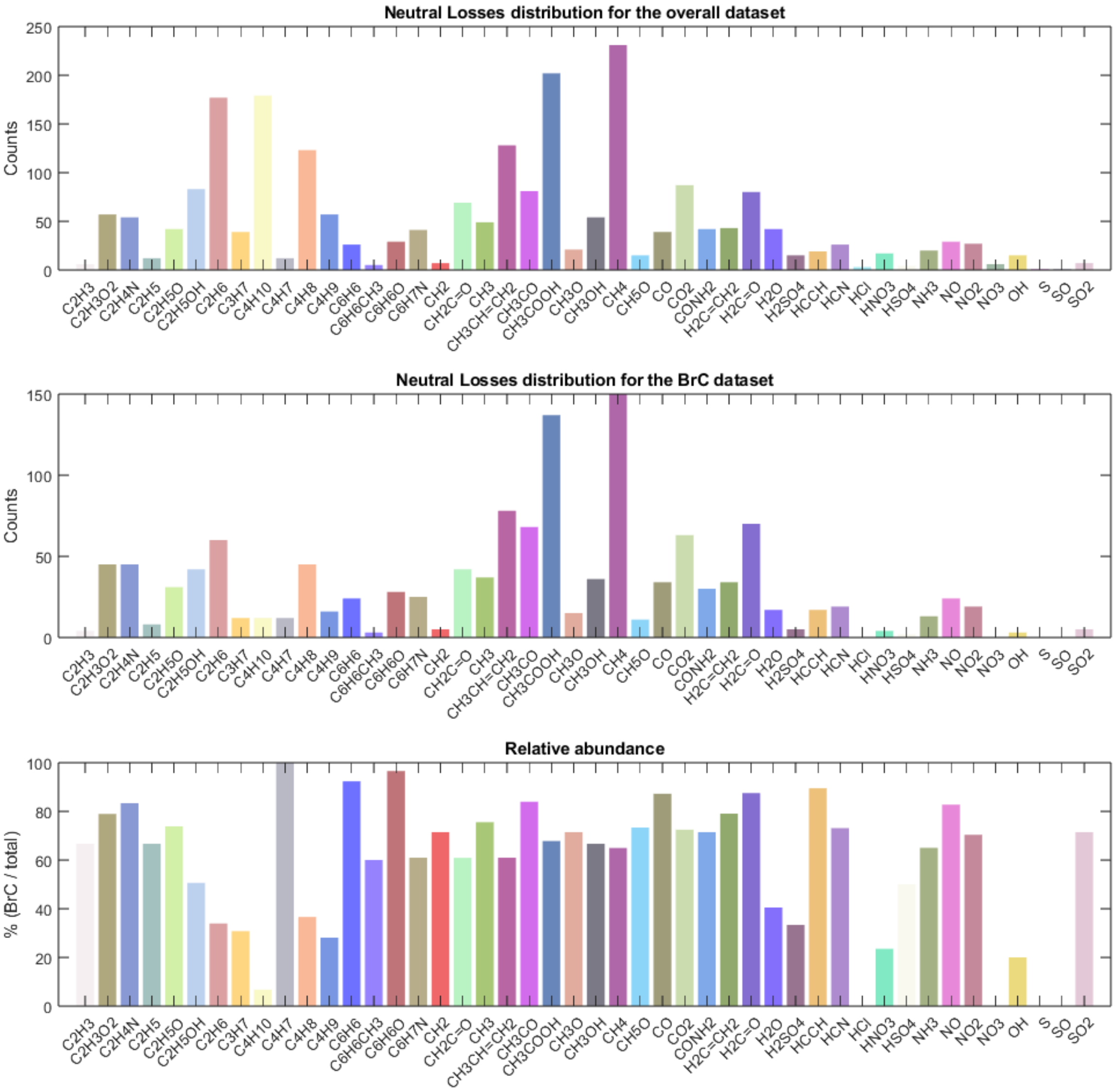

Figure R1: : bar charts of neutral losses identified via Compound Discoverer Neutral Losses node for the entire dataset (upper plot), potential BrC dataset (centre), and relative abundance of BrC neutral losses in respect to the entire dataset.

Comment 6: ***"****Lines 228-232: "When averaging intensity by compound families (Figure S2), it is observed that BrC at the urban site contributes more strongly to nTSI, mainly due to CHN species (8.8 % vs 3.7 % at MI and SKI, respectively, in summer; 17.1 % vs 7.9 % in winter), whereas the agricultural site is more influenced by CHNO (23.9 % vs 33.9 % and 46.2 % vs 51.5 % in summer and winter, respectively)." It is unclear why the discussion focuses exclusively on CHN species when interpreting BrC contributions, while other compound families (e.g., CHNO or CHOS) are not discussed. Please clarify whether CHN compounds dominate BrC by definition or by observation in this dataset.*__*"*__

Reply to Comment 6:

Thank you for pointing out this ambiguous sentence. We modify the text to clarify these observations (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 7: “*Lines 296-298: “According to the temporal patterns, three clusters at both sites showed a clear increase in intensity during the colder season. This could suggest either a source activation during the winter, an amplification of the impact due to a lowering of the mixing layer height, a gas-to-particle partitioning phenomenon, or photochemical degradation during summer.” The logic here is unclear, as the first sentence refers to colder-season enhancement while the explanation invokes summertime photochemical degradation. Please clarify whether the authors propose enhanced wintertime sources/accumulation or active summertime photochemistry removing these compounds or their precursors.***”**

Reply to Comment 7:

The sentence intends to propose a possible explanation for a such temporal pattern. Higher intensity values during wintertime with respect to summertime suggest higher anthropogenic contribution amplified by meteorological conditions but also the possible depletion of specific compounds during summertime due to stronger photooxidation, causing a decrease in their abundance. Since in this paper section 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 8: “*Lines 335-338: “Many tracers attributed to traffic exhaust in the literature are found here: e.g. $C_4H_6O_4$ (succinic acid, L4, Lui et al. (2023)), $C_7H_{12}O_7$ (L4, Thoma et al. (2022)), and $C_9H_8O_4$ (methylphthalic acid, L4, Ikemori et al. (2021)). In addition, N-*

containing features enrich the so-called "MI-TrOA" (Traffic OA) cluster, including aliphatic amines such as C8H18N, C7H17N, C9H21N (as reported in Cao et al. (2023))." The term "TrOA" is introduced here for the first time, although it already appears in earlier figures (e.g., Figure 3 and Figure S7). Please introduce and define this terminology consistently at its first occurrence to avoid confusion."

Reply to Comment 8:

As stated in the reported sentence, "TrOA" means "Traffic OA". We have modified and anticipated the abbreviation "Tr" in the Introduction section at line 60-63, together with a better explanation of the cited findings:

"For example, Perrone et al. (2012) performed a source apportionment on $PM_{2.5}$ samples collected at urban and rural sites over a three-year period (2006–2009), identifying the local contribution of traffic (Tr), the widespread influence of biomass burning (BB), and the importance of secondary aerosols (both organic and inorganic) particularly during spring and summer."

Comment 9: ***"****Figure S10 is not cited in the main text. Please check that all supplementary figures are properly referenced and that the numbering and order of Figures S9-S18 are consistent between the manuscript and the SI."*

Reply to Comment 9:

Figure S10 (now Figure S11), together with S17 (now Figure S18), indicates the biogenic secondary organic aerosols clusters, peaking during summertime. In the first submitted version of the manuscript, they are cited at line 441 *"The molecular fingerprints of these two clusters (Figures S10 and S17) are very similar.*" at the beginning of Section 3.2.2 "Summertime clusters". Figures in the Supplement are divided in function of the sampling site and then sorted in function of the citing order in the manuscript.

Comment 10: ***"****Lines 411-414: "Many of these were also listed in Zhang et al. (2023a), and attributed to wood burning (L4). Although the identification level is only 4 (unequivocal molecular formula), we hypothesize that these compounds are rising during summertime from oxidized BBOA, because of the meteorological and climatic conditions, such as the higher concentrations of oxidants species (O3, NO3 and OH radicals) induced by higher solar activity in this season." This interpretation appears contradictory and requires clarification. Moreover, attributing increased NO3 radical concentrations to higher solar activity is chemically incorrect, as NO3 is rapidly photolyzed during daytime, and this explanation should be revised."*

Reply to Comment 10:

Thank you for allowing us to better explain our statement. As first, we change the word "solar activity" with "solar radiation". Then, the presence of possible wood burning compounds during summertime, although they are detected in a season when no heating is needed, might be due to burning of agricultural residue or, in general, biomass burning as shown in David et al., (2025) and previously demonstrated in Ferrero et al. (2018, 2021a, b). In addition to primary

BBOA compounds belonging to this cluster, we also take into account the possibility that oxidants – higher in concentration during summertime – might affect the atmospheric concentrations of such compounds, resulting in higher intensity of secondary products during the warm season. In this regard, as the samples are collected for 24 hours (change at midnight), we expect to collect aerosols influenced both by both daytime and nighttime chemistry, with the latter driven by radical NO_3. After your request, we revised the manuscript as follows (now lines: 455-463):

"Alongside the CHO and CHOS compounds, a considerable amount (that are 205 and 104 compounds, which represent 13.8 % and 6.5 % of the total compounds in BSOA cluster for MI and SKI, respectively), even with lower nTSI, are N-containing compounds detected in positive ion mode. Many of these were also listed in Zhang et al. (2023a), and attributed to wood burning (L4). Although the identification level is only 4 (unequivocal molecular formula), we hypothesize that these compounds are rising during summertime from oxidized BBOA. In this season, the oxidative capacity of the atmosphere is enhanced by higher solar radiation, which leads to higher concentrations of oxidants species both during daytime (mainly OH radicals and O_3*) and nighttime (*NO_3 *radicals). In this regard, due to the 24 hour time-resolution, a contribution of both daytime and nighttime oxidation is expected to alter the OA composition. The presence of BBOA during summer has been previously demonstrated (Ferrero et al., 2018, 2021a, b)."*

Comment 11: "*Lines 428-430: "Due to the large number of undetected compounds in the SKI-BSOA and in other clusters, the temporal pattern and the mix of both biogenic and anthropogenic SOA, we can only speculate that this cluster has a contribution due to VCP SOAs." This attribution appears highly speculative, as excluding biogenic and anthropogenic SOA does not necessarily imply a VCP origin. Please provide stronger evidence or rephrase this statement to better reflect the uncertainty***"**

Reply to Comment 11:

Thank you for highlighting the uncertainty of this speculation. The cluster labeled 'MI–Summer B/ASOA' includes about 900 compounds showing higher intensities during the summer period. Among these, 46% were detected only at the urban site (i.e. site-specific compounds), while 22% were also assigned to the SKI-BSOA cluster. The presence of matches (L4) with compounds of biogenic origin, including some not assigned to the agricultural site, suggests the influence of biogenic emission sources or sources emitting similar volatile organic compounds that can then further react in the atmosphere. For example, monoterpenes (e.g. limonene) is known to be emitted in indoor environments as volatile chemical products (VCPs) from cleaning products and air fresheners (Carslaw and Shaw, 2022; McDonald et al., 2018; Sarwar et al., 2004; Singer et al., 2006; Steinemann, 2016). An additional compound found in indoor environment (García et al., 2007; He et al., 2018) is tributyl phosphate ($C_{12}H_{27}O_4P$), commonly used as flame retardant, industrial solvent, plasticizer, and antifoaming agent, hence a VCP par excellence. Our HCA approach shows a summertime-peaking of tributyl phosphate (L4) at the urban background site only, which populates the MI-Summer B/ASOA cluster. In this respect, it noteworthy that recently Zhou et al. (2025) demonstrated that the sources of VCPs in the atmosphere are rapidly changing showing that indoor environments contribute significantly to the levels of outdoor volatile compounds implying that indoor-to-outdoor emissions significantly contribute to urban VCP levels, rivalling traditional urban sources, e.g., power generation and biomass burning. The co-presence of these compounds let us speculate a common provenance in the atmosphere, suggesting a role—although not a dominant one—of VCPs. Based on this, we modified the manuscript at current lines 473-488:

"*However, more than 40 % are features not detected at SKI, of which 70 % are detected in positive mode, like* $C_9H_{20}O_4$ *and* $C_{13}H_{24}O_4$*, which instead are found in Qi et al. (2019) in a urban site in Zurich and apportioned to cigarette smoke OA and cooking OA, respectively. Because of this strong mix of both biogenic and anthropogenic source assignments, we labeled this cluster as "MI-Summer B/ASOA". Although terpenes are traditionally considered volatile organic compounds of predominantly biogenic origin, it is well established that fragranced consumer products, including cleaning agents, air fresheners, and personal care products, can contain and emit these compounds (Carslaw and Shaw, 2022; McDonald et al., 2018; Sarwar et al., 2004; Singer et al., 2006; Steinemann, 2016). In parallel, this cluster includes* $C_{12}H_{27}O_4P$*, corresponding to tributyl phosphate (L4), which does not exhibit a similar seasonal pattern at the rural site. Tributyl phosphate is commonly used as a flame retardant additive, solvent, plasticizer, and antifoaming agent. It has also been reported in aerosol samples collected in indoor environments, such as residential settings and transportation microenvironments (García et al., 2007; He et al., 2018). The co-occurrence of this mixture of compounds suggests a contribution from volatile chemical products (VCPs) and, more broadly, from compounds emitted in indoor environments that undergo transformation and diffusion into the urban atmosphere. In this respect, it noteworthy that recently Zhou et al. (2025) demonstrated that the sources of volatile organic compounds in the atmosphere are rapidly changing showing that indoor environments contribute significantly to the levels of outdoor volatile compounds implying that indoor-to-outdoor emissions significantly contribute to urban VCP levels, rivaling traditional urban sources, e.g., power generation and biomass burning.*"

Comment 12: "*Many of the molecular formulae the authors have found in their chamber experiments were found at both MI and SKI sites, mainly attributed to BSOA clusters, likely due to the increasing availability of H2SO4 during summertime. Nevertheless, most of the S-containing compounds attributed to SKI-Agricultural activities are not detected at MI site. Thus, we speculate that isomers with these formula, such as C4H8O8S, C8H16O8S, C16H26O3S, C7H12O7S (L4), could be attributed to agricultural tractors emissions***". ***The attribution here is unclear and potentially contradictory. Please clarify whether identical molecular formulas appear in multiple clusters or whether different isomers with the same formulas are classified differently and provide justification or references for attributing these compounds to agricultural tractor emissions*."

Reply to Comment 12:

Thank you for letting us to clarify this point.

First, our analytical setup enables the discrimination of not only isobars but also isomers. Features with the same mass-to-charge ratio (and thus the same molecular formula) can be distinguished based on their different retention times on the C18 reversed-phase chromatographic column prior to Orbitrap MS detection. Throughout the manuscript, when we refer to a molecular formula or assign a tentative compound name using the term "isomer," we indicate either: (i) that the compound has been identified using an analytical standard, but the specific feature under discussion does not correspond to that standard, or (ii) that no analytical standard is available and the identification is at level 4 (L4). In both cases, the term "isomer" is used to explicitly acknowledge this uncertainty.

Second, the same molecular formula may occur across multiple clusters, highlighting the importance of distinguishing between isomers. These features cannot correspond to the same compound, as individual isomers are characterized by distinct retention times. Accordingly, when comparing the two sites and assigning a given compound, we refer to the same isomer, defined by both identical molecular formula and retention time.

Third, 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" and Blair et al., (2017) findings. 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 this 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 it 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 (level 4, 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 Aerosolomic database, in order to more confidently link compounds to specific sources.*"

Comment 13: **"***Lines 461-463: "Moreover, observing the relation between the chromatographic retention time and the molecular mass, we infer that a subset of these features is likely due to dimers from high-NOx terpene oxidation Thoma et al. (2025)." Please check and standardize the reference formatting throughout the manuscript***"**

Reply to Comment 13:

Thank you for highlighting this typo. We have corrected in the manuscript at current line 524.

Comment 14: ***"****Lines 508-510: "Figure 5 illustrates the contribution to the monthly nTSI of each cluster at both sites. As expected, during wintertime the nTSI explained by the site-specific compounds (in darker colors) is lower than in the other seasons." Please clearly indicate in the figure legend which colors correspond to site-specific compounds, as this is not currently evident.****"***

Reply to Comment 14:

We have changed the legend adding the darker colors next to the light colors to let the reader to better understand the caption of Figure 5.

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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.

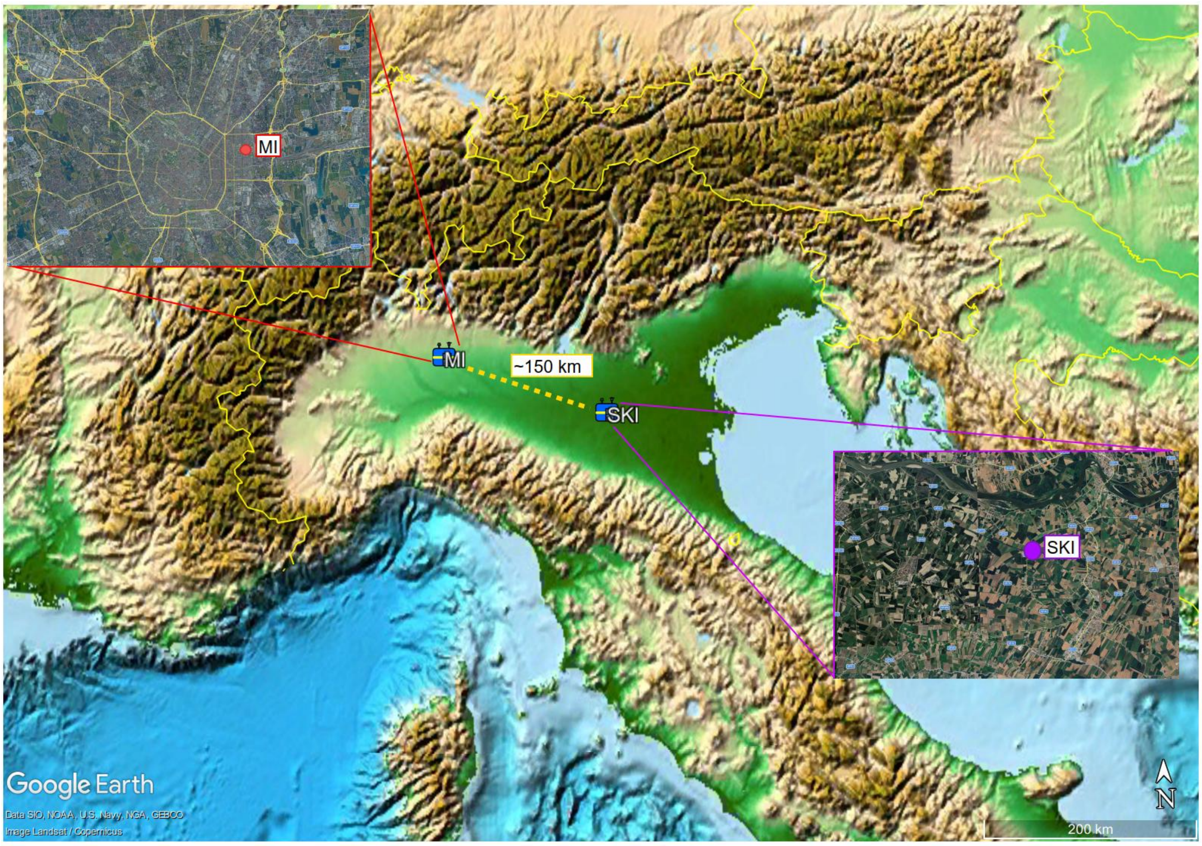

Figure S1: Map of Northern Italy. The Po Valley area is clearly visible, including the orography that often prevent incoming air masses able to abate the high aerosol concentrations that affect the basin. In the map the location of the two sampling sites considered in this work are also shown: MI (the 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. |ΔOC| < 2 μg m^{-3} and |Δ 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).*"

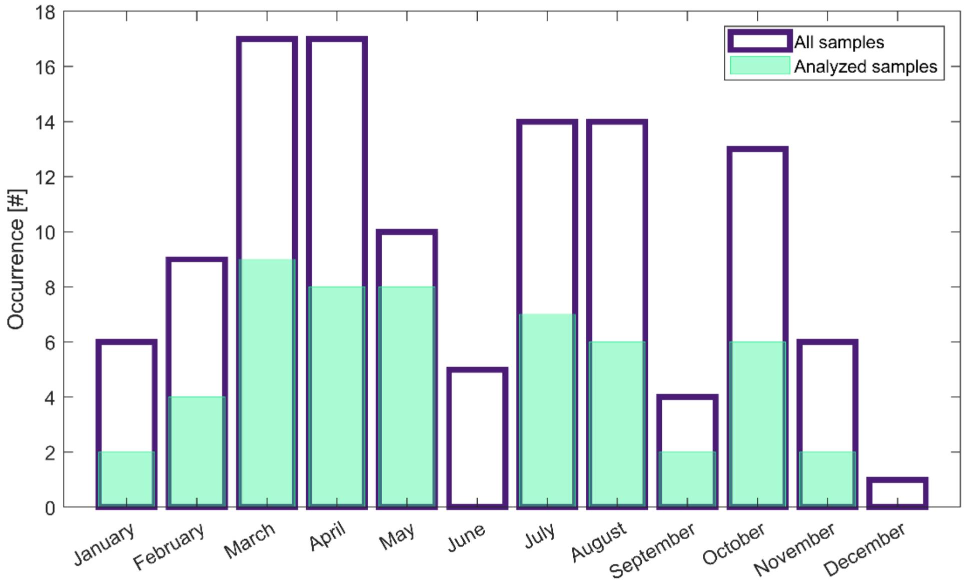

Figure 2: *Frequency histogram of samples (collected on the same day) that meet the criteria to be defined as 'similar samples,' grouped by month. The blue bars represent the entire dataset of samples collected throughout the year, whereas the green bars indicate the pairs of samples that were actually extracted and analyzed in this study.*

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