

We thank all the reviewers for their evaluation of the manuscript, and for their valuable and constructive feedback. Referee comments are given in black italics and the replies to the individual comments are directly added below them in regular black typeset. Changes made in the manuscript are in blue and marked with underlines. Page and line numbers refer to the original manuscript text.

Responses to Comments by Reviewer #1

This manuscript investigates the molecular characteristics of combustion-derived organic aerosols (OA) and their contribution to PM_{2.5} oxidative potential (OP) in Weifang, a medium-sized city in the North China Plain. The authors combine FIGAERO-CIMS molecular characterization, PMF source apportionment, hierarchical cluster analysis, and dithiothreitol (DTT)-based oxidative potential measurements to identify OA components associated with coal combustion, biomass burning, vehicle emissions, and secondary formation. The manuscript argues that combustion-related OA, particularly high-DBE aromatic compounds, plays a dominant role in enhancing PM_{2.5} oxidative potential. The monitoring technique is novel as the authors integrated online CIMS, PMF, and OP measurements. Although the topic is relevant and the dataset contains potentially valuable molecular information, the major scientific claims rely heavily on correlations, indirect source assignments, and assumptions about molecular toxicity without sufficient experimental validation. The work would be improved if further convincing mechanistic evidence can be provided besides the currently represented analytical evidence.

Major Comment 1: *The manuscript repeatedly claims that combustion-derived OA enhances PM_{2.5} OP and identifies high-DBE compounds as key contributors. However, most evidence is based on statistical correlations between FIGAERO-CIMS signals and DTT-based OP measurements. Correlation between molecular abundance and OP does not establish that these compounds are chemically responsible for oxidative activity. There may be covary issues due to common emission sources or atmospheric processing*

pathways. For example, the manuscript states that high-DBE compounds, likely aromatic derivatives, are major contributors to OPv based on enhanced correlations between DBE and OP. However, DBE is only a structural indicator and cannot distinguish among redox-active quinones, nitroaromatics, polycyclic aromatic hydrocarbons, sulfur-containing compounds, or thermally generated fragments. Without targeted quantification of representative compounds, authentic standard testing, or fractionation experiments, the proposed molecular drivers remain speculative and may be an overestimation.

Response: Thanks for reviewer's comments. This study aims to investigate how organic molecular compositions contribute to the OP in a medium-sized city in the North China Plain (NCP), **an area where the most of population in NCP residence, however, the chemical components, toxicity, and sources of PM_{2.5} in these regions have been scarcely investigated** in previous studies.

We applied two multidimensional data-reduction techniques (HCA and PMF) to both offline organic and online PM_{2.5} chemical component data to characterize OA compositions and their variable concentrations, as well as to examine their correlation with OP across different groups to identify potential sources. We fully acknowledge that the correlations between OA and OP, even when validated by OP experimental tests for some selected compounds, cannot entirely avoid uncertainties caused by the covariance of OA compounds with different OP reactivities. Nevertheless, the correlations between specific OA compounds, sources and OP provide valuable insights into the likely origins of these compounds in this understudied yet populated NCP city.

Consequently, similar correlation-based approaches are widely applied as a preliminary estimation of OA toxicity characteristics, particularly for OP analyses in Chinese cities, where numerous components may act synergistically. For example, OP activation between some OA species (e.g., PAHs and BFRs) was investigated in Guangzhou (Zhang et al., 2025); OP was found to be more correlated with Mn, K, and nitrate in six Chinese cities (Ye et al., 2024), and OP was found to be driven by

carbonaceous aerosols in Beijing (Li et al., 2024). Correlations between PM sources and OP have been reported to help pinpoint dominant local or regional toxic sources for OP, such as indoor biomass burning (Zhang et al., 2024a), residential coal combustion (Luan et al., 2022; Li et al., 2019a), and source apportionment sources, especially for primary combustion sources (Kim et al., 2025; Cao et al., 2026).

We understand that previous studies have typically focused on PM_{2.5} inorganic components or a limited selection of OA compounds in correlation-based OP analyses, especially in the NCP region. To address the gap between OP and the numerous OA species driving PM toxicity, this study presents over 1,000 OA compounds. By grouping them via HCA and correlating them with major PM_{2.5} sources, we draw attention to heavy air pollution in medium-sized NCP cities. Furthermore, we investigated OP activity across OA groups and sources to screen for OP-modulating factors and identify priority sources for control.

Therefore, we believe our study have elucidated the correlations between OP and OA chemical components, as well as their origins in medium-sized cities within the NCP, which feature high population densities but have received much less scientific attention. Building on these findings, future research should further explore the underlying toxicological mechanisms. Ultimately, our results provide a valuable reference for developing efficient control strategies aimed at these key emission sources.

As suggested by the reviewer, to better elucidate the implication of our study and and clarify the limitation of correlation-based approach, we have carefully revised the manuscript as follows:

Line 610-614:

Two distinct pollution episodes accounted for the peak OP_v levels (Fig. 1b). The episode on January 12 was characterized by substantial secondary inorganic contributions (50 %) and levoglucosan (0.59 $\mu\text{g m}^{-3}$; 1.9 % of OA), indicative of strong secondary aerosol formation and biomass burning emissions. While the increasing proportion of secondary inorganics tends to suppress OP_m, the peak OP_v level was likely impacted by the high contribution of biomass burning suggested by elevated levoglucosan.

Line 622-624:

Such a similarity indicates that OP driven by OA during biomass burning events could rival the toxicity levels driven by transition metals during firework events.

This similarity suggests that OA-driven OP during biomass burning events may reach OP levels comparable to those driven by transition metals, which are widely recognized as key contributors to OP in Weifang.

Line 117-130:

Identifying OP-active OA compounds is difficult due to the complexity of the composition, functional groups, and structures of the tens of thousands of OA compounds. Therefore, correlation-based methods have commonly been applied to identify potential candidate OP-active compounds and their sources in China (Zhang et al., 2025; Ye et al., 2024; Li et al., 2024). These methods provide valuable information regarding key sources and further highlight key compounds for toxicological studies to investigate their structures and biological responses, enabling policymakers to formulate effective control policies. For example, correlations between PM sources and OP have been used to help pinpoint dominant local or regional toxic sources of OP, such as indoor biomass burning (Zhang et al., 2024a), residential coal combustion (Luan et al., 2022; Li et al., 2019a), and source apportionment sources, especially for primary combustion sources (Kim et al., 2025; Cao et al., 2026).

***Major Comment 2:** The identification of coal combustion-, biomass burning-, and vehicle-related OA compounds is primarily based on correlations between molecular formulas and PMF-derived source factors. This approach has substantial uncertainty because PMF factors themselves are derived from bulk chemical tracers rather than direct OA molecular measurements. The assignment of sulfur-containing compounds to coal combustion is particularly questionable. The manuscript argues that increased sulfur oxidation states indicate coal combustion-related chemistry, but atmospheric*

oxidation and heterogeneous processing can generate similar sulfur-containing products from multiple sources. Likewise, compounds correlated with biomass burning are interpreted as combustion tracers, but biomass burning and coal combustion are known to co-occur in the North China Plain, making source separation difficult. The moderate correlation of levoglucosan with biomass burning is acknowledged by the authors, but the manuscript does not adequately quantify the uncertainty introduced by mixed combustion sources.

Response: We agree with the reviewer that there may be uncertainties in linking the PMF-based source apportionment of bulk PM_{2.5} to the source identification based on OA molecular composition in this study. We want to clarify that, in this study, **the PMF analysis was used to help identify sources that were consistent with those derived from OA-HCA, rather than to quantitatively compare the source contributions between the two methods.**

Meanwhile, wintertime PM_{2.5} in Weifang is largely derived from primary emissions, especially from biofuel combustion, which emits a large fraction of organic matter, in contrast to megacities in the NCP such as Beijing. Therefore, OA and PM_{2.5} share several common sources in Weifang during the sampling period. This is also supported by the MEIC emission inventory, which suggests that more than 90% of primary OC originates from biofuel burning. In addition, regional transport further enhances this co-elevated influence on both total PM_{2.5} and carbonaceous aerosols due to residential coal burning in NCP (Li et al., 2020).

Regarding the reviewer's point that organic tracers such as sulfur-containing organics may also originate from heterogeneous reactions, and that biomass burning and coal combustion can be co-emitted in the NCP region, we fully acknowledge that such uncertainties cannot be neglected given the the limitation of current measurement setting and the analysis using source apportionment methods. Therefore, in the revised manuscript, we have rephrased the content about **the indicative meaning of these tracers and added more discussion of the uncertainties for both organic and inorganic tracers**, as follows:

Line 300-306:

For typical medium-sized northern cities in Shandong Province like Weifang, atmospheric PM_{2.5} mass concentrations are predominantly influenced by combustion sources, through pathways including both primary emissions and regional transport. Accordingly, the present study focuses on the distinction between PM_{2.5} source apportionment based on combustion sources and the source classification of OA, simultaneously.

Line 478-481:

However, sulfur-containing organics may also form via heterogeneous reactions in the NCP region (Le Breton et al., 2018); thus, a combined influence of coal combustion and heterogeneous reactions cannot be fully excluded.

Major Comments 3: The manuscript combines several established methods, including FIGAERO-CIMS molecular identification, PMF source apportionment, hierarchical clustering, and DTT assays. However, the conceptual advance is unclear. Previous studies have already demonstrated that oxygenated organic aerosols, combustion-derived aromatic compounds, and nitroaromatic species influence aerosol oxidative potential. The manuscript does not introduce a new mechanistic framework, a new molecular toxicity indicator, or a predictive model that substantially improves understanding beyond previous work. The authors concluded that combustion-derived OA contributes to PM toxicity simply based on existing literature. To justify publication in a high-impact journal, the authors need to demonstrate what fundamentally new knowledge is obtained from this dataset.

Response: We would like to clarify that, rather than developing and representing a novel analytical methods to identify highly toxic individual OA compounds, we centered our attention on the OA characteristics in the world's most densely populated region: the North China Plain (NCP), which has a population exceeding 340 million (Kulmala et al., 2021). Specifically, **we targeted medium-sized cities (e.g., Weifang), which have been scarcely investigated compared to megacities (e.g., Beijing).**

As stated in the revised manuscript, most previous studies on OA composition and its health impacts in the NCP have focused on megacities like Beijing and Tianjin (Ma et al., 2018; Zheng et al., 2026; Zhou et al., 2019). Consequently, the key toxic components and underlying health impact mechanisms of OA in broader NCP regions, particularly in medium-sized cities, remain poorly constrained. Considering that over 80% (> 260 million) of the NCP population resides in over 50 medium-sized cities similar to Weifang, **this research gap must be urgently addressed**. This is especially critical given the broader context of decreasing PM_{2.5} (from 72 $\mu\text{g m}^{-3}$ in 2013 to 34 $\mu\text{g m}^{-3}$ in the 2020s (Chen et al., 2024)) and declining oxidative potential (OP) (from 150 $\text{pmol min}^{-1} \mu\text{g}^{-1}$ in 2015 to 24 $\text{pmol min}^{-1} \mu\text{g}^{-1}$ in the 2020s (Zheng et al., 2026)) in the Chinese megacities. Therefore, it remains unknown whether PM_{2.5} and OP in medium-sized cities have declined as sharply as in Beijing, which has enacted strict regulations on residential combustion.

Here, we report that severe PM_{2.5} pollution events were frequently observed in Weifang, with seven identified episodes during which hourly levels exceeded 200 $\mu\text{g m}^{-3}$ and peaked at 985 $\mu\text{g m}^{-3}$. This indicates that despite the general decline of PM_{2.5} in megacities like Beijing (Chen et al., 2024; Dai et al., 2023; Chen et al., 2025), autumn and wintertime air pollution remains substantial across the broader NCP, especially in medium-sized cities.

Building on this, the current study focuses on these high-PM_{2.5} episodes to determine the dominant OA components, the differences between pollution and clean periods, and the potential OP-active OA compounds along with their corresponding sources. This information is crucial for understanding the broader implications of OA pollution and toxicity, ultimately aiding policymakers in developing effective control strategies. Bridging this knowledge gap is vital for accurately evaluating the health risks to populations in these densely populated, medium-sized areas in the NCP region.

Major Comment 4: The interpretation of oxidation state and the role of oxygen on OP is internally inconsistent. The manuscript reports that OP_v increases with increasing O ratio, while OP_m increases initially and then decreases at higher O ratios. The authors

attribute this to highly oxygenated OA becoming less toxic during haze evolution. However, this explanation is not sufficiently supported. Oxidation state alone does not determine oxidative potential. Aging can both generate and remove redox-active structures depending on precursor composition and reaction pathways. The manuscript does not distinguish between increased oxygenation caused by functionalization and oxygenation caused by fragmentation. Additional evidence, such as Van Krevelen analysis combined with molecular-level identification of redox-active species, is required.

Response: We understand the reviewer's concern and fully acknowledge that separating functionalization from fragmentation is not possible with our current offline CIMS method. However, we would like to clarify that, instead of concluding definitively that the lower mass-normalized OP is caused by aging, this study presents the mass-normalized OP and volume-normalized OP as a function of oxidation state, O:C ratios, and DBE values to indicate a potential reason for this phenomenon.

Specifically, the lower OP_m coincided with strongly enhanced abundances of low-molecular-weight compounds during the haze period (e.g., diacids and polyols, as previously reported in the NCP), along with higher O:C ratios and oxidation states. While the formation of these low-OP_m compounds is validated by our DTT tests, their formation pathway remains uncertain, as it may occur either through OA fragmentation during aging or through heterogeneous reactions. These compounds lead to the apparently lower OP_m associated with higher oxidation states and O:C ratios. Therefore, **the presence of these compounds does not simply demonstrate that aging reduces OP activity.**

To clarify this point, we have revised the manuscript as follows:

Line 666-679:

the low molecular weight highly oxygenated OA (e.g. diacids and polyols) likely formed in the extremely haze periods may exhibit lower OP activity in Weifang City, which is also validated by our test experiment using standard chemicals. The apparently lower OP_m associated with higher oxidation states and O:C ratios were likely caused by

the formation of such OA compounds via fragments or heterogeneous reactions. Our findings are consistent with the spatial variations reported by Liu et al. (2024a), who showed that while highly oxygenated OA dominates OP activity in megacities like Beijing, primary emitted or moderately oxygenated OA compounds play a more important role in driving OP_m in rural areas of the NCP. It should be noted that this phenomenon should not be simply interpreted as evidence that the aging process reduces OP-activity. Rather, it suggests that low molecular weight acids and aldehydes, which have low OP_m, likely influence the overall OP_m of OA during haze periods.

Additionally, to better elucidate the variation of OP_m with compounds within homologous series, we have also added Kendrick mass defect plots and their relationship with OP_m to the supplementary information, as suggested by the reviewer. We analyzed commercial standard compounds with different OP_m, including fulvic acid, D(-)-salicin, ethoxycarbonylmethyl ethyl phthalate, and nitroaniline (75 – 490 pmol min⁻¹ μg⁻¹), as well as compounds with relatively low OP_m, including glyceric acid (C₃H₆O₄, 8.8 pmol min⁻¹ μg⁻¹) and malic acid (C₄H₆O₅, 22 pmol min⁻¹ μg⁻¹). During the haze episode from January 6 to January 12, the signal intensities of less OP-active compounds, such as C₃H₆O₄ and C₄H₆O₅, increased from 0.07% to 0.12%, whereas those of highly OP-active compounds, such as C₁₄H₁₂O₈ and C₁₃H₁₈O₇, decreased from 0.09% to 0.06% and 0.08% to 0.07%, respectively.

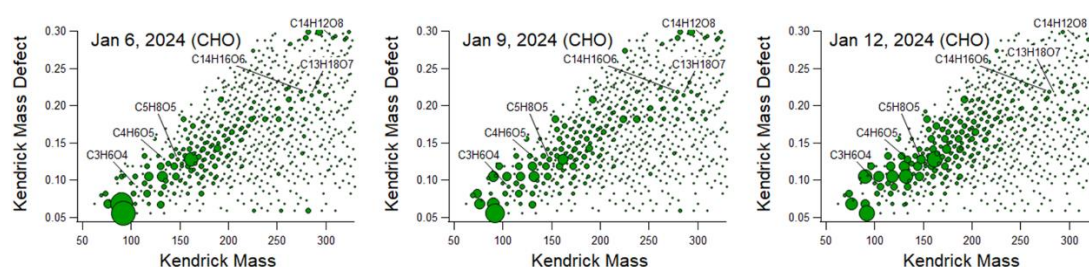


Figure R1 (Figure S13). Kendrick mass plots of the CHO compounds on January 6, 9, and 12, 2024. The compounds tested with the DTT assay are marked. The sizes of the markers are proportional to their relative signal intensities of CHO_X

Major Comment 5: *The manuscript lacks stronger validation linking ambient OA composition to health relevance. The DTT assay provides a chemical measure of oxidative potential, but the manuscript interprets OP changes as indicators of aerosol toxicity. This connection requires caution. DTT activity represents only one oxidative*

mechanism and does not directly represent cellular toxicity, inflammatory response, or health impacts. The conclusions should be limited to oxidative potential rather than implying broader toxicological effects. Ideally, the study should include complementary oxidative assays or biological responses to support stronger health-related claims.

Response: We thank the reviewer for this valuable comment. We agree that DTT activity reflects only one oxidative mechanism and does not directly indicate cellular toxicity. The manuscript has been revised accordingly to soften the toxicity-related statements as suggested.

To better illustrate the core meaning of this part, we have modified the following text in the revised manuscript.

Line 33:

However, characterizing OA composition, the ~~toxicity~~ potential health impacts, and sources remains challenging.

Line 44:

~~To evaluate toxicity~~ Additionally, we determined the oxidative potential (OP) in Weifang.

Line 624-625:

To accurately compare OA activity, Feb 11 was excluded from further analysis, as its ~~toxicity~~ oxidative potential was dominated by firework metals rather than OA.

Line 770-771

indicating that a minority of high-abundance compounds drive OA oxidative potential.

Nevertheless, oxidative potential has been widely used as an important metric for characterizing the toxic effects of ambient fine particulate matter, analogous to health risk assessment models for carcinogenic elements. Previous studies have shown that OP exhibits stronger associations with certain health endpoints than mass concentration alone, and it has accordingly been proposed as a key indicator of the potential toxicity of inhaled particulate matter (Salana et al., 2024; Weichenthal et al., 2016; Abrams et al., 2017; Delfino et al., 2013; Korsiak et al., 2022). For instance, short-term OP exposure exhibited stronger correlations with multiple cardiorespiratory health endpoints (e.g., forced expiratory volume, asthma, and rhinitis), than PM_{2.5} mass

concentration (Bates et al., 2019). whereas long-term exposure may lead to additional health effects such as metabolic disorders, reproductive diseases, and inflammation (He and Zhang, 2023).

Additionally, in another unpublished study conducted at the same sampling site, we investigated the relationship between OP exposure and the biological responses of BEAS-2B cells (cellular ROS response) using PM_{2.5} samples collected in Weifang city as suggested by reviewer. In that study, BEAS-2B cells were exposed to the same mass concentration but at different OP_m value levels. Samples were divided into the control (without PM exposure), low OP_m, and high OP_m groups based on OP_m values, and cellular ROS levels were then measured using the DCFH-DA method by confocal laser microscopy. The results showed that the high OP_m group exhibited higher cellular ROS concentrations, which is indicated by fluorescence intensity than the low OP_m group (Fig. R2). Therefore, we can safely propose that OP during our sampling period can serve as an important indicator of the external-exposure impacts of PM_{2.5} in Weifang.

Following this rationale, the present study adopted and extended this framework, while acknowledging that OP does not directly represent health effects.

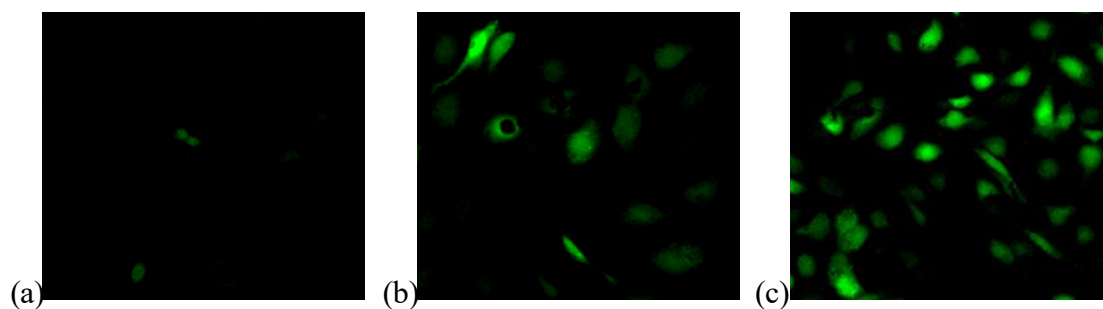


Figure R2. Cellular ROS concentration based on BEAS-2B cells' exposure to different OP_m values' PM_{2.5}. (a) control group, without PM_{2.5} exposure; (b) low OP_m PM_{2.5} exposure, averaged OP_m = 24 pmol min⁻¹ μg⁻¹; (c) high OP_m PM_{2.5} exposure, averaged OP_m = 46 pmol min⁻¹ μg⁻¹.

Minor comments

Minor Comment 1: Lines 146–150 (Page 6): *The authors introduce the integration of*

FIGAERO-CIMS, OP assays, cluster analysis, and PMF source apportionment as the methodological framework. However, the rationale for combining these approaches is not sufficiently explained. The authors should clarify how each method addresses a distinct scientific question rather than simply providing parallel datasets.

Response: While previous studies have been conducted, OA composition, sources, and oxidative potential in medium-sized cities of the NCP remain poorly constrained. To fill this gap, we integrated PMF source apportionment with OP assays and FIGAERO-CIMS coupled with HCA to identify the origins of highly OP-active compounds. This multi-method framework links bulk PM_{2.5} source apportionment to OA molecular-level characterization, providing scientific evidence for targeted control strategies.

To better clarify this analytical framework, we have modified the following text to the revised manuscript:

Line 159-164. We integrated PMF source apportionment and OP assays, focusing specifically on the OA-dominated water-soluble components. Furthermore, molecular OA characterization via FIGAERO-CIMS was coupled with Hierarchical Cluster Analysis (HCA) to identify the specific origins of highly OP-active compound clusters. This multi-method framework links bulk PM_{2.5} source apportionment to molecular-level characterization.

***Minor Comment 2:** Lines 168–177 (Page 6): The sampling description lacks important QA/QC information. Although the authors state that “all data have undergone strict quality control,” specific details regarding field blank correction, filter storage conditions, extraction recovery, and possible sampling artifacts should be provided.*

Response: We have added the following information regarding to quality control.

Line 192-197. Three field blanks were also collected during the sampling period. After sampling, filters were wrapped in aluminum foil, sealed in individual bags, stored at –20 °C for 5 months, and subsequently analyzed in the laboratory. Method uncertainties and potential artifacts, including sample handling and storage, are described in our previous literature (Cai et al., 2023).

Minor Comment 3: Lines 204–223 (Page 7): The manuscript identifies 1630 compounds using FIGAERO-CIMS and applies semi-quantitative calibration based on levoglucosan and succinic acid. However, the uncertainty associated with applying only two calibration standards across a broad chemical space (m/z 120–500) should be discussed. The authors should provide an estimate of uncertainty introduced by this calibration approach.

Response: We used levoglucosan and succinic acid to classify compounds into two groups: those reacting with reagent ions near the collision limit and those reacting significantly below it. Levoglucosan represents the high-efficiency group, as it is reported to react with iodide near the collision limit (20 cps ppt⁻¹, (Lopez-Hilfiker et al., 2016)). These compounds are typically larger, multifunctional organics with sufficient binding energy to remain stable. Conversely, the latter group consists of compounds that form clusters easily dissociated in the instrument, such as simple, lower molecular weight carboxylic acids. We applied succinic acid to represent these lower molecular weight compounds, which tend to have lower charging efficiencies. Nevertheless, we have added this information to the revised manuscript to better elucidate the quantification and its uncertainties.

Line 225-228. And the calibrations were conducted with levoglucosan (C₆H₁₀O₅) and succinic acid (C₄H₆O₄). The former approaches the collision limit with I⁻, while the latter represents species that bind less efficiently with reagent ions.

Line 249-255. The reproducibility of this method is 9% for filter samples, based on our previous work (Cai et al., 2023). However, quantification uncertainties may be larger, as the collision limit was applied to most compounds; accurate uncertainties cannot be determined due to the lack of standards for all OA compounds. In previous literature, the uncertainty for absolute concentration using a similar method was estimated to be approximately ±50% (Ehn et al., 2014).

Minor Comment 4: Lines 212–220 (Page 7): The statement that CHO_x species can be regarded as oxygenated compounds because I⁻ ionization favors moderately

oxygenated OA requires more careful explanation. The authors should clarify the potential bias against highly oxygenated or less oxygenated compounds introduced by the ionization scheme.

Response: Iodide CIMS was found to be more sensitive to moderately oxygenated compounds compared to proton-transfer, nitrate, or amine-CIMS in the α -pinene ozonolysis system (Riva et al., 2019). Additionally, iodide CIMS captured the majority of the reacted carbon, suggesting broad sensitivity to most OVOCs. However, it was less sensitive to highly oxygenated compounds (containing more than 9 oxygen atoms in the α -pinene system) than nitrate-CIMS, and less sensitive to less polar compounds (containing fewer than 4 oxygen atoms) than proton-transfer CIMS. We have added the following statement as suggested:

Line 233-239

These CHOX species were considered as oxygenated species since I- ionization tends to select toward moderately oxygenated OA (Riva et al., 2019). Most oxygenated organics were found to undergo reaction with iodide in the α -pinene ozonolysis system. Meanwhile, highly oxygenated organics, such as ultra-low-volatility organic compounds (ULVOCs), and less oxygenated organics, such as PAHs, exhibited lower sensitivity.

***Minor Comment 5:** Lines 224–250 (Page 8): The DTT assay methodology is described, but the manuscript should clarify whether extraction efficiency was evaluated. Since the authors acknowledge that water-insoluble components, including EC, insoluble organics, and insoluble metals, were excluded (Lines 232–234), the potential impact of this limitation on total PM oxidative potential should be discussed more explicitly.*

Response: We acknowledge the limitation of using water to extract the OP-active compounds; however, this choice was based on water-soluble species, especially water-soluble organic carbon (WSOC), in particulate matter are key drivers of OP in urban environment (Bates et al., 2019), and FIGAERO-CIMS is more suitable for

characterizing oxygenated OA, which is typically water-soluble (Lopez-Hilfiker et al., 2014).

It should also be noted that the contribution of water-insoluble components may vary with season, regions, sources, and components. For example, approximately 80% of the OP of PM_{2.5} was contributed by water-soluble components in Atlanta (Gao et al., 2020), 77% in Fairbanks (Yang et al., 2024) and 65% in Shanghai (Wu et al., 2022). Meanwhile, several other studies have suggested an even higher contribution of water-insoluble components to total OP near the roadside (Tang et al., 2022; Zhang et al., 2024b) or for the coarse mode particles (Wang et al., 2023; Frezzini et al., 2022). Therefore, it is difficult to quantify the contribution of water-insoluble components to OP of PM_{2.5} in Weifang during our sampling period.

To make it clear, we have revised Line 232 as suggested.

Line 264-270. Therefore, it should be noted that water-insoluble components, including elemental carbon (EC), water-insoluble organics (e.g., humic acid) and insoluble metals, were not analyzed in the DTT analyses in this study. The influence of water-insoluble components on OP would be difficult to quantify, as it may vary across sites, seasons, particle sizes and sources (Gao et al., 2020; Yang et al., 2024; Wu et al., 2022; Tang et al., 2022; Zhang et al., 2024b; Wang et al., 2023; Frezzini et al., 2022).

Minor Comment 6: Lines 252–264 (Page 8): The HCA and PMF methodology requires additional statistical justification. The authors should provide sensitivity tests showing whether the six HCA clusters and selected PMF factor number remain stable under different clustering parameters or factor numbers.

Response: In this study, the hierarchical cluster analysis (HCA) was applied to the mass spectrometry data to simplify the dataset comprising a large number of individual observations (274 high-intensity compounds for 45 samples). Specifically, the Euclidean distances between compounds were calculated in a 45-dimensional space corresponding to the number of samples, and Ward's minimum variance method was used as the linkage criterion, merging the two candidate clusters that yielded the

smallest increase in total within-cluster variance (i.e., the minimum Ward distance) of the merged cluster.

Additionally, to evaluate the stability of HCA, we performed bootstrap resampling ($n = 1000$) using the Jaccard coefficient method implemented in the R package `fpc` (function `clusterboot`, (Hennig, 2007)). Mean Jaccard similarity values across the seven clusters exceeded 0.6, a threshold generally considered indicative of robust clustering, suggesting that the HCA results were acceptably stable overall. The only exception was Cluster D (Jaccard = 0.39), likely due to its compounds may share similar characteristics between secondary formation and primary emissions.

Table R1. Stability assessment of the hierarchical clustering solution based on bootstrap resampling ($n = 1000$)

Cluster	Jaccard_mean	Dissolved_count
A	0.64	193
B	0.65	379
C	0.67	180
D	0.39	851
E	0.89	39
F	0.74	209

To better elucidate the methodology, we have added detailed information in the revised Supplementary Information.

SI: [Euclidean distance](#) was used to quantify dissimilarities, combined with Ward's minimum variance method as the linkage criterion. [Euclidean distance is defined as the square root of the sum of squared differences between the time series of a pair of compounds, A and B, across all time steps. Ward's minimum variance method was employed as the linkage criterion; this approach merges the two candidate clusters that result in the smallest increase in total within-cluster variance \(i.e., the minimum Ward distance\) for the new merged cluster \(Priestley et al., 2021\).](#)

These identified clusters represent distinct OA molecular regimes and serve as the basis for subsequent analyses. [Additionally, we performed bootstrap resampling \(\$n =\$](#)

1000) to evaluate the stability of the HCA with the Jaccard coefficient method implemented in the R package *fpc* (function cluster boot; Hennig, 2007). An overall acceptable stability for the HCA results was observed (Table S2). Meanwhile, Cluster D, which was highly correlated with secondary sources, exhibited relatively lower stability, which may cause by a greater overlap in the OA characteristics this type and other primary emissions.

Regarding the PMF results, we have also included the 4-factor and 6-factor solutions in the Supplementary Information (Figure R3). The 4-factor solution merged the dust cluster into other factors, which may lead to significant uncertainty in the characterization of primary combustion emissions. Conversely, adding an extra factor resulted in a noisy factor characterized by high metal content, likely attributable to instrumental noise from the metal analyzer. Therefore, the 5-factor PMF solution was selected as the optimal model. We have also added a detailed discussion of this selection process in the Supplementary Information.

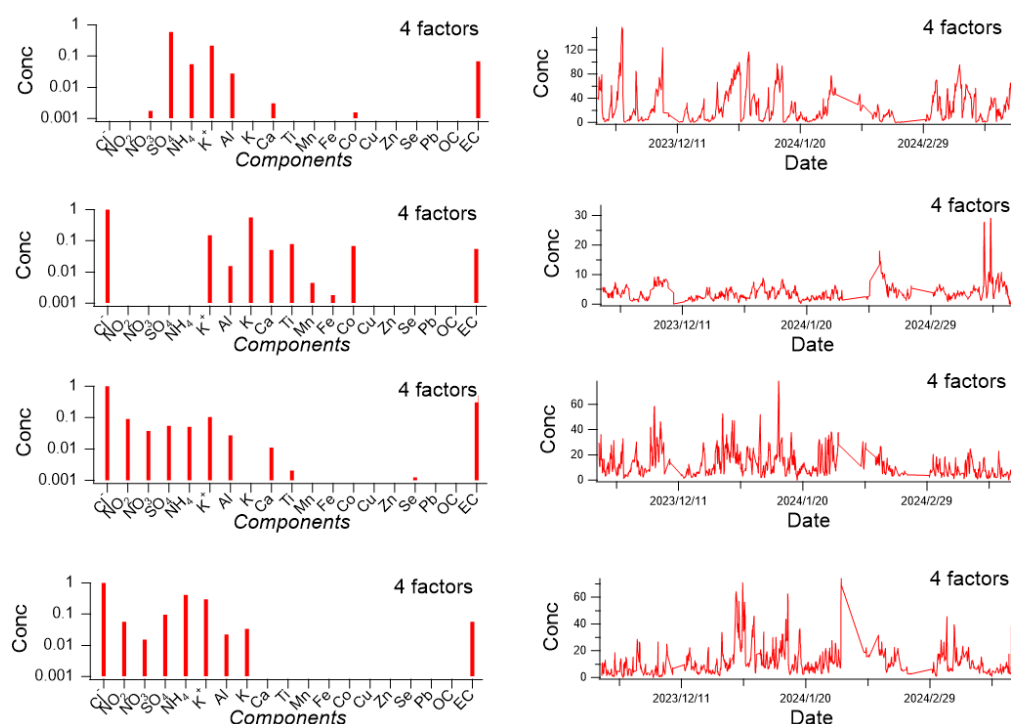


Figure R3 (Figure S5). Source profiles and time series of 4-factor PMF results

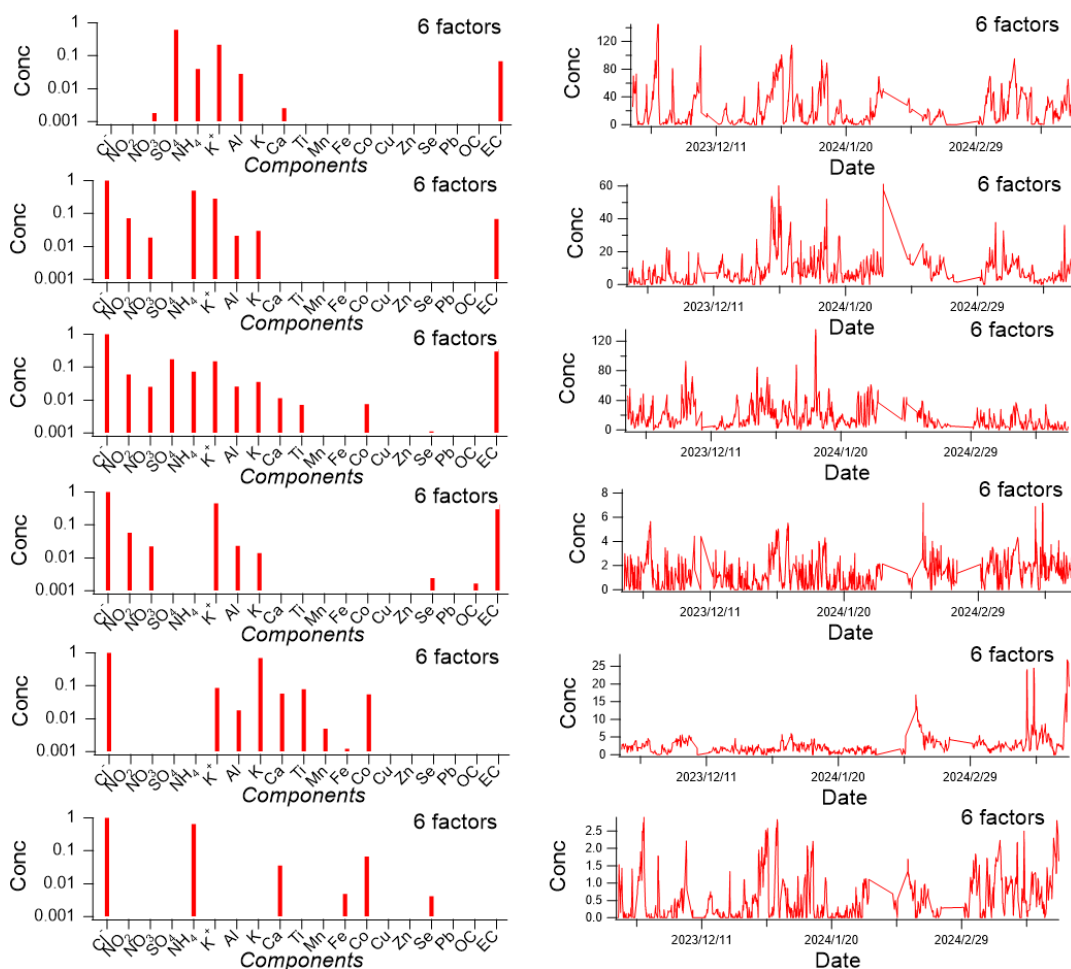


Figure R4 (Figure S6). Source profiles and time series of 6-factor PMF results

SI: [PMF was performed for 2 to 8 factors, and the 5-factor solution was selected due to its low \$Q/Q_{\text{exp}}\$ value and its ability to provide a robust interpretation of the factors. In the 4-factor solution, the dust cluster was mixed with other factors, leading to potentially high uncertainty in the characterization of primary combustion emissions. Meanwhile, the 6-factor solution resulted in a noisy factor characterized by metal elements, likely attributable to instrumental noise from the metal analyzer. Therefore, the 5-factor PMF solution was selected as the optimal results.](#)

Minor Comment 7: Lines 317–326 (Page 10–11): The comparison among Weifang, Beijing, and Wangdu is potentially valuable, but the authors should clarify whether differences in sampling periods, meteorological conditions, and sampling locations may influence the observed OA composition differences.

Response: The data compared in Figure 2 were collected during the heating season

(autumn and winter) at various sites across the NCP. For comparison, we selected autumn filter samples from Weifang to compare with those from Beijing and Wangdu. The Beijing samples were collected on the Beijing University of Chemical Technology (BUCT) campus in central Beijing. The Weifang samples were collected in residential areas near Shandong Second Medical University, which are influenced by vehicle emissions and residential sources. The Wangdu samples were collected in residential areas of Wangdu County, in Heibei Province where agricultural activities and vehicle emissions are dominant.

We acknowledge that differences in sampling years and local emission sources may influence the results. However, such a comparison remains valuable for highlighting the regional variations in OA pollution and toxicity across the NCP. Consequently, these findings underscore the importance of developing broader regional control strategies

To better present the sampling information and uncertainties for the comparison among different sites, we have added the following information in the revised manuscript:

[Line 367-370](#)

[Samples were obtained at the Beijing University of Chemical Technology \(BUCT\) campus in central Beijing, a residential site near Shandong Second Medical University in Weifang \(influenced by traffic and residential emissions\) and residential areas in Wangdu County \(dominated by agricultural and vehicular emissions\), respectively.](#)

Minor Comment 8: Lines 429–432 (Page 14): Figure 3 contains a large number of molecular formulas, but important marker compounds are not explicitly labeled. The authors should annotate representative compounds to improve interpretation and readability.

Response: In the original Figure 3, we presented all identified compounds. To improve interpretation, the revised Figure 3 displays only those compounds showing a relative high positive correlation with their corresponding sources ($r > 0.6$), highlighting the

representative compounds for the sources as follows:

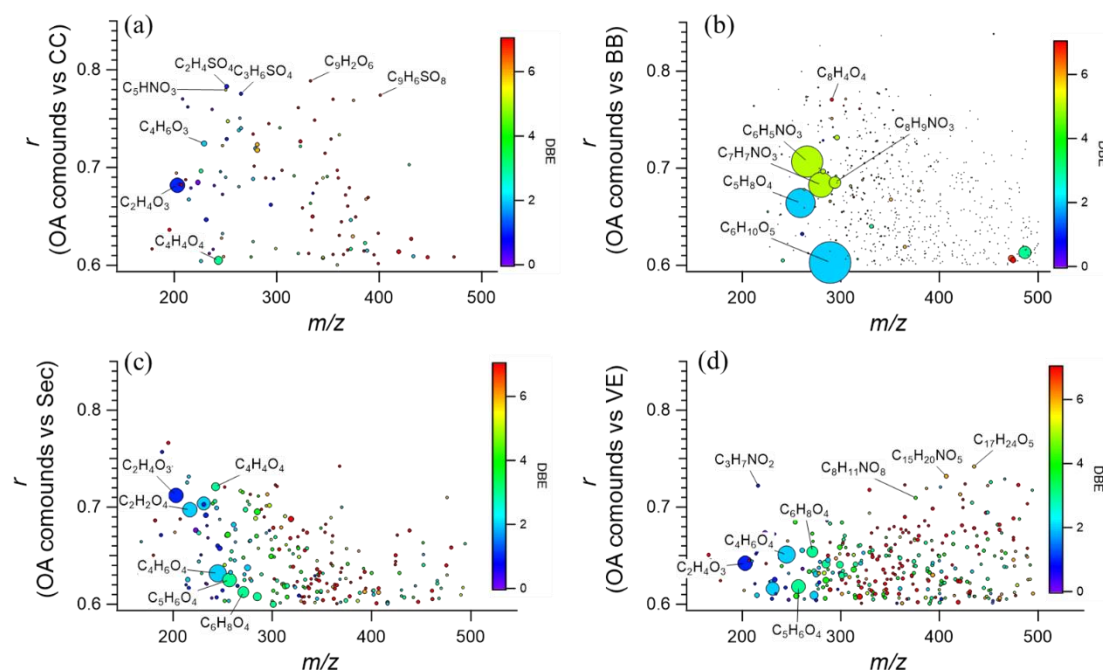


Figure R5 (Figure 3). Correlation coefficients between OA compound signals and different sources: (a) coal combustion, (b) biomass burning, (c) secondary inorganics, and (d) vehicle emissions ($r > 0.6$). Dot sizes are proportional to the square root of the signal intensity for the corresponding compounds, and dots are color-coded by the DBE number of each compound. Correlation coefficients for dust source are shown in Fig. S15.

Minor Comment 9: Lines 480–485 (Page 16): *The criteria for selecting high-abundance compounds (>0.05% of total CHOX signal and twice background level) should be justified. The authors should explain whether different thresholds significantly alter the HCA results.*

Response: The 274 selected compounds constitute the majority (56%) of the total CHOX signal intensity, meeting the criteria of exceeding 0.05% of the total signal and being at least twice the background intensity. The 0.05% threshold is generally consistent with previous work that selected compounds based on 10% of the maximum compound intensity (Daellenbach et al., 2024). Compared the maximum compound intensity threshold aforementioned, the actually threshold (8.2%) used in our HCA analyses is slightly lower (10%), thereby including even more compounds in this study.

We applied the threshold of twice the background level to account for offline FIGAERO-CIMS analyses (Cai et al., 2023), which largely measure the desorption of

semi-volatile or low-volatile compounds adsorbed on instrument surfaces. In this context, the background is defined by the second ramping process; therefore, valid compounds must exhibit signals at least twice as high as this background. A lower threshold risks including compounds influenced by thermal desorption artifacts.

Additionally, we applied a different threshold for maximum compound intensity (10%, (Daellenbach et al., 2024)), yielding 228 compounds, and found that the resulting compound categories were generally consistent with our previous results. In Figure R6, compounds identified in the previous HCA analysis (274 compounds) are marked with their corresponding colors, and their categories in the new HCA results (228 compounds) are indicated at the head of each category. This suggests that the categories are broadly consistent across the two runs.

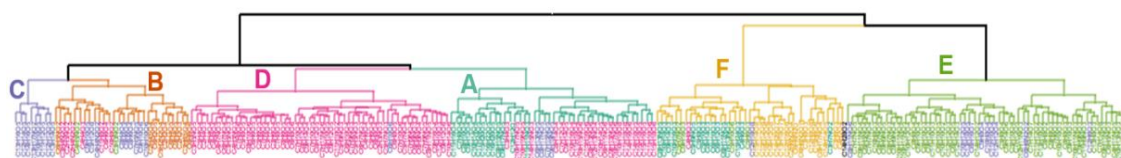


Figure R6. The comparison between the HCA results obtained with a compound selection threshold of >10% maximum compound intensity (indicated by the letter at the head of each category) and those from our previous study, which used a threshold of >0.05% of all OA compounds (indicated by the corresponding colors).

Minor Comment 10: Lines 513–518 (Page 17): The authors interpret Cluster F compounds as thermal fragments based on thermogram behavior. Since thermal decomposition may affect a broader range of FIGAERO-CIMS compounds, the authors should discuss whether other clusters may also be influenced by thermal artifacts.

Response: We calculated the average desorption temperature at which the maximum signal intensity of a compound is observed ($T_{\max}$) for each cluster, which serves as an indicator of compound volatility. The average $T_{\max}$ values for Clusters A to D are $100^{\circ}\text{C} \pm 27^{\circ}\text{C}$, $141^{\circ}\text{C} \pm 30^{\circ}\text{C}$, $112^{\circ}\text{C} \pm 28^{\circ}\text{C}$, $119^{\circ}\text{C} \pm 23^{\circ}\text{C}$, and $117^{\circ}\text{C} \pm 24^{\circ}\text{C}$, respectively.

However, Cluster F showed a much lower average $T_{\max}$ ($60^{\circ}\text{C} \pm 12^{\circ}\text{C}$) for most compounds, suggesting high volatility and possible influence of gaseous artifacts. The exception was two compounds with low molecular weights (e.g., $\text{C}_3\text{H}_6\text{O}_3$ and $\text{C}_4\text{H}_2\text{O}_4$)

but high $T_{\max}$ values exceeding 140°C, accompanied by biopeaks in the thermogram (Figure S5); since such low-molecular-weight compounds are expected to desorb at significantly lower temperatures, they are likely thermal fragments derived from larger precursors. Overall, the $T_{\max}$ distribution indicates that Cluster F is dominated by highly volatile compounds or fragments of larger molecules, unlike the compounds in other clusters.

Line 578-586:

Additionally, we calculated the desorption temperature at maximum intensity ($T_{\max}$) as an indicator of compound volatility. Except for the aforementioned low molecular weight compounds with high $T_{\max}$ over 140 °C (e.g., $C_3H_6O_3$ and $C_4H_2O_4$), the average $T_{\max}$ ($60 \pm 12^\circ\text{C}$) for the rest of the compounds in Cluster F was significantly lower than that of other clusters. This suggests that, compared to compounds in other clusters, the compounds in Cluster F are more likely to be fragments of larger molecules or highly volatile compounds that could be potential contaminants.

Minor Comment 11: Lines 815–823 (Page 28): The authors acknowledge that PMF and HCA cannot fully separate primary emissions from aging processes. This limitation should be emphasized earlier in the discussion because it directly affects the interpretation of source-specific OP contributions.

Response: We have addressed the discussion on methodological uncertainties in the revised manuscript.

Line 699-703:

However, it should be noted that, with online $PM_{2.5}$ chemical component and FIGAERO-CIMS analyses, we cannot fully separate primary emissions from their subsequent aging processes. This limitation exists because certain OA compounds may originate from primary emissions, aging processes or secondary formation.

Line 883-886:

High OP_m episodes cannot be explained by primary emissions alone, indicating that

secondary processes such as post-emission oxidation and SOA formation are also crucial to OP activity during the heating season in Weifang.

Minor Comment 12: Figures 5 and 7 (Lines 570–575 and 719–722): The figures contain extensive molecular-level information but lack sufficient guidance for readers. The authors should improve figure legends by defining abbreviations, explaining color coding, and identifying representative compounds.

Response: We have improved figure legends as suggested.

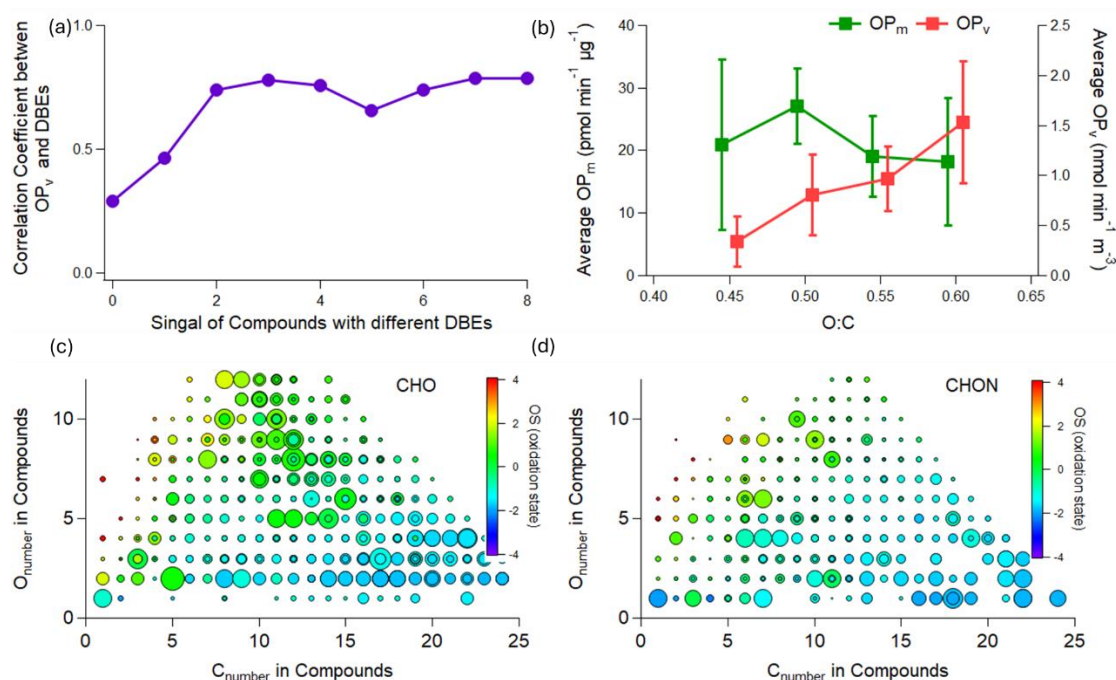


Figure R7. (Revised Figure 5). (a) Spearman correlation coefficients between OP_v and the total signal for compounds with different DBEs; (b) OP_m and OP_v variation across different O:C ratio for CHO compounds (c) Spearman correlation coefficients between OP_m and the signal intensities of CHO compounds with varying O and C numbers. Compound markers are color-coded according to their average oxidation state; (d) Spearman correlation coefficients between OP_m and the signal intensities of CHON compounds with varying O and C numbers. Compound markers are color-coded according to their average oxidation state.

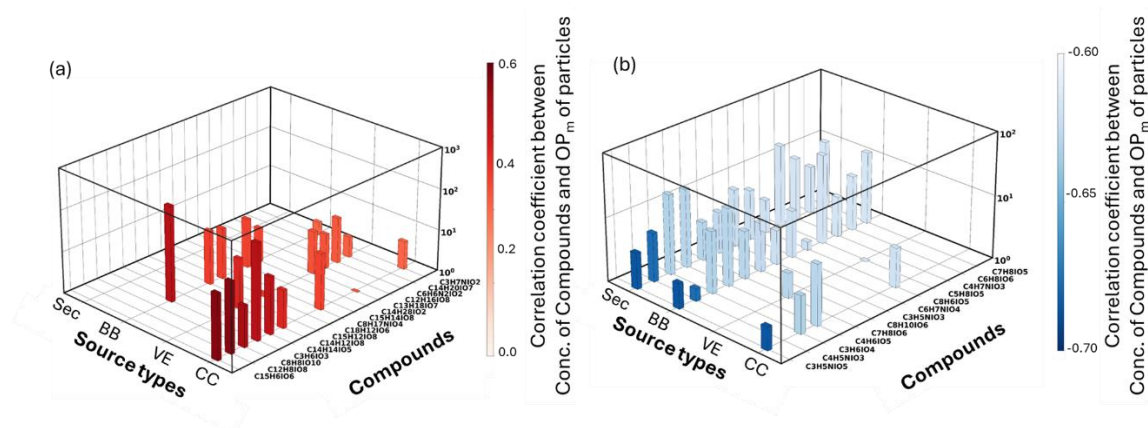


Figure R8 (Revised Figure 7). Spearman correlation coefficients of compounds significantly positively and negatively correlated with OP_m : (a) positively correlated compounds and (b) negatively correlated compounds. The x-axis shows the compounds that are significantly correlated with OP_m ; the y-axis represents the dominant source types, which are defined as the source with the positive coefficient for each compound, determined by the multiple linear regression model. Sec, BB, VE, and CC represent secondary sources, biomass burning, vehicle emissions, and coal combustion, respectively. The z-axis shows the coefficients for each source of corresponding compounds from the multiple linear regression, and the color scale represents the correlation coefficients with OP_m .

Reviewer 2

The manuscript by Cai et al. investigates the chemical composition, sources, and toxicity of organic aerosol and PM_{2.5} in a representative medium-sized NCP city, based on FIGAERO-CIMS mass spectrometer and DTT measurements in addition to source apportionment and data analysis methods including HCA, PMF, and MLR. The topic of this manuscript is interesting. However, the manuscript needs major improvement in the texts to support its statements, as a lot of the statements didn't show any data or figures. Besides, major revision on the discussions and interpretation are also needed before its possible publication on ACP. Please see my comments and questions below.

Response: We thank the reviewer for the constructive suggestions and the response to the comments have been shown below.

Major: The manuscript is about dominant contributors from different OA types to OP, but then the OA source apportionment is done through linking/correlating HCA clusters to PM_{2.5} PMF source factors with input data of BC, TC, metals, and secondary

inorganics. It would be make more sense to (try to) run PMF on the OA measured by FIGAERO-CIMS even though it's probably only ~40 filters in the 4 months campaign. This would be more convincing than the correlations of OA compounds with the PM2.5 source factors since for example OA cannot originate from secondary inorganics or dust. Besides, the authors have concluded several times (e.g. Line 302-307, Line 536-542) about dominant role based on the strong correlation coefficient, such as key OA role in PM2.5 and OC role in OPm. However, strong correlations only mean variations in A parameter are more closely associated with variations in B parameter, but does not necessarily imply about it being a key/dominant driver. Please avoid overinterpretation of the correlations for dominance. The manuscript may focus on what the manuscript and introduction says about the research question/gap on dominant contributors from different OA types to OP at this site.

Response: In this study, a total of 274 high-intensity compounds were used as input for the HCA analysis, which substantially exceeds the number of samples collected during the campaign (40 filters). The positive matrix factorization (PMF) model typically requires an input matrix composed of a sufficiently large number of samples to yield reliable solutions (Scerri et al., 2019); specifically, the number of samples should considerably exceed the number of chemical species. For example, previous studies have suggested that the number of chemically characterized samples should be at least 50 (Belis et al., 2019). In addition, the US EPA PMF 5.0 user guide notes that datasets with fewer than 100 samples are more likely to suffer from increased rotational ambiguity (Norris, 2008). Therefore, the PMF method was not applied to our offline FIGAERO-CIMS dataset in this study **considering the large number of chemical species and limited number of samples.**

Additionally, as the reviewer noted, OA is unlikely to originate from dust or inorganics, consistent with this, we did not observe strong correlations between OA clusters from HCA and the major dust-related species in the PMF analysis. Although OA is also unlikely to come directly from secondary inorganic species, the high positive correlations between Clusters A and D from HCA results and secondary inorganics

reported in the manuscript do not imply that these two clusters originate from a secondary inorganic factor resolved by PMF. Rather, they suggest that these two OA types co-varied with secondary inorganic species, likely reflecting OA formations from photochemical processing or heterogeneous reactions during haze events.

As for the research question/gap on dominant contributors from different OA types to OP at this site, we have replied in Reviewer 1's Major Comment 1 and we also presented here:

In this study, we targeted medium-sized cities (e.g., Weifang), which have been scarcely investigated compared to megacities (e.g., Beijing). As stated in the revised manuscript, most previous studies on OA composition and its health impacts in the NCP have focused on megacities like Beijing and Tianjin (Ma et al., 2018; Zheng et al., 2026; Zhou et al., 2019). Consequently, **the key toxic components and underlying health impact mechanisms of OA in broader NCP regions, particularly in medium-sized cities, remain poorly constrained**. Considering that over 80% (> 260 million) of the NCP population resides in over 50 medium-sized cities similar to Weifang, this research gap must be urgently addressed.

Here, we report that severe PM_{2.5} pollution were frequently observed in Weifang, with seven identified episodes during which hourly levels exceeded 200 $\mu\text{g m}^{-3}$ and peaked at 985 $\mu\text{g m}^{-3}$. This indicates that despite the general decline of PM_{2.5} in megacities like Beijing (Chen et al., 2024; Dai et al., 2023; Chen et al., 2025), autumn and wintertime air pollution remains substantial across the broader NCP, especially in medium-sized cities. Building on this, we focuses on these high-PM_{2.5} episodes to determine the dominant OA components, the differences between pollution and clean periods, and the potential OP-active OA compounds along with their corresponding sources. This information is crucial for understanding the broader implications of OA pollution and toxicity, ultimately aiding policymakers in developing effective control strategies. Bridging this knowledge gap is vital for accurately evaluating the health risks to populations in these densely populated, medium-sized areas.

Additionally, for the uncertainties in correlation between compounds and OP method, we have added the following discussions:

Line 117-130

Identifying OP-active OA compounds is difficult due to the complexity of the composition, functional groups, and structures of the tens of thousands of OA compounds. Therefore, correlation-based methods have commonly been applied to identify potential candidate OP-active compounds and their sources in China (Zhang et al., 2025; Ye et al., 2024; Li et al., 2024). These methods provide valuable information regarding key sources and further highlight key compounds for toxicological studies to investigate their structures and biological responses, enabling policymakers to formulate effective control policies. For example, correlations between PM sources and OP have been used to help pinpoint dominant local or regional toxic sources of OP, such as indoor biomass burning (Zhang et al., 2024a), residential coal combustion (Luan et al., 2022; Li et al., 2019a), and source apportionment sources, especially for primary combustion sources (Kim et al., 2025; Cao et al., 2026).

Specific:

Line 37. Is the overall air quality improvement compared to other cities at the same measurement period or same location but in previous years? Please specify.

Response: We took the air quality improvement in Weifang as an example of the North China Plain region. According to the Weifang Statistical Yearbook (2015 – 2023) and the China National Environmental Monitoring Center (CNEMC) data for urban Weifang (2023 – 2024), the yearly averaged PM_{2.5} concentration decreased dramatically from 78 $\mu\text{g m}^{-3}$ in 2014 to 33 $\mu\text{g m}^{-3}$ in 2024 (Figure S1).

To clarify it, we revise the following expression:

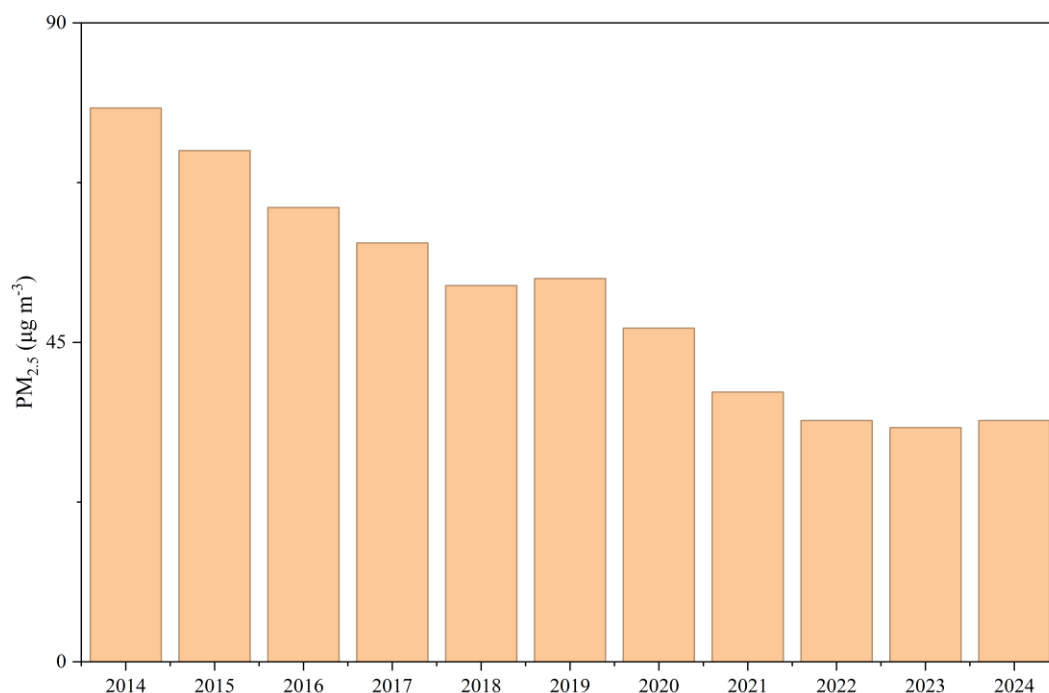


Figure R9 (Revised S1). Annual PM_{2.5} mass concentration (µg m⁻³) data from the Weifang Statistical Yearbook (2015 – 2023) and Weifang monitor site from China National Environmental Monitoring Center (CNEMC)

Line 41-43. The linking part of OA sources to the PM_{2.5} sources. Does it mean none of the OA measured come from any biogenic origins? And also, how can the OA sources originate from secondary inorganics and dust? It seems weird to me to do the source apportionment of OA based on correlations with PM_{2.5} sources with PMF input data of BC, TC, metals, and secondary inorganics.

Response: For biogenic OA, previous studies have shown that in the North China Plain (NCP) region, biogenic-origin OA remains a relatively small fraction of total OA in summer. In winter, more than half of the OA is secondary, with much of this SOA associated with solid-fuel emissions, and primary OA is also dominated by solid-fuel combustion (Daellenbach et al., 2024). Moreover, a previous study combining factor analysis with ¹⁴C analysis suggested that biogenic emissions are likely negligible in Beijing during winter due to low temperatures (Huang et al., 2014). Therefore, biogenic-origin OA can be considered negligible in our study period.

We agree with the reviewer that OA does not originate from dust. This is further

supported by the weak correlations between the major OA factors and the dust aerosol factor identified by PMF ($r = -0.14$ to 0.10 , Fig. 4b). The purpose of presenting the correlations between the OA factors and PMF factors was not simply to link their source types; rather, we intended to highlight the similarities and differences between the source profiles of OA and PM_{2.5}. This comparison is valuable because PM_{2.5} source information is available in emission inventories and is readily accessible for designing control policies. Through this analysis, biomass burning, coal combustion, and vehicle emissions were identified as major sources for both PM_{2.5} and OA. Such information is particularly useful for evaluating the health risks to populations in these densely populated, medium-sized cities.

Line 80-82. Do quinones and semiquinone generate ROS without ascorbic acid and iron? In Line 75-77, it seems they can generate ROS on their own.

Response: Semiquinone radicals are capable of generating reactive oxygen species (ROS), mainly superoxide anion ($\cdot\text{O}_2^-$), via direct electron transfer to molecular oxygen (O_2). Ascorbic acid and iron can serve as accelerators of ROS production during the redox cycling between semiquinone and quinone (Song and Buettner, 2010; Shang et al., 2012). Even without ascorbic acid and iron, quinones can still cause DTT consumption. For example, Fang et al. (2024) found that 2-methoxyhydroquinone exhibited an OP of $125.8 \pm 1.7 \text{ pmol min}^{-1} \mu\text{g}^{-1}$.

To avoid potential misunderstanding, we have revised the following statement in the revised manuscript:

Line 74-75

semiquinones can generate ROS, while ascorbic acid and iron can enhance their generation in this process.

Line 130-131. Are the results of SOA dominating OP in Beijing from Zhou et al (2019) contradictory with the results from Ma et al (2018) in Line 126-128 who identifies solid fuel combustion, vehicle emissions and secondary formation as the dominant drivers of OP?

Response: We think the differences in the dominant sources or species of OP between these two studies can be explained by the following reasons:

Although both studies were conducted in Beijing, their sampling periods differed. The sampling in Ma et al. (2018) covered an entire year during 2012–2013, before China's air quality control measures were implemented, whereas Zhou et al. (2019) was carried out in the winter of 2015, after primary emission controls had been implemented in the North China Plain. This difference in sampling periods is therefore one potential reason for the discrepancy between the two studies.

The analytical methods, molecular tracers, and source apportionment approaches also differed between the two studies. Ma et al. applied one-year offline sampling combined with gas chromatography-mass spectrometry to quantify water-soluble HULIS, including 12 aromatic acids, 5 nitrophenol analogues, 3 aliphatic acids, and 5 biogenic secondary organic aerosol (BSOA) tracers. Specifically, 4-methyl-5-nitrocatechol and 3-methyl-6-nitrocatechol were used as tracers for anthropogenic SOA (ASOA), while 3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid, 3-methyl-1,2,3-butanetricarboxylic acid, 3-isopropylglutaric acid, and 3-acetylglutaric acid were used as tracers for BSOA. In contrast, Zhou et al. used an aerosol mass spectrometer and an online ROS analyzer to quantify the source contributions to OP in Beijing over one month in winter, using oxygenated organic aerosol (OOA) as a proxy for SOA. Consequently, the identification and quantification of SOA in the two studies may differ.

Nevertheless, both studies strongly suggested that anthropogenic emissions, including primary emissions and subsequent gas-to-particle conversion, were the dominant contributors to OP in Beijing, which is consistent with the findings of our study.

To avoid any misunderstanding, we have revised it in the revised manuscript:

Line 134

in the [one-year-long \(2012-2013\) period](#)

Line 137:

and Zhou et al. (2019) demonstrated that SOA dominates OP, contributing 60% of the total OP with online aerosol and OP measurement in winter Beijing.

Line 167. Is the heightened exposure to elevated concentrations of fine particulate matter compared to other cities in NCP region or same location but in previous years? Please specify.

Response: This question can be referred to Minor Comment 1.

We took the air quality improvement in Weifang as an example of the North China Plain region. According to the Weifang Statistical Yearbook (2015 – 2023) and the China National Environmental Monitoring Center (CNEMC) data for urban Weifang (2023 – 2024), the yearly averaged PM_{2.5} concentration decreased dramatically from 78 $\mu\text{g m}^{-3}$ in 2014 to 33 $\mu\text{g m}^{-3}$ in 2024 (Figure S1). However, it should still be noted that during the winter period, the elevated concentrations of PM_{2.5} still matters.

To clarify it, we revise the following expression:

Line 180-182. Consequently, despite overall improvements in air quality (Figure S1), dense population in Weifang remains heavily exposed to fine particulate matter pollution due to recurring PM_{2.5} pollution events in winter.

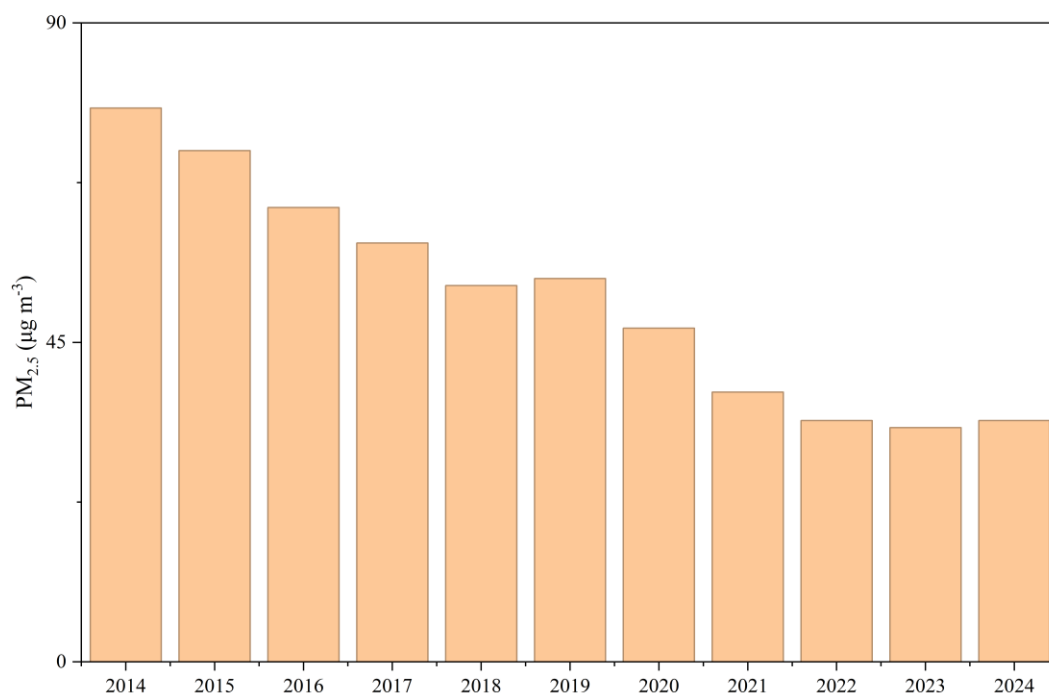


Figure R10 (Figure S1). Annual PM_{2.5} mass concentration (µg m⁻³) data from the Weifang Statistical Yearbook (2015 – 2023) and Weifang monitor site from China National Environmental Monitoring Center (CNEMC)

Line 175-177. What do you mean “strict quality control”? Please elaborate a bit more.

Response: We have answered this question in Reviewer 1’s minor comment 2 and listed as below:

We have added the following information ragared to quality control.

Line 192-197. Three field blanks were also collected during the sampling period. After sampling, filters were wrapped in aluminum foil, sealed in individual bags, stored at – 20 °C for 5 months, and subsequently analyzed in the laboratory. Method uncertainties and potential artifacts, including sample handling and storage, are described in our previous literature (Cai et al., 2023).

Line 215-220. Please add the sensitivity you obtained from the calibrations of levoglucosan and succinic acid. Also, please discuss the uncertainties in CHOX mass

concentrations calculated using this method described here.

Response: we have added the sensitivity we calculated in the revised manuscript as follows:

Line 244-246: as its sensitivity approaches the collision-limit of the FIGAERO-CIMS (Lopez-Hilfiker et al., 2016). The sensitivity for C₆H₁₀O₅ and C₄H₆O₄ in our study is 357 count μg^{-1} and 41 count μg^{-1} , respectively.

For the uncertainties in CHOX mass concentrations, we answered Reviewer 1's comments in minor comments 3 and we have added the following information as follows:

Line 225-228. And the calibrations were conducted with levoglucosan (C₆H₁₀O₅) and succinic acid (C₄H₆O₄). The former approaches the collision limit with I⁻, while the latter represents species that bind less efficiently with reagent ions.

Line 249-255. The reproducibility of this method is 9% for filter samples, based on our previous work. However, quantification uncertainties may be larger, as the collision limit was applied to most compounds; accurate uncertainties cannot be determined due to the lack of standards for all OA compounds. In previous literature, the uncertainty for absolute concentrations using a similar method was estimated to be approximately $\pm 50\%$ (Ehn et al., 2014).

Line 232-235. Could you comment on the toxicity of these water-insoluble components including HULIS and how do they compare to the water-soluble ones, since you talked about ROS from HULIS in Line 76 and 82?

Response: The contribution of water-insoluble components may vary with season, regions, sources, and components. For example, approximately 80% of the OP of PM_{2.5} was contributed by water-soluble components in Atlanta (Gao et al., 2020), 77% in Fairbanks (Yang et al., 2024) and 65% in Shanghai (Wu et al., 2022). Meanwhile, several other studies have suggested an even higher contribution of water-insoluble components to total OP near the roadside (Tang et al., 2022; Zhang et al., 2024b) or for the coarse mode particles (Wang et al., 2023; Frezzini et al., 2022). Therefore, it is

difficult to quantify the contribution of water-insoluble components to OP of PM_{2.5} in Weifang during our sampling period.

To make it clear, we have revised Line 232 as suggested.

Line 264-270. Therefore, it should be noted that water-insoluble components, including elemental carbon (EC), water-insoluble organics (e.g., hulic acid) and insoluble metals, were not analyzed in the DTT analyses in this study. The influence of water-insoluble components on OP would be difficult to quantify, as it may vary across sites, seasons, particle sizes and sources (Gao et al., 2020; Yang et al., 2024; Wu et al., 2022; Tang et al., 2022; Zhang et al., 2024b; Wang et al., 2023; Frezzini et al., 2022).

Line 277-283. Please add the gaseous pollutant plots in the manuscript or SI to show what you are talking about.

Response: We have added the gaseous pollutant time series plot as suggested by the reviewer in the revised SI.

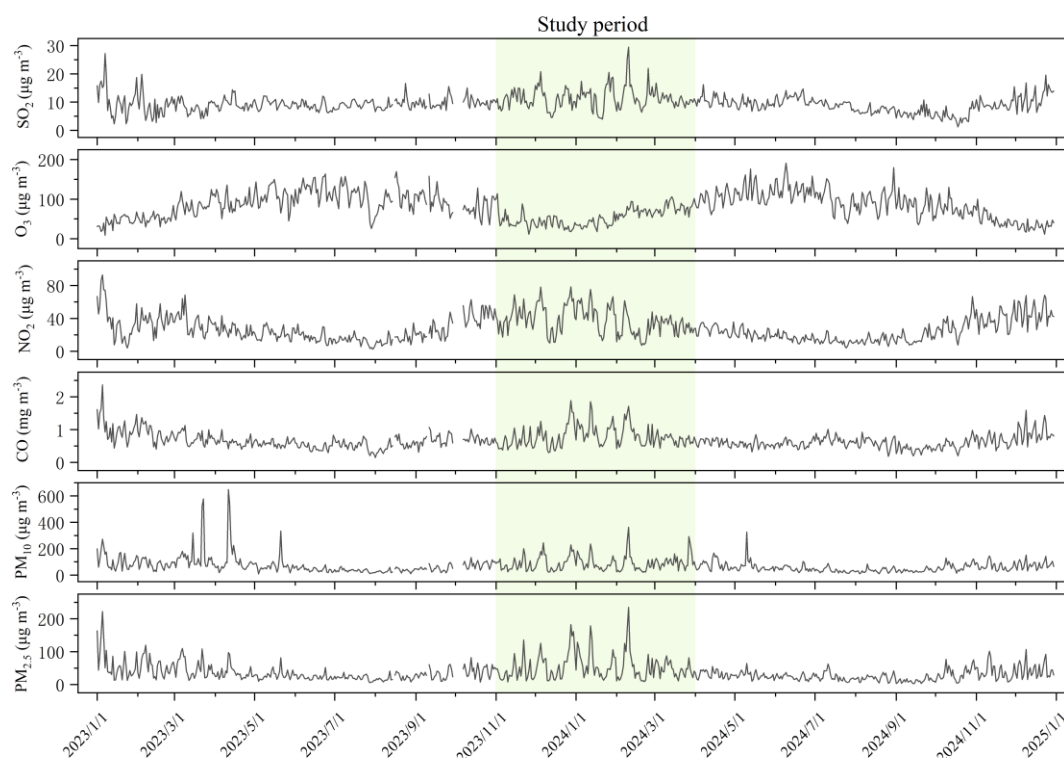


Figure R11 (Figure S9). Concentration of gaseous (SO₂, O₃, NO₂, CO) and particulate pollutants (PM₁₀ and PM_{2.5}) in Weifang from Jan 2023 to Jan 2025.

The gaseous pollutant concentrations for Beijing and Tianjin for comparison has

been listed in the manuscript.

Line 332-335. During the same observation period (Nov 2023 to Mar 2024), Weifang's SO₂ (5 ppb) and NO₂ (17 ppb) levels were approximately twofold higher than those in Beijing (1.4 and 9.7 ppb, respectively) and Tianjin (2.5 and 10 ppb)

Line 294-297. Why did Weifang exhibit this distinct daily cycle? Is this distinct daily cycle only shown after January 2024, and if so why? Please also add the daily cycle both from Weifang before January 2014 and from Beijing to show that Weifang daily cycle after January 2024 is distinct.

Besides, please add the gaseous pollutants diurnal cycle in Fig S2 for better comparison.

Also, why is Fig. 3 mentioned here to show the emission influences? I didn't get it. Please clarify.

Response: We present the diurnal cycles of PM_{2.5} in Weifang before and after Jan 2024 for comparison. The results show that a distinct diurnal pattern of PM_{2.5} existed in both periods, while the morning peak was more obvious in the period after Jan 2024. As for the diurnal cycle of PM_{2.5} in Beijing, it has been well documented in our previous studies (Cai et al., 2020) and is therefore beyond the scope of this study. These patterns may be attributed to both the increase in boundary layer height during the afternoon and the strong primary emissions during the nighttime and early morning. The diurnal cycles of the gaseous pollutants CO and SO₂ have been added to the revised Figure S10 for comparison.

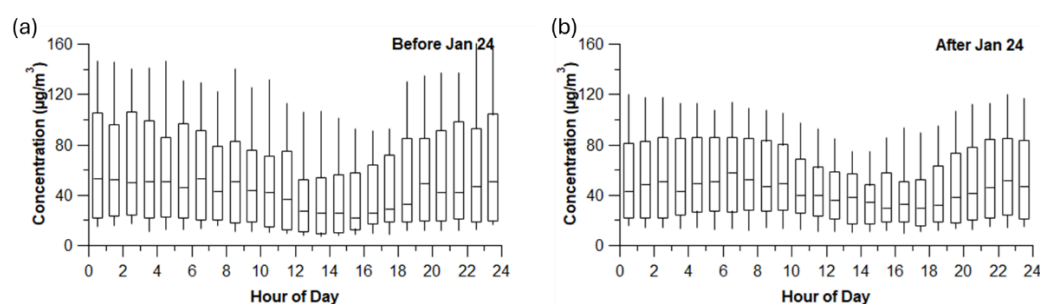


Figure R12. Diurnal variation of PM_{2.5} (a) before and (b) after January 2024 in Weifang .

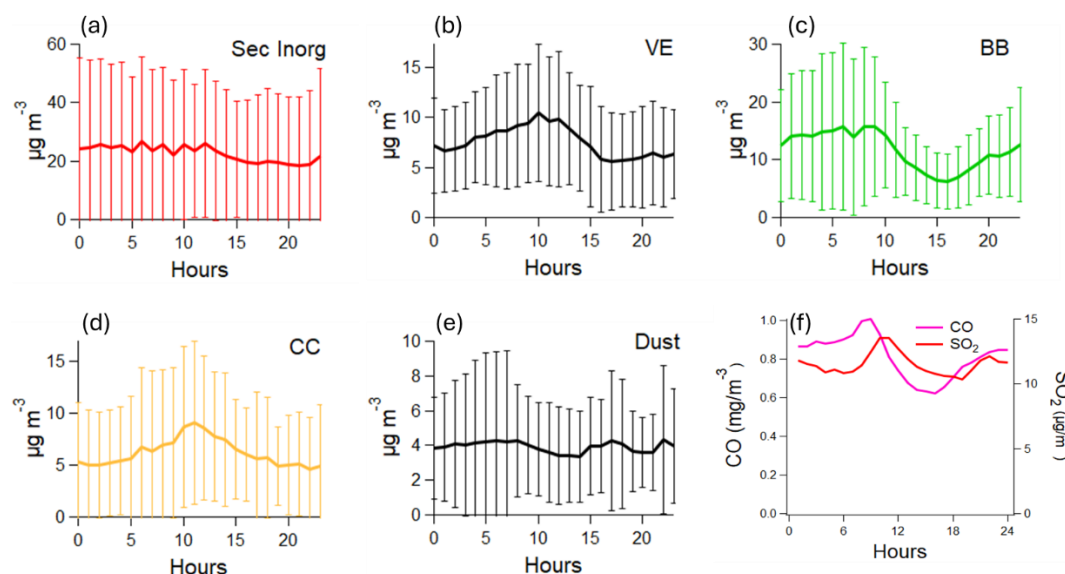


Figure R13 (Figure S10). Diurnal variation of resolved sources and gaseous pollutants: (a) secondary inorganics (Sec Inorg), (b) vehicle emissions (VE), (c) biomass burning (BB), (d) coal combustion (CC), (e) dust emission (Dust), and (f) CO and SO₂.

Figure 3 presents the OA compounds and their correlations with different sources, showing that primary emissions were positively correlated with most of the OA compounds. We agree with the reviewer that, although related, the statement regarding primary emission influences and Figure 3 were not closely linked. Therefore, the citation of Figure 3 has been removed in the revised manuscript.

Line 349. morning with gaseous pollutants (Fig. S7, Fig. S10), underscoring the emissions influences (Fig. 3).

Line 302-307. Please add a pie chart for PM_{2.5} contributions, and also scatter plot and the correlations for PM_{2.5} vs OA and PM_{2.5} vs nitrate to show what you are talking about.

Besides, a stronger correlation between OA and PM_{2.5} does not necessarily imply that OA emissions are the key driver. It just indicates that variations in OA are more closely associated with variations in PM_{2.5} than are variations in nitrate. One example is in Line 391-395, as you stated secondary inorganics dominated the pollution.

Response: We have added the pie chart for PM_{2.5} contribution and the scatter plots as suggested in the revised supplementary information.

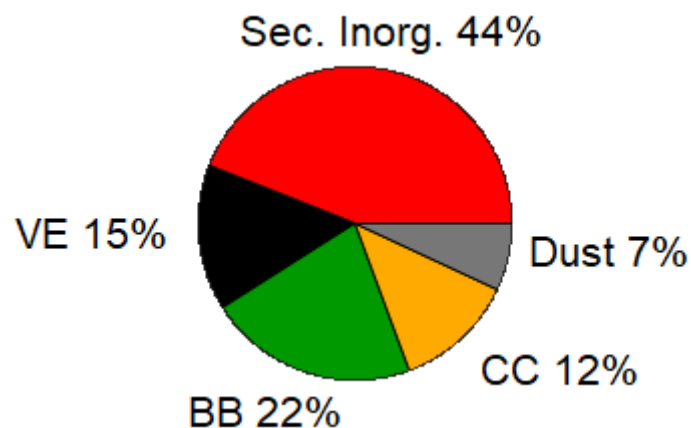


Figure R14 (Figure S8 (f)). The source contribution of each source type to PM_{2.5} in Weifang during the whole sampling period. Sec, BB, VE, and CC represent secondary sources, biomass burning, vehicle emissions, and coal combustion, respectively.

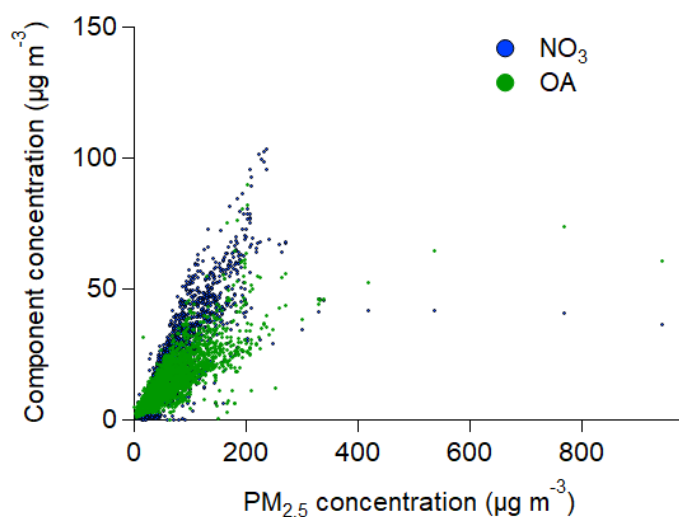


Figure R15 (Figure S3). The correlation between PM_{2.5} and OA and NO₃ concentrations

We appreciate the reviewer's insightful comment on the correlation between OA and PM_{2.5}. We agree with this assessment and have removed the relevant statement suggesting that OA emissions are the primary driver of PM_{2.5} in the revised manuscript.

Line 355-359: the broader NCP region. Specifically, nitrate was the most abundant species in PM_{2.5} (16.6 µg m⁻³, 29 %), followed by OA (12.3 µg m⁻³, 22 %) and sulfate (7.6 µg m⁻³, 13%). However, in Weifang, the correlation coefficient between PM_{2.5} and OA ($r = 0.80$) was stronger than that with nitrate ($r = 0.71$. Fig. S3), underscoring that OA emissions are the key driver to fine PM pollution, especially during extreme episodes.

Line 335. Please add the residential burning fraction in Weifang.

Response: We have added the fraction for residential burning in Weifang as suggested:

Line 388-390. It is consistent with the emission inventories (MEIC) which suggest residential burning is the dominant OC source in Weifang (62% and reached 80% during wintertime).

Line 336-338. What are the compounds with the largest signal in Weifang in Fig 1c (i.e., the compound in blue and purple with DBE<2)? They don't seem to be the levoglucosan nor compounds with DBE>4.

Besides, why are you using number fraction of CHOX? I think signal fraction would make more sense.

Response: The compound that the reviewer suggested is C₂H₄O₂, likely acetic acid formed in secondary reactions.

Additionally, in Line 336, we referred signal fraction rather than number amount fraction of CHOX as the reviewer suggested. Therefore, we revised the manuscript to make it clear for the readers.

Line 390-394:

Wangdu (87%) but substantially higher than in Beijing (54%). Consistent with this, a large fraction of levoglucosan (0.9 % in signal intensity) and compounds with DBE>4 in signal intensity (39%) during the measurement period (Fig. 1c), exceeding previously reported fractions in Beijing (13%).

Line 350-353. The naming of the factors for Fig S3 was described in SI. But their high correlation with organic and inorganic tracers as stated in Line 357 and SI should be included to support.

Besides, in SI it says "A total of seven sources were resolved in this study, including secondary inorganic aerosols, vehicle emissions, coal combustion, biomass burning, fireworks and related emissions, industrial emissions, and dust." But then in the two paragraphs afterwards, it says "The variation in Q/Q_{exp} values suggested that five

factors could explain the majority of the residuals”. It’s confusing how many factors were resolved.

Response: The correlations between PMF factors and organic tracers have been discussed in Section 3.3. The correlations between PMF factors and inorganic tracers were not further discussed, as the source profiles containing inorganic species have already been presented in Figure S3. Since these results were resolved based on those inorganic elements, the typical inorganic tracers were not discussed further.

We thank the reviewer for pointing out the incorrect expression regarding the source apportionment results in the SI. We have corrected these mistakes in the revised SI.

Revised SI:

PMF was performed for 2 to 8 factors, and the 5-factor solution was selected due to its low Q/Q_{exp} value and its ability to provide a robust interpretation of the factors. In the 4-factor solution, the dust cluster was mixed with other factors, leading to potentially high uncertainty in the characterization of primary combustion emissions. Meanwhile, the 6-factor solution resulted in a noisy factor characterized by metal elements, likely attributable to instrumental noise from the metal analyzer.

Line 377-381. CO seems to reach max at 8-9 am instead of max vehicle emissions at 10 am. Is CO the best indicator still? How about the timing of the max NO_x in the morning? Would it match better the timing of the max vehicle emissions?

Response: Indeed, unique tracers for vehicle emissions remain limited, especially in the particle phase. Although previous molecular-level studies have used hopanes and steranes (e.g., cholestanes) as tracers for gasoline and diesel vehicle emissions (Schauer and Cass, 2000), these compounds are subject to photochemical reactions in the atmosphere and cannot be measured by our FIGAERO-CIMS, which targets oxygenated OA. Therefore, we used the diurnal pattern of CO to reflect the emission pattern of vehicle emissions.

It should be noted, however, that CO is a gaseous pollutant, whereas vehicle emissions were apportioned by PMF using particulate BC and OC. Their atmospheric lifetimes and diurnal variations, influenced by photochemical reactions and boundary layer dynamics, may therefore differ. In addition, CO, as well as particulate BC and OC, can originate from multiple primary combustion sources; for instance, we cannot rule out a contribution from coal combustion in the morning, as resolved by PMF and indicated by elevated SO₂.

As the reviewer pointed out, CO in our study peaked at 8 – 9 am, about one hour earlier than the vehicle emission factor resolved by PMF, which increased at 8 am and peaked at around 10 am. This discrepancy may be explained by two factors. First, the PMF-resolved vehicle factor may be mixed with other primary sources, such as coal combustion due to the lack of unique tracers as discussed above. Second, the morning rush hour in Weifang City can typically last 3 – 4 hours, so traffic-related emissions were likely elevated throughout this period, during which the exact peak time may vary from day to day. Nevertheless, vehicle emissions exhibited an earlier morning peak than any other resolved primary sources, and therefore the morning CO enhancement is more likely attributable to vehicle emissions than to other primary sources.

NO would potentially be a better indicator of primary vehicle emissions, because NO₂ we measured can be affected by O₃ titration during the daytime. However, NO was not measured during our sampling period. Consequently, we consider that the diurnal variation of CO provides supportive evidence for the identification of the traffic source impact that peaked in the morning, even though the peak times indicated by CO and by the PMF factor differ slightly.

Line 391-395. On Jan 12, solid fuel burning didn't dominate the pollution based on Fig 2, as secondary inorganics still dominated with a contribution of 46%. Besides, solid fuel burning contributions seem not to be 36% if I summed up the coal combustion of 9% with biomass burning of 25%.

Response: We have corrected the manuscript as the reviewer suggested:

Line 447-452. During extremely polluted days, such as November 22 ($\text{PM}_{2.5}$: $136 \mu\text{g m}^{-3}$) and January 12 ($178 \mu\text{g m}^{-3}$), secondary inorganics (79%) and solid fuel burning (34%) were among the most important factors during the pollution episodes, respectively, with concentrations significantly higher than during the post-heating period. During the heating season, mean concentrations of biomass burning ($15 \mu\text{g m}^{-3}$) and coal combustion ($8 \mu\text{g m}^{-3}$) significantly exceeded spring season averages ($6 \mu\text{g m}^{-3}$ for both).

Line 395-399. For biomass burning and coal combustion comparisons, it seems heating season didn't include the spring-heating season, while for dust comparisons the spring-heating season was included in the heating season. Is spring period of March 1-March 15 (Line 384) heating season or not? It's quite confusing.

Response: In the original manuscript, the heating season has covered the spring period. We revised the manuscript to make it clear:

Line 441-442. During the heating season (Nov 15 to Mar 15),

Line 400-402. Please show the PM_{10} data to support your statement. I only found $\text{PM}_{2.5}$ in figs 1 and 2. PM_{10} measurement was never mentioned in the method as well.

Response: Thanks for the reviewer for pointing out the missing of PM_{10} measurement in the methodology. We have now added it in the revised manuscript.

Line 198-201, Online chemical components of $\text{PM}_{2.5}$ and PM_{10} along with gaseous pollutants including SO_2 , NO_2 and O_3 were measured in another near site covering the whole sampling period with a time resolution of 1 hour (see SI for a detailed description).

Line 406. It would be nice to show the correlations between identified OA compounds with the dust source in the SI, at least for post-heating season when dust source is important.

Response: we have added the correlation plot between OA compounds and dust from PMF as suggested, it shows that dust is not the dominant source of OA.

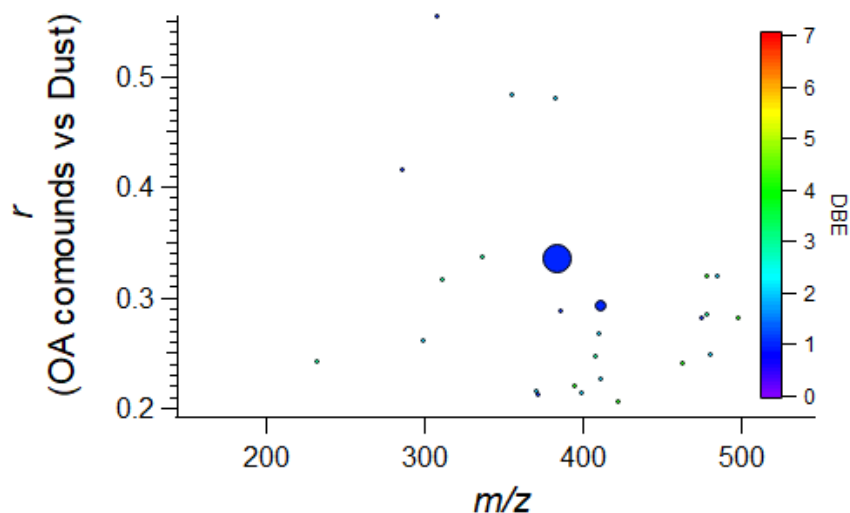


Figure R16 (Figure S15). Correlation coefficients between OA compound signals and dust source. Dot sizes are proportional to the square root of the signal intensity for the corresponding compounds, and dots are color-coded by the DBE number of each compound.

Line 423-425. Why not showing the thermograms with $T_{\max}$ to validate this for these ions?

Response: We have added the $T_{\max}$ for the 10 most highly correlated with coal combustion source as suggested.

Table R2 (Table S2). $T_{\max}$ for the 10 most highly correlated with coal combustion source

Compounds	$T_{\max}$	m/z
C ₉ H ₂ O ₆	136.2	332.89
C ₂ H ₄ SO ₄	131.8	250.89
C ₅ HNO ₃	119.3	249.90
C ₃ H ₆ SO ₄	145.8	264.90
C ₉ H ₆ SO ₈	105.3	400.88
C ₈ H ₂₀ O ₄ S	107.6	208.11
C ₈ H ₄ O ₈	122.5	354.90
C ₇ H ₄ O ₁₀	115.8	374.89
C ₅ H ₁₀ O	85.8	212.99
C ₈ H ₂ O ₆	148.2	320.89

Line 434-436. Here you are choosing the well-known biomass burning tracers to compare even though their correlations are below 0.75. However, for coal combustion case the OA compound correlations discussed are above 0.75 (Line 406-409). Same for vehicle emission comparisons for the C₁₅H₂₀NO₅ and C₁₇H₂₄O₅ which seem to have

correlations below 0.6 (Line 449-452) from Fig 3d. It feels subjective what compounds to choose to compare. Maybe PMF can do a better job for OA source apportionment.

Response: PMF did not perform well with such a large number of OA variables and the limited number of offline samples. As noted in our response to the major comment, the US EPA PMF 5.0 user guide indicates that datasets containing fewer than 100 samples are more likely to suffer from increased rotational ambiguity (Norris, 2008).

Regarding the two compounds ($C_{15}H_{20}NO_5$ and $C_{17}H_{24}O_5$) that the reviewer referred to, they showed correlation coefficients of 0.73 and 0.74 with vehicle emissions, respectively. These two compounds were among those with the highest correlations, which have shown in the revised Figure 3.

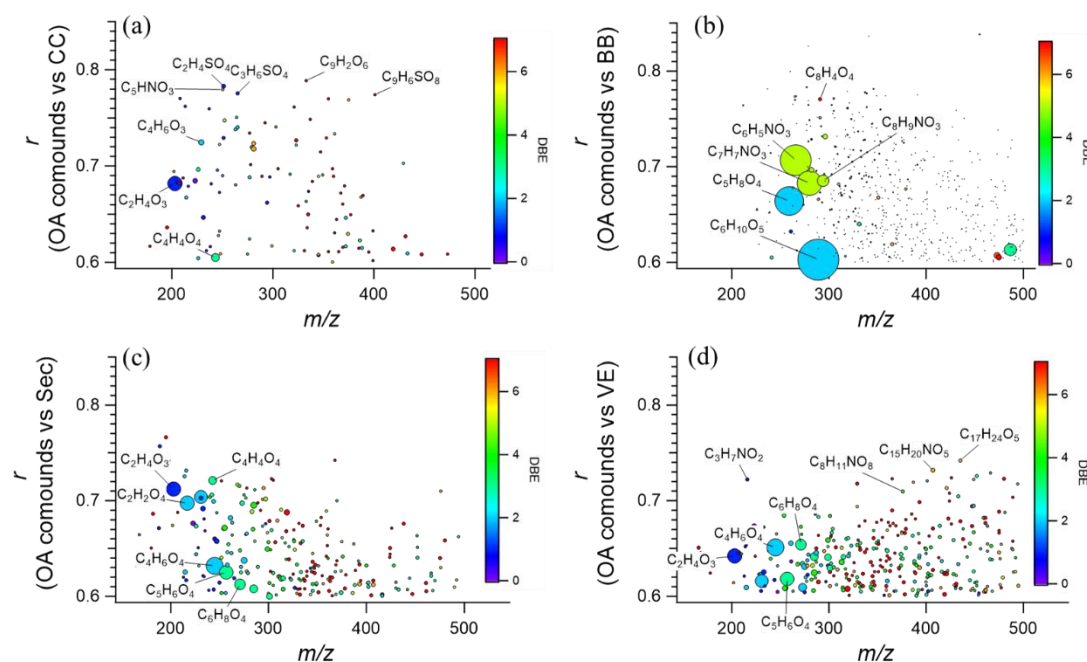


Figure R17 (Figure 3). Correlation coefficients between OA compound signals and different sources: (a) coal combustion, (b) biomass burning, (c) secondary inorganics, and (d) vehicle emissions ($r > 0.6$). Dot sizes are proportional to the square root of the signal intensity for the corresponding compounds, and dots are color-coded by the DBE number of each compound. Correlation coefficients for dust source are shown in Fig. S15.

Line 443-445. What do you mean of “one in fourth of the levoglucosan-to-OA ratio”? Please rephrase it.

Response: We have rephrased the expression as follows:

Line 501-505. During our whole sampling period, $C_6H_{10}O_5$ constituted 0.9 % of total

OA. Meanwhile, the primary levoglucosan-to-OA ratio in fresh biomass burning plume is about 4% (Mazzoleni et al., 2007), highlighting the significance of fresh biomass burning to ambient.

Line 460-461. It's not very straightforward in Fig 3c to see the differences of DBE and MW between different panels of fig 3. Maybe can show pearson's r-weighted DBE vs pearson's r-weighted molecular masses for OA with different PM2.5 sources as the Fig 3?

Response: We thank the reviewer for pointing out that the original Figure 3 was not straightforward. In the original Figure 3, we presented all identified compounds with correlation coefficients ranging from -0.40 to 0.85, which indeed weakened the key point regarding the compounds that were strongly correlated with different PM_{2.5} sources. To improve the interpretation, the revised Figure 3 displays only those compounds showing a positive correlation with their corresponding sources ($r > 0.6$), thereby highlighting the representative compounds for each source. In the revised Figure 3, the compounds that were highly correlated with the different sources varied in molecular weight, DBE value, and mass, as follows:

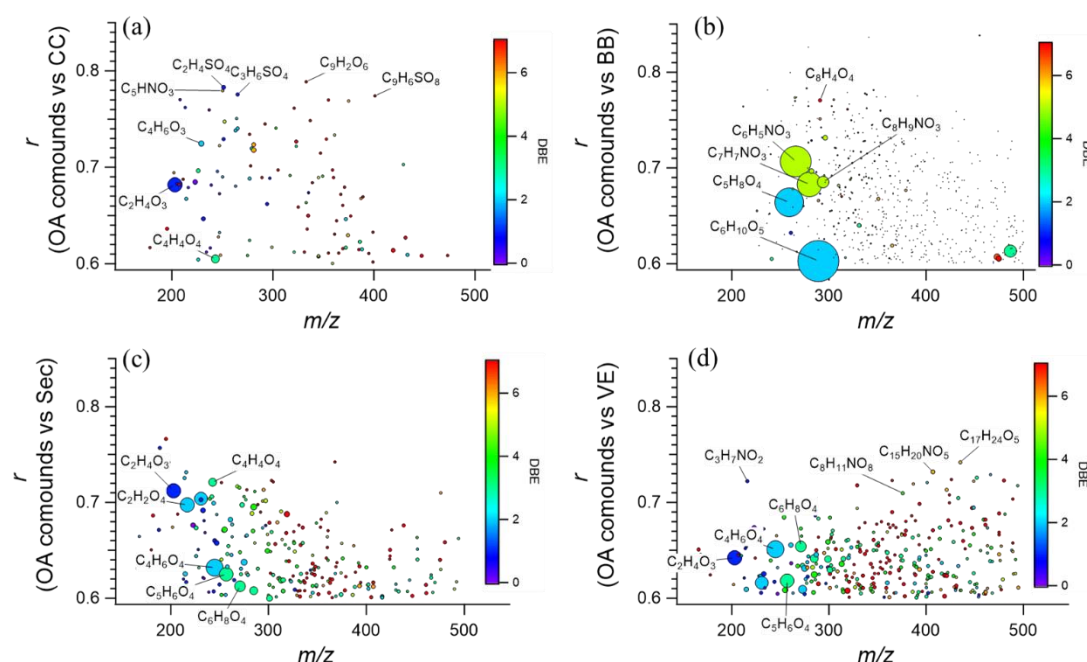


Figure R18 (Figure S3). Correlation coefficients between OA compound signals and different sources: (a) coal combustion, (b) biomass burning, (c) secondary inorganics, and (d) vehicle emissions ($r > 0.6$). Dot sizes are proportional to the square root of the signal intensity for the corresponding compounds,

and dots are color-coded by the DBE number of each compound. Correlation coefficients for dust source is exhibited in Fig. S15

Line 480-487. Do the compounds discussed in Fig3 (in Line 409-410, 420-421, 435-436, 452, and 462) fall into this 274 high-abundance compound list?

Besides, I think Fig 4 says more than Fig 3 in terms of OA sources and correlations with PM_{2.5} source factors. Is it really necessary to have Fig 3 and relevant discussions? However, the best way to talk about OA sources would be to run PMF on OA and show factor correlations, instead of OA cluster correlations to PM_{2.5} PMF factors.

Response: Not all compounds discussed in Figure 3 are included in the 274 high-abundance compounds; the full list is provided in the revised SI (Table S3). The compounds discussed in Figure 3 were selected solely because of their high correlations with different source types, which helps to validate the PMF source apportionment results for PM_{2.5}. In contrast, the list of 274 high-abundance compounds applied in HCA in Figure 4 was selected based on their high signal intensities and therefore provides less indication of sources. We first present the correlations between the compounds and the source apportionment results in Figure 3 in order to validate the PMF results. This suggests that the PM_{2.5} sources identified by PMF can be independently validated by the organic compounds measured with FIGAERO-CIMS. On this basis, we can further compare the OA clusters from HCA with the PM_{2.5} sources to investigate the typical OA types and their potential sources in Figure 4. Therefore, Figures 3 and 4 are not duplicated; rather, they are logically connected within the analysis.

Line 519-530. Dust itself is most minerals, but dust transport can also bring over OA together as you stated in Line 654 when they are mix with anthropogenic emissions in NCP (Zhang et al., 2026). Have you tried to run the HCA for the post-heating season to check, since this period was dust dominated?

Response: The number of samples for the post-heating season is only 4, which is significantly lower than the number of high-intensity compounds (274) used in the HCA analyses. With such a small sample size, the variations of different OA compounds cannot be fully captured, and the degrees of freedom provided by the 4

samples are insufficient to separate dust-related OA compounds with HCA. Therefore, we did not attempt to run the HCA for the post-heating season alone.

Line 536-542. Does Fig S6 show the correlations of all days or excluding Feb 11 since it's not very clear from the text and Fig S6 caption?

Besides, a stronger correlation between OP_m and OC does not necessarily imply that OC are the key driver. It just indicates that variations in OC are more closely associated with variations in OP_m than are variations in transition metals. As you also stated in Line 538, metals are typically one of the OP drivers; if you focus on Feb 11 firework case, then your conclusion would be different.

Response: Feb 11 was excluded from Figure S6 and this is now noted in the figure caption: "Correlation between OP_v (DTT) and Cu, Fe, Mn, and OC during the sampling period (February 11 excluded)".

We agree with the reviewer's comment that both metal components and organic carbon make substantial contributions to OP, and that their interaction is also an important factor influencing OP. As the reviewer suggested, in some extreme cases, such as the Diwali festival in India (Lakhani et al., 2021) the Spring Festival in China (Zheng et al., 2026), firework-related emissions significantly contributed to the OP of fine atmospheric particles. However, such metal emissions are characterized by high concentrations and intensity, typically last for only a relatively short period, and can be easily controlled through targeted strategies.

As a typical medium-sized city in the North China Plain, Weifang is still frequently affected by pollution episodes in autumn and winter, even though the overall air quality has been substantially improved. During these episodes, however, the types, categories, and sources of the abundant organic aerosol compounds, as well as their contributions to OP, remain unconstrained. Therefore, firework emissions and their related metal contributions to OP are not the focus of this study, as this topic has been addressed in our previous study (Zheng et al., 2026); accordingly, we have removed the corresponding samples from our dataset.

Line 543-554. Please show the OP time series figure. It's difficult to relate if there is no data supporting the statement. Also, is Feb 11 the only day having elevated SO₂ and metal levels since you excluded only Feb 11 due to this reason?

Response: We have added the time series of OP as suggested in the revised supplementary information.

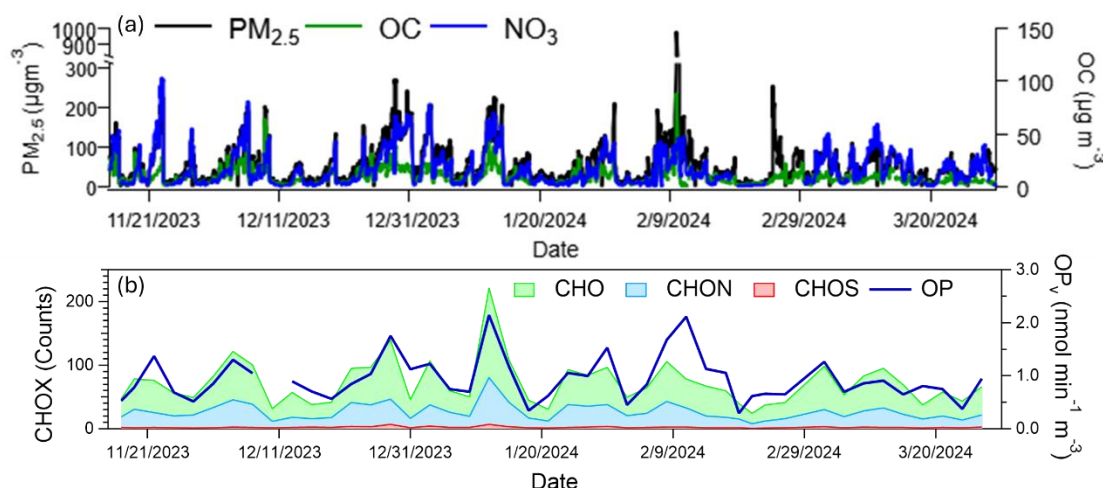


Figure R19 (Figure S2). Time series of (a) PM_{2.5} NO₃ and OC, (b) CHO, CHON, CHOS of CHOX groups and volume-normalized OP of PM_{2.5} during the sampling period

We consider that Feb 11 was strongly influenced by fireworks, as SO₂ and firework-related metals, such as Ba and Cu, were extremely high compared with other periods. For example, Ba and Cu reached their highest levels across the entire sampling period, with concentrations on Feb 11 being 21 and 12 times higher, respectively, than the averages of the remaining sampling days.

Line 555-556. I don't understand why Fig S7 shows some OA species are important in driving the OPm? Fig 5c-d probably show better? Fig S7 only shows the signal ratio of Feb 17 to Jan 12. Why are these two days chosen and why are OA compound signal ratios larger than 1 are shown and how does this relate to importance in OPm? Please explain more.

Response: We selected those two days (Jan 12 2024 and Feb 17 2024) because that they exhibited 5 times different PM_{2.5} (160 µg m⁻³ and 32 µg m⁻³) and OC levels (19.6 µg m⁻³ and 3.9 µg m⁻³), yet their volume-normalized OP values differed by only a factor of 2 (2.1 mol min⁻¹ m⁻³ and 1.1 mol min⁻¹ m⁻³). This suggests that the OA compounds on Feb 17 were more OP-active; that is, a small subset of OA compounds with higher

OP_m may have driven the generally elevated OP_v on Feb 17 (Fig. S7). To better illustrate this point, we have revised the manuscript as follows:

Line 627-631. Although the PM_{2.5} and OC levels on Jan 12 and Feb 17 differed by approximately a factor of five, the volume-normalized OP values differed by only a factor of two. Comparison of the identified OA signals revealed that only a small subset of OA compounds was more abundant on Feb 17, which likely contributed to its elevated intrinsic OP_m (Fig. S14).

Figure 5c-d. I assume the size of the compound markers refer to the spearman correlation coefficient? Does smallest marker refer to strongly negative correlation and biggest one strongly positive correlation? Please specify.

Response: Indeed, we plotted the compound group markers with their sizes scaled according to the correlation coefficients, which ranged from -0.65 to 0.60 for the different compound groups.

We have revise the Figure 5 c and d caption as follows:

Line 653-654. Compound markers are color-coded according to their average oxidation state and sized by their correlation coefficients with OP_m (ranging from -0.65 to 0.60) in (c) and (d).

Line 579-581. I can see the relationship from more aged OA to higher O:C ratio, but more discussions are needed to explain why is there a difference trend for OP_m vs O:C compared to OP_v vs O:C, because the difference of OP_m and OP_v is probably the density (Line 237-247). Maybe some literature on OP_v vs O:C from the literature similar to your discussions of OP_m vs O:C from Liu et al (2024a).

Response: We have now added more discussion and references about the reason for the different trend for OP_v versus O:C ratio of the OA compounds as suggested.

Line 659-663. The continuous enhancement in OP_v with increasing O:C is likely driven by PM concentration. At higher PM levels, OA compounds undergo more atmospheric aging, resulting in higher O:C ratios. A similar enhancement of OP during the aging of aerosols in haze episodes has been reported in previous studies (Li et al., 2019b; Sun et

[al., 2016\).](#)

Line 593-597. How would it look like when correlating with OP_v? Could add it in SI.

Response: We have added the following information in the manuscript.

Line 684-686. [Those highly oxygenated compounds \(OS_c > 2\), however, generally showed positive correlations with OP_v \(\$r = -0.2 - 0.7\$, with average of 0.4\)](#)

Line 597-603. Could you explain more the connection of group (1) C₁₀-15H₁₀O₁₀ compounds and group (2) C_{>15}H_{O<5} compounds to solid fuel burning emissions and traffic emissions, respectively from section 3.3? Based on fig 5b, group (1) may be from BB only since cluster C and E correlated with BB also exhibited long carbon chains of C₉-10. However, group (2) doesn't seem to relate with vehicle emissions which only exhibited relatively higher correlations with cluster A and D with carbon chain of C₈,11.

Response: We agree with the reviewer that group 1 is likely associated with biomass burning. As shown in Figure 4b, both clusters C and E, with long carbon chains, are highly correlated with biomass burning. In addition, according to the revised Figure 3, the OA compounds with m/z values around 300 – 400, typically corresponding to carbon numbers of ~10, were more strongly correlated with biomass burning. In contrast, group 2, characterized by high m/z ratios (>400), carbon numbers greater than 15, and the presence of nitrogen, was more strongly correlated with vehicle emissions.

We note that the clusters presented in Figure 4 represent the average formulas of the clusters and thus do not correspond exactly to the individual compounds, which is likely lead to misunderstandings. To better illustrate the results, we have revised the manuscript as follows:

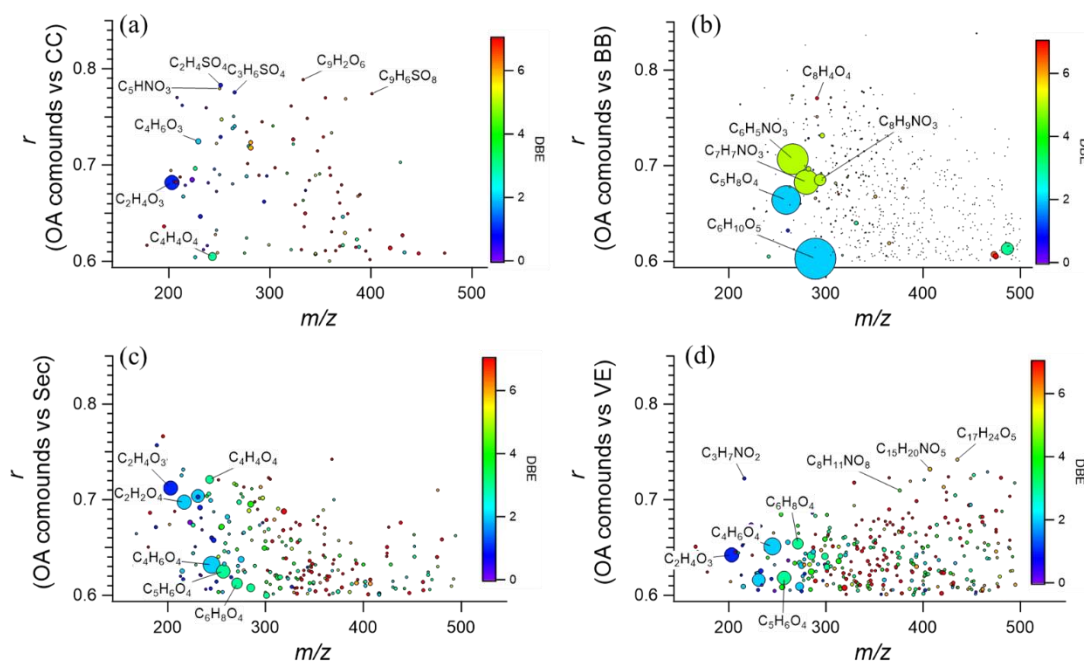


Figure R20 (Figure 3). Correlation coefficients between OA compound signals and different sources: (a) coal combustion, (b) biomass burning, (c) secondary inorganics, and (d) vehicle emissions ($r > 0.6$). Dot sizes are proportional to the square root of the signal intensity for the corresponding compounds, and dots are color-coded by the DBE number of each compound. Correlation coefficients for dust source are shown in Fig. S15.

We have added more discussion about the group

Line 687-692:

In contrast, the most highly positive correlated OA compounds fall into two groups: (1) $C_{10} - C_{15}$ with ~ 10 oxygen atoms and m/z around 300 (likely oxygenated aromatics linked to the solid fuel burning emissions in Section 3.3, [shown in Figure 3b](#)), and (2) long-chain species ($> C_{15}$) with less than 5 oxygen atoms ([shown in Figure 3d](#)).

Line 610-613. The four days are also not the same four days in Fig 2a. It seems the day choice of data is also a bit subjective. Would it make more statistical sense if you just do the average for the autumn-winter heating season, spring-heating season, and post-heating season? Or give out the reasoning for different choices of days selected.

Response: We selected these four days because each reached a high $PM_{2.5}$ level of over $150 \mu g m^{-3}$ and exhibited distinct source characteristics: November 22 was dominated by secondary sources, January 12 by biomass burning, March 3 by vehicle and coal

combustion, and March 28 by dust. These four days were therefore chosen to compare the source variations among the different periods. Since the strong dust and biomass burning episodes each lasted for only two periods, we consider it more appropriate to analyze individual episodes rather than to take the average over the autumn–winter heating season, the spring heating season, and the post-heating season.

Line 615. Are 76% and 47% the average contributions for the two episodes?

Response: The two percentages represent the average contributions for the two days, namely Nov 22 and Mar 28, respectively. We have clarified this point in the revised manuscript.

Line 706-709. Nov 22 ($\text{PM}_{2.5}$: $122 \mu\text{g m}^{-3}$, OP_m : $11 \text{ pmol min}^{-1} \mu\text{g}^{-1}$), Jan 6 ($\text{PM}_{2.5}$: $20 \mu\text{g m}^{-3}$, OP_m : $38 \text{ pmol min}^{-1} \mu\text{g}^{-1}$), Jan 21 ($\text{PM}_{2.5}$: $15 \mu\text{g m}^{-3}$, OP_m : $37 \text{ pmol min}^{-1} \mu\text{g}^{-1}$), Mar 18 ($\text{PM}_{2.5}$: $24 \mu\text{g m}^{-3}$, OP_m : $27 \text{ pmol min}^{-1} \mu\text{g}^{-1}$) and Mar 28 ($\text{PM}_{2.5}$: $73 \mu\text{g m}^{-3}$, OP_m : $15 \text{ pmol min}^{-1} \mu\text{g}^{-1}$).

Line 619-626. OP_m from vehicle emissions also seem to be elevated on these two days (seen also in Fig 6a). Would it make sense to include it when talking about dominant contributors to OP_m ? In particular, compounds from this group also correlated with OP_m as stated in Line 686-688.

Response: We agree with the reviewer' point that vehicle emissions may also elevated on the episode from Jan 6 to Jan 12 2024. Therefore, we have revised this section accordingly.

Line 714-717

“In contrast, on Jan 6 and Jan 21, fine PM was dominated by biomass burning, coal combustion, and vehicle emissions; together, these primary combustion and combustion-like sources accounted for up to 60 – 80% of the total mass.”

Line 639-644. Continuing about OP_m from vehicle emissions: do you mean the concurrent accumulation of secondary inorganic formations cancelled out some OP_m from vehicle emissions at high vehicle emission source contributions?

Response: During stagnant weather conditions, primary emissions from vehicle

sources and contributions from secondary inorganic aerosol sources accumulate simultaneously. SIA components exhibit much lower OP activity, thereby likely reducing the overall OP_m of PM_{2.5}, despite the high OP_m particles derived from vehicle emissions and subsequent secondary formation. Therefore, the increase in SIA with low OP_m may cancel out the contribution of vehicle emissions to the total PM_{2.5}.

Accordingly, we have revised the manuscript.

Line 736-742: “This decline is likely attributable to stagnant meteorological conditions during high-PM_{2.5} episodes, which promote the concurrent accumulation of both vehicle emissions and secondary inorganic formations. A higher fraction of low-OP-activity secondary inorganic aerosols may cancel out the influence of vehicle emissions on total PM_{2.5}, causing the apparent contribution of vehicle emissions to the total OP_m to decline during haze periods.”

Line 647-654. If the anthropogenic emissions are related to the OP_m decrease at high dust source contributions, are they likely to be the primary solid fuel combustion as stated in Line 625?

Response: During typical days in our sampling periods, the dust contribution was very limited (8.3%) to PM_{2.5} compared with that on strongly dust-influenced days (e.g., Mar 28: 47%); therefore, OP_m was unlikely to be attributed to dust aerosols in general during our sampling period. On typical days, dust aerosols themselves should have contributed very little to OP_m, since most of the mineral components in dust aerosols are water-insoluble, whereas a water-extraction DTT assay was applied to estimate OP in our study.

However, a recent study showed that the solubility of dust aerosols could increase significantly when they are transported over polluted regions and mix with anthropogenic emissions (e.g., primary solid fuel combustion, as suggested by the reviewer), potentially leading to high OP values in the NCP (Zhang et al., 2026).

Line 677-683. Please show the data. Besides, are these high O:C compounds significantly correlating with OP_m contradictory to what was shown in Fig 5b and Line

581-590 about decline in OP_m at higher O:C?

Response: We have added the correlation coefficients as suggested:

Line 772-774: Concurrently, these OP-active species showed a significantly negative correlation with secondary inorganic sources ($r = -0.29$ to -0.68 , t-test, $p < 0.05$).

In Line 774-779, we aimed to show that the compounds significantly and positively correlated with OP_m were high-DBE compounds, among which a higher O:C ratio led to a stronger correlation with OP_m. However, as shown in Fig. 5b and Line 581, we suggested that a generally higher O:C ratio would lead to a decline in OP_m, which is likely caused by the formation of lower-molecular-weight and lower-DBE compounds, possibly through heterogeneous reactions. To clarify this, we have revised Line 774-779.

Line 777-782. the latter of which was primarily attributed to the species containing high oxygen number (typically associated with primary sources, especially biomass burning and coal combustion), which is different from the compounds with low DBE and high O:C ratios likely formed in the heterogeneous reactions during haze period.

Line 704. Can you show the temperature and RH data to support?

Response: We have now added the temperature and RH data as the reviewer suggested as follows:

Line 802-806. Under the low temperature (6.0 °C in autumn and 0.36 °C in winter) and low relative humidity environment (54% in autumn and 59 % in winter) during our sampling period in Weifang that typically predominant the NCP during autumn and winter, aromatic compounds tend to stabilize their benzene ring structures under such conditions (Cao et al., 2026).

Fig 8: Feb 11 (one day after Chinese New Year) exhibited high OP_m caused by transition metals during firework events (in Line 543-554). Where would this date sit in this plot? And for this day, I assume the conclusion of dominant OP_m contributors would be different since you also stated in Line 538 that transition metals are typically

being considered as one of the drivers of OP?

Response: In this study, we used the water extraction method combined with the DTT assay to estimate the OP_m of the PM_{2.5} samples, as described in the Methods section. Since firework emissions are heavily enriched with water-insoluble transition metals, adding the OP_m of the firework event would bias the results in Weifang and outscope of this study. Therefore, we did not include Feb 11 when intense firework emissions occurred in our analysis. However, we compared our dataset with previously reported OP_m values of standard water-soluble metal ions (Figure S16), which suggested that these typical transition metals were less OP-active than the OP-active OA compounds we identified and tested with standards.

In addition, firework events occurred only over a short period, typically around the Chinese New Year, with extensive emissions. For example, the concentrations of Ba and Cu during the autumn and winter periods were an order of magnitude lower than those on February 11, indicating that the influence of transition metals during typical (non-firework) periods was much weaker in Weifang during our sampling period. Therefore, we believe our conclusions remain valid.

Line 770-774. It's difficult to see from Fig 8. The different color shades illustrating the standard deviation ranges of previously reported OP_m values from various sources are overlapping on top of each other, in particular biomass burning, traffic emissions, and SOA_{bio}. Please try to make the figure more clear.

Response: Following the reviewer's suggestion, we have revised the color shades in Figure 8 to make the ranges of the various sources more visible, as shown below:

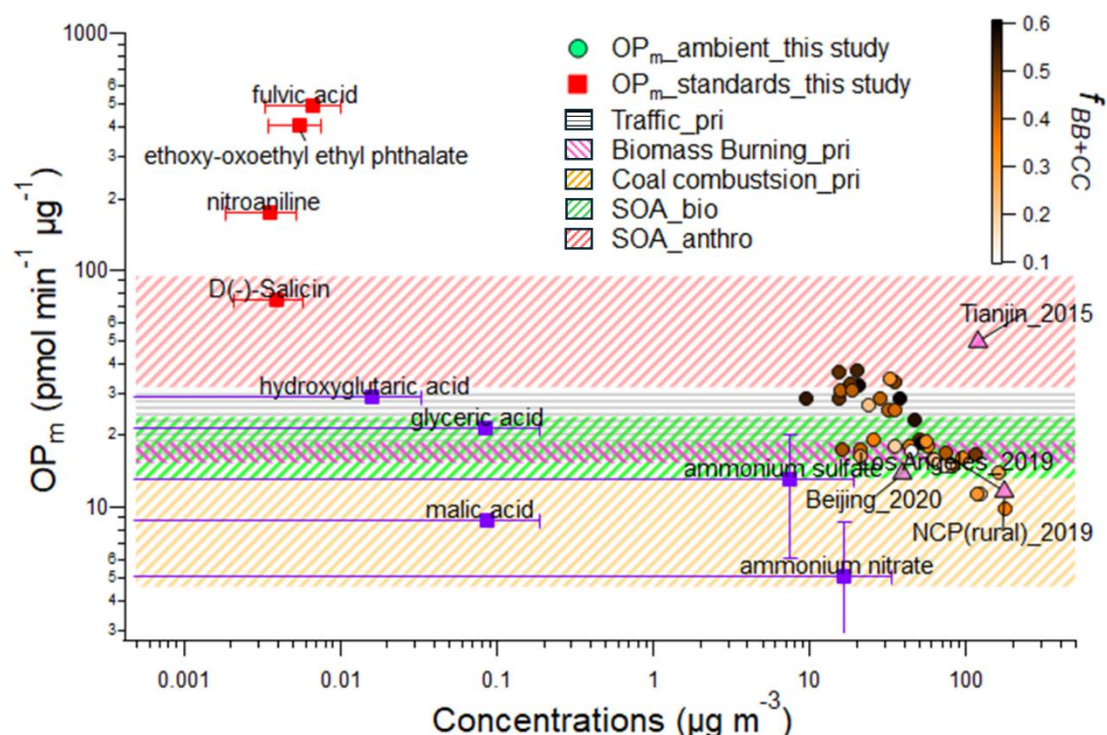


Figure R21 (Revised Figure 8). Mass-normalized oxidative potential (OP_m) derived from offline samples and chemical standards in the study. Offline samples collected during the campaign are represented by brown circles, color-coded according to the fractional contribution of solid fuel (biomass burning plus coal combustion). OP_m data previously measured in the NCP are shown in pink triangles, including Beijing in 2020 (Li et al., 2024; Zheng et al., 2026), Tianjin in 2015 (Liu et al., 2018) and NCP rural area in 2019 (Liu et al., 2024b). Chemical standards measured in this study are shown as squares, with red and purple representing compounds positively and negatively correlated with OP, respectively, and error bars represent the standard deviations. Additionally, the standard deviation ranges of previously reported OP_m values from various sources are illustrated using different color shades. These include primary OP_m from traffic (Traffic_pri), biomass burning (Biomass_burning_pri), and coal combustion (Coal_combustion_pri), as well as SOA from biogenic precursors (SOA_bio) and from two aromatic precursors (m-xylene and naphthalene). The data sources are derived from the following references: Liu et al. (2024b); Bates et al. (2019); Cheung et al. (2010); Fushimi et al. (2017); Jiang et al. (2016); Mcwhinney et al. (2013); Tuet et al. (2017)

Line 774-783. If the biomass and coal fraction are positively scaled with OP_m plus primary OA such as coal combustion exhibited so low OP_m compared to other sources (Fig 8), is it still solid to say primary solid fuel combustion (stated in Line 625) is the dominant driver of OP_m ? Have you tried plotting biomass fraction alone since it's OP_m is much higher? Aren't primary biomass burning and all anthropogenic SOA the dominant contributors to OP_m based on the color shades in Fig 8?

Response: We agree that primary combustion played an important role in OP_m in

Weifang. However, secondary anthropogenic emissions cannot be ignored, as some of the ambient samples exhibited higher OP_m than any of the reported primary sources, falling within the region of m-xylene and naphthalene SOA in Figure 8. Therefore, in the manuscript, we stated that “primary solid fuel combustion and oxygenated OA associated with solid-fuel combustion are the dominant contributors to OP_m .” Additionally, as suggested by the reviewer, we have replotted Figure 8 with the samples color-coded by the fraction of biomass burning alone. The results show that a high biomass burning fraction alone cannot explain the higher OP_m of the particles. Therefore, we consider primary solid fuel combustion and associated secondary anthropogenic organic aerosols to be the dominant factors contributing to OP_m in Weifang.

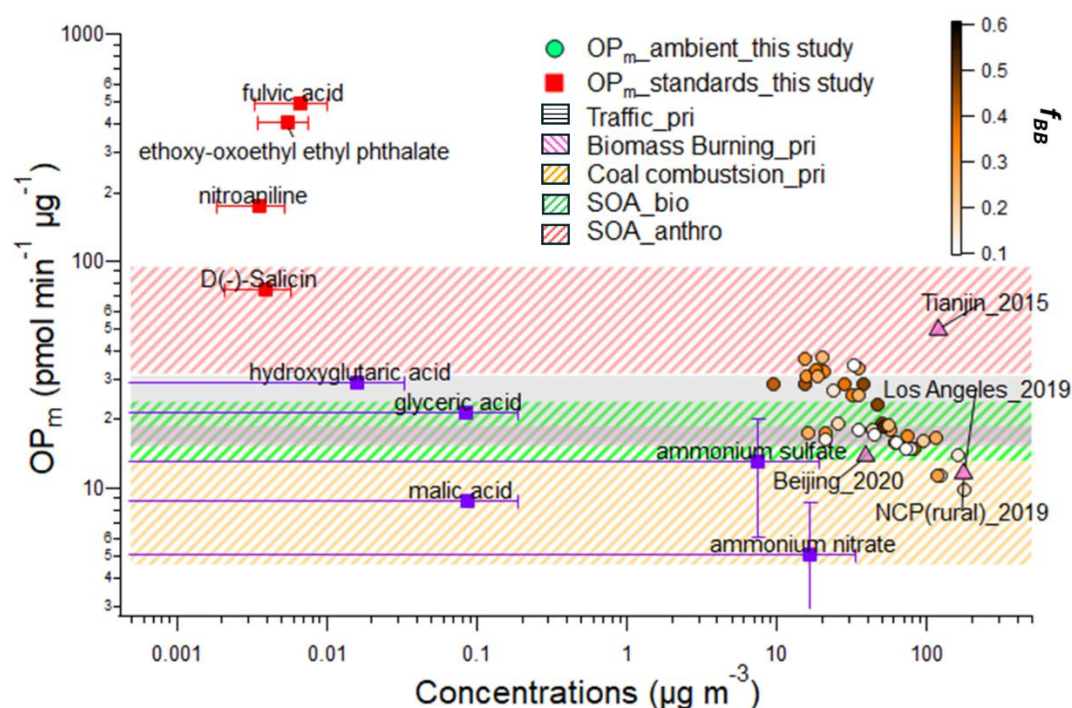


Figure R22. Mass-normalized oxidative potential (OP_m) derived from offline samples and chemical standards in the study. Offline samples collected during the campaign are represented by brown circles, color-coded according to the fractional contribution of solid fuel (biomass burning plus coal combustion). OP_m data previously measured in the NCP are shown in pink triangles, including Beijing in 2020 (Li et al., 2024; Zheng et al., 2026), Tianjin in 2015 (Liu et al., 2018) and NCP rural area in 2019 (Liu et al., 2024b). Chemical standards measured in this study are shown as squares, with red and purple representing compounds positively and negatively correlated with OP , respectively, and error bars represent the standard deviations. Additionally, the standard deviation ranges of previously reported OP_m values from various sources are illustrated using different color shades. These include primary OP_m from

traffic (Traffic_pri), biomass burning (Biomass_burning_pri), and coal combustion (Coal_combustion_pri), as well as SOA from biogenic precursors (SOA_bio) and from two aromatic precursors (m-xylene and naphthalene). The data sources are derived from the following references: Liu et al. (2024b); Bates et al. (2019); Cheung et al. (2010); Fushimi et al. (2017); Jiang et al. (2016); Mcwhinney et al. (2013); Tuet et al. (2017)

Line 790-795. Aren't the OP_m differences and comparisons just due to measurements in different years which related to different stages of air quality mitigation implementation, instead of emission source differences in megacities vs median/small-sized cities?

Response: We compared our data with those from other megacities such as Beijing and Tianjin, as well as medium-sized cities. The implementation of air quality mitigation measures indeed improved the air quality in the NCP overall and led to a lower OP_m. However, considering the substantial differences in OA compositions and sources discussed in Section 3.1, spatial variation in OP_m still persisted, although we were unable to compare data from exactly the same sampling year across sites due to limited data availability. For example, we compared our Weifang data in 2023 with those from Beijing in 2020, when air quality had both improved considerably. Weifang also exhibited a stable interannual variation in PM_{2.5} over the past five years (Figure R10).

Line 803-804. Is this statement based on higher correlations of OP with OA (fig S6)? But can high correlation necessarily lead to high importance? As you also stated in Line 543-554, Feb 11 (one day after Chinese New Year) exhibited similarly high OP_m caused by transition metals during firework events.

Response: We have answer the question about the correlation between OP and OA in Reviwer 1's Major Comment 1 and we presented briefly here: We fully acknowledge that the correlations between OA and OP, even when validated by OP experimental tests for some selected compounds, cannot entirely avoid uncertainties caused by the covariance of OA compounds with different OP reactivities. Nevertheless, the correlations between specific OA compounds, sources and OP provide valuable insights into the likely origins of these compounds in this understudied yet populated NCP city.

Consequently, similar correlation-based approaches are widely applied as a

preliminary estimation of OA toxicity characteristics, particularly for OP analyses in Chinese cities, where numerous components may act synergistically. For example, OP activation between some OA species (e.g., PAHs and BFRs) was investigated in Guangzhou (Zhang et al., 2025); OP was found to be more correlated with Mn, K, and nitrate in six Chinese cities (Ye et al., 2024), and OP was found to be driven by carbonaceous aerosols in Beijing (Li et al., 2024). Correlations between PM sources and OP have been reported to help pinpoint dominant local or regional toxic sources for OP, such as indoor biomass burning (Zhang et al., 2024a), residential coal combustion (Luan et al., 2022; Li et al., 2019a), and source apportionment sources, especially for primary combustion sources (Kim et al., 2025; Cao et al., 2026).

To better elucidate the novelty of our study and tuned down the conclusions from correlations, we have revised the manuscript as follows:

Line 610-616:

Two distinct pollution episodes accounted for the peak OP_v levels (Fig. 1b). The episode on January 12 was characterized by substantial secondary inorganic contributions (50 %) and levoglucosan ($0.59 \mu\text{g m}^{-3}$; 1.9 % of OA), indicative of strong secondary aerosol formation and biomass burning emissions. While the increasing proportion of secondary inorganics tends to suppress OP_m , the peak OP_v level was likely impacted by the high contribution of biomass burning suggested by elevated levoglucosan.

Line 622-624:

~~Such a similarity indicates that OP driven by OA during biomass burning events could rival the toxicity levels driven by transition metals during firework events.~~

This similarity suggests that OA-driven OP during biomass burning events may reach toxicity levels comparable to those driven by transition metals, which are widely recognized as key contributors to OP in Weifang.

Line 117-130:

Identifying OP-active OA compounds is difficult due to the complexity of the

composition, functional groups, and structures of the tens of thousands of OA compounds. Therefore, correlation-based methods have commonly been applied to identify potential candidate OP-active compounds and their sources sources in China (Zhang et al., 2025; Ye et al., 2024; Li et al., 2024). These methods provide valuable information regarding key sources and further highlight key compounds for toxicological studies to investigate their structures and biological responses, enabling policymakers to formulate effective control policies. For example, correlations between PM sources and OP have been used to help pinpoint dominant local or regional toxic sources of OP, such as indoor biomass burning (Zhang et al., 2024a), residential coal combustion (Luan et al., 2022; Li et al., 2019a), and source apportionment sources, especially for primary combustion sources (Kim et al., 2025; Cao et al., 2026).

Line 824-826. Considering the similar OP_m in Fig 8 for Beijing and Weifang, is it still solid to say OP activity vary significantly across NPC region between Beijing and Weifang? Instead, would it mean OP can be very similar despite of different OA composition and origins?

Response: The OP_m values presented in our study were derived from ambient samples collected in different sites, as well as from standards and source samples; they therefore span a wide range and are plotted on a logarithmic scale. In Weifang, the daily ambient OP_m values varied by a factor of 4: although the lowest sample (10 pmol min⁻¹ μg⁻¹) was close to the average of Beijing (13 pmol min⁻¹ μg⁻¹), the highest sample (38 pmol min⁻¹ μg⁻¹) was nearly 3 times higher. Overall, the average OP_m value in our study was 60% higher than that in Beijing, indicating spatial heterogeneity in OP_m across the NCP region.

We would also like to note that even at the same sampling site, OP_m values can vary considerably depending on the sources, PM levels, and PM and OA compositions. For example, during the period dominated by solid fuel combustion, characterized by a high abundance of moderately oxygenated OA with high DBE values (shown in Figures 4, 6, and 8), the OP_m levels in Weifang were significantly higher than the average of Beijing. Meanwhile, during the haze periods, the formation of secondary inorganic

aerosols and less OP-active OA compounds, led to a decline in the mass-normalized OP, resulting in OP_m values similar to those of Beijing. Therefore, comparing the absolute values of OP_m alone is not sufficient to draw conclusions on toxicity; the underlying chemical composition and sources must be considered.

Based on the information above, we believe that our statement, that OP activity varied significantly across the NCP region, and that OA compounds and their sources played an important role still hold.

Technical:

Line 68-70. It seems repetitive from the sentence in Line 62-64. You may consider keeping only one of them.

Response: We have deleted the expression as suggested:

~~Epidemiological studies have indicated strong associations between OA and adverse outcomes, including respiratory and cardiovascular hospital visits, morbidity, and mortality (Pye et al., 2021).~~

Line 151. What do you mean “near-molecular”?

Response: We have revised the expression to “molecular”

Line 213-216. It seems repetitive from the sentence in Line 204-209. Please remove one of them.

Response: We have deleted the repetitive expression

~~The OA compounds identified with FIGAERO-CIMS can be regarded as oxygenated since it is more favored to charge moderately oxygenated OA.~~

Figure 1. why is the size area of the dots in panel c-e proportional to the “fourth” square root of corresponding integrated signals (Line 313)?

Also why are the data shown in panel c-e “in autumn” (Line 313) since in Line 321 the data from Wangdu are from January 2019?

Response: We plotted the dots using the fourth root of the integrated signals, as these signals varied considerably among different OA compounds. Line 313 has been revised as follows:

Line 364-365 : The size area of dots was proportional to the fourth root of

corresponding integrated signals.

The description of the season for the Wangdu data has also been revised.

Line 363-364: from Beijing (BJ, autumn), Wangdu (WD, winter), and Weifang (WF, autumn, this study)

Line 543. I think you meant fig 1a here instead of fig 1b.

Response: We have changed the figure citation in the revised manuscript.

Line 610-611. Two distinct pollution episodes accounted for the peak OP_v levels (Fig. S2).

Responses to Comments by Reviewer #3

Overall assessment

This manuscript presents a comprehensive characterisation of the molecular composition, sources, and oxidative potential (OP) of PM_{2.5} during the heating season in Weifang. The combination of online measurements, molecular characterization using FIGAERO-CIMS, PMF source apportionment, hierarchical clustering, and DTT measurements provides a valuable dataset for investigating the sources and molecular characteristics associated with aerosol OP. The manuscript contains substantial analysis, and the overall dataset appears suitable for addressing the research questions. However, I found that several interpretations, particularly those concerning the identification of compounds and sources driving OP, are stated more strongly than the statistical analyses directly demonstrate. Since a considerable part of the manuscript relies on correlations between PM components, molecular compounds, source factors, and OP, I think the distinction between association, source attribution, and contribution to OP needs to be made more clearly. Some reorganisations of the Results would also considerably improve the flow of the manuscript. I therefore have the following comments.

Response: We thank the reviewer for the constructive suggestions and the response to the comments have been shown below.

Major comments

1. Interpretation of PM_{2.5}–OA and PM_{2.5}–nitrate correlations

Around lines 302–307, the authors report correlations of PM_{2.5} with OA ($r=0.80$) and nitrate ($r=0.71$) and use the stronger OA correlation to suggest that OA is a key driver of PM_{2.5} pollution. The correlations are useful for showing that these components covary with PM_{2.5}, but I am not convinced that the difference between ($r=0.80$) and ($r=0.71$) by itself supports the stronger interpretation concerning their relative importance. This is particularly relevant because OA and nitrate are both components of PM_{2.5}, and nitrate is reported to contribute approximately 29% of PM_{2.5} compared with approximately 22% for OA.

If the intention is to establish that OA has a particularly important role in PM_{2.5} pollution,

I suggest that the authors clarify the basis for this conclusion rather than relying mainly on the difference between these two correlation coefficients. If additional analyses presented later in the manuscript support this interpretation, connecting them more explicitly here would strengthen this discussion.

Response: We thank the reviewer for the insightful suggestion. Indeed, similar suggestions have also been given by the Reviewer 2, and **we fully agree with both reviewers that the representativeness of correlation analysis should carefully assessed and comprehensively discussed in the paper.** To address this, we have softened the related statements and added more discussion on this issue as suggested.

Line 357-358: However, in Weifang, the correlation coefficient between PM_{2.5} and OA ($r = 0.80$) was stronger than that with nitrate ($r = 0.71$, Fig. S3), underscoring that OA emissions are the key driver to fine PM pollution, especially during extreme episodes.

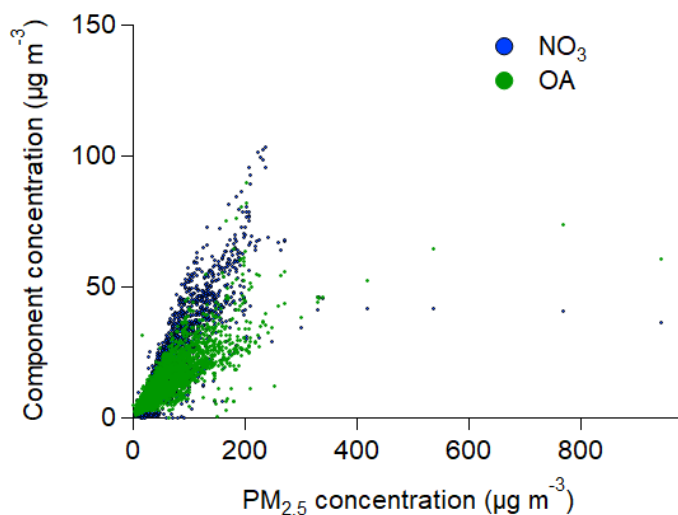


Figure R23 (Figure S3). The correlation between PM_{2.5} and OA and NO₃ concentrations

We suggest that OA may contribute more to PM_{2.5} pollution in Weifang because, in some cases, particularly during periods influenced by solid fuel combustion in autumn and winter, PM_{2.5} was more closely correlated with primary emissions than during non-heating periods ($r = 0.87$ from Nov 15 to Dec 15, and $r = 0.63$ from Mar 15 to 29), as reflected by the higher correlation coefficient with OA. However, during

episodes of heavy secondary aerosol pollution, such as Dec 27–30 and the non-heating period (March 15–29), PM_{2.5} pollution was more likely driven by secondary inorganic aerosol formation and was therefore more strongly correlated with NO₃ ($r = 0.87$). We agree with the reviewer's point that the difference between these two correlation coefficients alone cannot demonstrate that OA plays a particularly more important role in PM_{2.5} pollution. To address this concern, we have added a figure to the revised supplementary information, which suggests that OA and NO₃ may play different roles in PM_{2.5} pollution during different episodes.

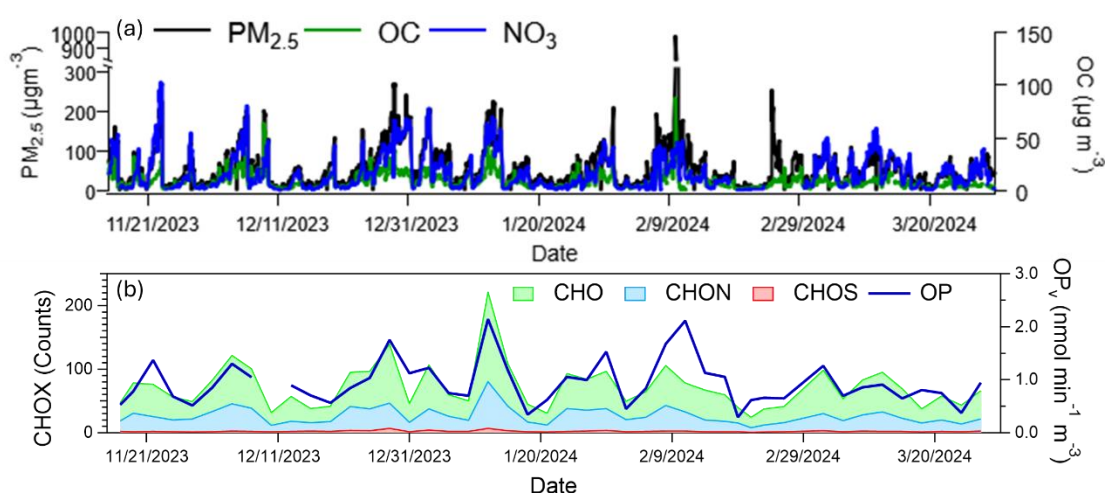


Figure R24 (Figure S2). Time series of (a) PM_{2.5} NO₃ and OC, (b) CHO, CHON, CHOS of CHOX groups and volume-normalized OP of PM_{2.5} during the sampling period

SI: During periods influenced by solid fuel combustion in autumn and winter, PM_{2.5} was more closely correlated with primary emissions than during non-heating periods ($r = 0.87$ from Nov 15 to Dec 15, and $r = 0.63$ from Mar 15 to 29), as reflected by the higher correlation coefficient with OA. However, during episodes of heavy secondary aerosol pollution, such as Dec 27–30 and the non-heating period (March 15–29), PM_{2.5} pollution was more likely driven by secondary inorganic aerosol formation and was therefore more strongly correlated with NO₃ ($r = 0.87$).

2. Statistical robustness and interpretation of the molecular-level OP analysis

A substantial part of the later analysis relates individual molecular compounds to OP. Around lines 660–662, compounds associated with OP_m are selected from the 274 high-abundance OA compounds based on their individual correlations with OP_m

($p < 0.05$). Given the relatively limited number of offline OP samples and the large number of compound correlations being evaluated, I think some additional clarification of the statistical treatment would be useful. In particular, when a large number of correlations are tested using $p < 0.05$, some compounds may be identified as significant simply by chance. Could the authors clarify whether this was considered when selecting the OPm-associated compounds? If not, I suggest that the authors consider an appropriate statistical approach or discuss this limitation, particularly since the selected compounds are subsequently used in the source-attribution analysis. The subsequent MLR analysis (lines 655–674) also requires some clarification regarding both the methodology and its interpretation. As I understand it, the authors use the MLR to determine which of the four sources is most strongly associated with each compound previously identified as correlated with OPm. This appears useful for identifying the likely source associations of these OPm-correlated compounds. However, at lines 669–674, the manuscript goes a step further and states that a source contributing strongly to a positively correlated compound thereby exerts a “significant positive influence on the overall OP”, whereas a source associated with a negatively correlated compound may exert a “negligible or suppressive effect” on OPm. It is not clear to me how these conclusions follow directly from the analysis. An association between a source and a compound that is itself correlated with OPm does not necessarily demonstrate that the source influences OPm through that particular compound. I suggest that the authors clarify the basis for this interpretation or use wording that more closely reflects the associations demonstrated by the analysis. In addition, the MLR is introduced in the Results, but I could not identify a corresponding methodological description of the analysis in the Methods. Please provide sufficient methodological information to explain how the MLR was performed, including how the regression coefficients were obtained and normalised and how their relative magnitudes were used for source attribution.

Response: We agree with the reviewer that relying on correlation coefficients and t-test values alone may lead to potentially incorrect conclusions, as some compounds may appear to be associated with OP merely by chance.

We fully acknowledge that the correlations between OA and OP, even when validated by OP experimental tests for some selected compounds, cannot entirely avoid uncertainties caused by the covariance of OA compounds with different OP reactivities. Nevertheless, the correlations between specific OA compounds, sources and OP provide valuable insights into the likely origins of these compounds in this understudied yet populated NCP city.

Consequently, similar correlation-based approaches are widely applied as a preliminary estimation of OA toxicity characteristics, particularly for OP analyses in Chinese cities, where numerous components may act synergistically. For example, OP activation between some OA species (e.g., PAHs and BFRs) was investigated in Guangzhou (Zhang et al., 2025); OP was found to be more correlated with Mn, K, and nitrate in six Chinese cities (Ye et al., 2024), and OP was found to be driven by carbonaceous aerosols in Beijing (Li et al., 2024). Correlations between PM sources and OP have been reported to help pinpoint dominant local or regional toxic sources for OP, such as indoor biomass burning (Zhang et al., 2024a), residential coal combustion (Luan et al., 2022; Li et al., 2019a), and source apportionment sources, especially for primary combustion sources (Kim et al., 2025; Cao et al., 2026).

To better elucidate the novelty of our study and tuned down the conclusions from correlations, we have revised the manuscript as follows:

Line 117-130:

Identifying OP-active OA compounds is difficult due to the complexity of the composition, functional groups, and structures of the tens of thousands of OA compounds. Therefore, correlation-based methods have commonly been applied to identify potential candidate OP-active compounds and their sources in China (Zhang et al., 2025; Ye et al., 2024; Li et al., 2024). These methods provide valuable information regarding key sources and further highlight key compounds for toxicological studies to investigate their structures and biological responses, enabling policymakers to formulate effective control policies. For example, correlations between

PM sources and OP have been used to help pinpoint dominant local or regional toxic sources of OP, such as indoor biomass burning (Zhang et al., 2024a), residential coal combustion (Luan et al., 2022; Li et al., 2019a), and source apportionment sources, especially for primary combustion sources (Kim et al., 2025; Cao et al., 2026).

We agree with the reviewer that a high correlation between OP_m and an OA compound cannot directly prove that a specific source affects OP_m through that compound. Meanwhile, such correlations do provide information on whether certain OA compounds, likely originating from specific sources as identified by the MLR method, are positively or negatively correlated with the overall OP_m of PM_{2.5}, thereby indicating whether they may contribute to or suppress OP_m. To clarify this point, we have revised the discussion in the manuscript as follows:

Line 761-768: Accordingly, for compounds positively correlated with OP_m, a higher regression coefficient for a specific source indicates that the source is the primary contributor to that compound, thereby potentially making a positive contribution to the overall OP_m. Conversely, for compounds negatively correlated with OP_m, a higher regression coefficient suggests that, while the abundance of this compound from certain source origins increases, the overall OP_m of total PM_{2.5} decreases, implying that such a compound may have a potentially negative contribution.

For the MLR method, we have added the following discussions in the revised manuscript.

Line 316-327. To quantitatively identify key OP-active compounds and their dominant sources, a multilinear regression model was applied. The input data consisted of time series of four major organic aerosol sources identified through cluster analysis: secondary inorganics, biomass burning, vehicle emissions, and coal combustion, which were previously determined using Positive Matrix Factorization. Additionally, signal intensities of OA compounds were included as input variables. This approach enabled the apportionment of OA compounds to their respective contributions from the four major OA sources. To facilitate comparison of the dominant source for each compound based on their MLR coefficients, the coefficients for each compound were normalized

to the maximum value among the four coefficients corresponding to the four OA sources.

3. Interpretation of the January 12 and February 11 high-OPv episodes

Around lines 543–554, the interpretation of the two high-OPv episodes is not entirely clear to me. On Jan 12, the authors report a secondary inorganic contribution of 5% and an elevated levoglucosan concentration ($0.59 \mu\text{g m}^{-3}$; 1.9% of OA), which are interpreted as evidence of strong secondary formation and solid-fuel-burning influence. In contrast, on Feb 11, SO_2 and metals associated with fireworks increased approximately tenfold above the campaign average. The similar OPv values during the two episodes are then used to conclude that OP driven by OA during biomassburning events could rival that driven by transition metals during fireworks. While levoglucosan indicates biomass-burning influence on Jan 12, I do not understand how the presented evidence (levoglucosan $\sim 1.9\%$) establishes that the high OPv on this day was specifically driven by biomass-burning OA. Similarly, the description of a 5% secondary inorganic contribution as “high” is unclear. Please clarify the source contributions on Jan 12 and the evidence supporting the attribution of its high OPv to biomass-burning OA.

Response: We apologize for the misunderstanding caused by a typo in Lines 543–554. The contribution of secondary inorganic species in January should be $\sim 50\%$ rather than 5% presented in the manuscript. As clearly shown in Figure 2, the PMF analysis indicates that secondary inorganics were the largest contributor to $\text{PM}_{2.5}$. It has been corrected in the revised manuscript.

Regarding the evidence for the significant impact of biomass burning, levoglucosan contributed approximately 1.9% of total OA during the episode, which is nearly half of the level observed in fresh biomass burning plumes (Mazzoleni et al., 2007), highlighting the importance of fresh biomass burning emissions in the ambient atmosphere, considering the contributions of secondary inorganics and other primary sources also existed in Weifang winter. In addition, Cubison et al. (2011) reported that f_{60} , an aerosol mass spectrometer (AMS) tracer representing the ratio of organics from

levoglucosan and similar species (mannosan, galactosan) from biomass burning to total OA, exceeding 0.3% indicates a non-negligible influence of biomass burning activities. Although a direct comparison is not possible due to the lack of AMS measurements in our study, the fraction of levoglucosan to OA on January 12 was substantially higher than this threshold value. Finally, the PMF results show that the contribution of biomass burning reached as high as 25% of total PM_{2.5} on January 12, significantly higher than in other heavy pollution episodes (5%–12%) that were dominated by other sources (Figure 2). Therefore, biomass burning was likely the key contributor to the elevated OP_v observed on January 12.

4. Interpretation of intrinsic OP measurements and the conclusion regarding “aged primary OA”

The discussion of the standard-compound measurements requires some clarification. Around line 739, malic acid is reported to have an intrinsic OP_m of approximately 22 pmol min⁻¹ μg⁻¹ and is described as having negligible activity. However, the campaignaverage ambient OP_m is reported as approximately 24 pmol min⁻¹ μg⁻¹. It is therefore unclear on what quantitative basis an intrinsic OP_m of 22 is considered “negligible.” Or is this supposed to be 2.2 pmol min⁻¹ μg⁻¹? Please clarify the criterion used for this terminology and revise it if appropriate. I also suggest reconsidering the interpretation around lines 779–783. The association of high OP_m with solid-fuel combustion, together with the moderately oxygenated character of OP-associated compounds is good. However, I am not convinced that the presented analyses uniquely demonstrate that this represents aged primary OA. For example, oxidation of VOCs emitted by solid-fuel combustion followed by SOA formation could potentially produce a similar association and molecular signature. If the authors can distinguish aged POA from combustion-derived SOA using the available measurements, the evidence should be explained more explicitly. Otherwise, terminology such as oxygenated OA associated with solid-fuel combustion may better reflect what is directly supported by the observations.

Response: This is a very helpful suggestion. The OP_m of malic acid measured in our

OP tests was $22 \text{ pmol min}^{-1} \mu\text{g}^{-1}$, which is close to that of secondary inorganic species with low intrinsic OP_m , such as ammonium sulfate ($13 \text{ pmol min}^{-1} \mu\text{g}^{-1}$), and considerably lower than that of the high- OP_m compounds in our OP tests ($75 - 490 \text{ pmol min}^{-1} \mu\text{g}^{-1}$). Moreover, considering that secondary inorganic species, which are widely recognized as compounds with low OP_m , accounted for over 50% of $\text{PM}_{2.5}$ (ammonium sulfate and ammonium nitrate combined), the intrinsic OP_m of the total OA fraction should be higher than the overall OP_m of bulk $\text{PM}_{2.5}$ ($24 \text{ pmol min}^{-1} \mu\text{g}^{-1}$). Therefore, OP_m of malic acid is relatively lower than other high OP_m OA compounds.

Nevertheless, we agree with the reviewer that the word “negligible” is misleading in the text, particularly given the OP_m value of $22 \text{ pmol min}^{-1} \mu\text{g}^{-1}$. We have therefore revised the wording throughout the manuscript to avoid such misunderstanding.

Line 840-843:

“Specifically, despite their relatively high abundance in OA during sampling period, glyceric acid ($\text{C}_3\text{H}_6\text{O}_4$, average: $84 \pm 10 \text{ ng m}^{-3}$) and malic acid ($\text{C}_4\text{H}_6\text{O}_5$, average: $90 \pm 10 \text{ ng m}^{-3}$) exhibited relatively lower OP_m values (8.8 and $22 \text{ pmol min}^{-1} \mu\text{g}^{-1}$, respectively).”

We thank the reviewer for suggesting the replacement of the term “aged primary OA” with “oxygenated OA associated with solid-fuel combustion.” As the reviewer pointed out, we cannot distinguish between aged primary OA and SOA formed from VOCs emitted by solid-fuel combustion with our current measurement methods. Such separation would be extremely difficult, as the compositions of the two are very similar (Kroll et al., 2011). Therefore, we have replaced “aged primary OA” with “oxygenated OA associated with solid-fuel combustion” throughout the revised manuscript.

Line 887-888. specifically oxygenated OA associated with solid-fuel combustion, plays a critical role in driving OP activity in the NCP.

Specific and technical comments

1. **Around line 346:** EC is subsequently referred to, but I could not identify an independent EC measurement in the described methods. The manuscript describes BC

measured by AE33, whereas EC is only explicitly mentioned elsewhere as a water-insoluble component excluded from the DTT analysis. Please clarify whether EC was independently measured or whether EC here refers to BC, and use BC/EC terminology consistently.

Response:

We also thank the reviewer for this suggestion. As the reviewer pointed out, we did not measure elemental carbon (EC) in this study; rather, we measured black carbon (BC) using an aethalometer. Accordingly, we have revised the relevant expressions throughout the manuscript to use “BC” consistently.

Line 400-401:

“Hourly online water-soluble ions, OC, BC, and trace elements data were utilized to resolve major PM_{2.5} sources in Weifang using the PMF method.”

2. Lines 377–379: The vehicle-emission factor appears to peak at approximately 10:00, whereas the CO maximum is described as occurring between 08:00 and 09:00. Please clarify this temporal difference if the CO profile is being used to support the vehicle-source attribution.

Response: Indeed, unique tracers for vehicle emissions remain limited, especially in the particle phase. Although previous molecular-level studies have used hopanes and steranes (e.g., cholestanes) as tracers for gasoline and diesel vehicle emissions (Schauer and Cass, 2000) these compounds are subject to photochemical reactions in the atmosphere and cannot be measured by our FIGAERO-CIMS, which targets oxygenated OA. Therefore, we used the diurnal pattern of CO to reflect the emission pattern of vehicle emissions.

It should be noted, however, that CO is a gaseous pollutant, whereas vehicle emissions were apportioned by PMF using particulate BC and OC. Their atmospheric lifetimes and diurnal variations, influenced by photochemical reactions and boundary layer dynamics, may therefore differ. In addition, CO, as well as particulate BC and OC, can originate from multiple primary combustion sources; for instance, we cannot rule out a contribution from coal combustion in the morning, as resolved by PMF and

indicated by elevated SO₂.

As the reviewer pointed out, CO in our study peaked at 8 – 9 am, about one hour earlier than the vehicle emission factor resolved by PMF, which increased at 8 am and peaked at around 10 am. This discrepancy may be explained by two factors. First, the PMF-resolved vehicle factor may be mixed with other primary sources, such as coal combustion due to the lack of unique tracers as discussed above. Second, the morning rush hour in Weifang City can typically last 3 – 4 hours, so traffic-related emissions were likely elevated throughout this period, during which the exact peak time may vary from day to day.

Nevertheless, vehicle emissions exhibited an earlier morning peak than any other resolved primary sources, and therefore the morning CO enhancement is more likely attributable to vehicle emissions than to other primary sources. Consequently, we consider that the diurnal variation of CO provides supportive evidence for the identification of the traffic source impact that peaked in the morning, even though the peak times indicated by CO and by the PMF factor differ slightly.

3. Around line 441: The discussion uses levoglucosan to support the attribution to coal/solid-fuel combustion. Please report the corresponding correlation coefficient with the relevant PMF factor, if this correlation forms part of the source-attribution evidence.

Response: The correlation coefficient has been added.

Line 499-501: and its moderate correlation with the biomass burning tracer ($r = 0.6$) can be explained by the co-emission of coal combustion alongside biomass burning in the NCP (Yan et al., 2017).

4. Lines 449 and 460: Please provide the corresponding r values for the correlations discussed.

Response: We have added the corresponding r values as suggested.

Line 508-509

Compounds that were highly correlated ($r > 0.7$) with vehicle emissions showing higher

molecular

Line 519-520

Compounds strongly correlated with secondary inorganic sources ($r > 0.7$) exhibited low DBE values (1 – 3) and lower molecular masses (200 – 300 Da).

5. Lines 591 and 597: Please report the corresponding correlation coefficients rather than describing the relationships only qualitatively.

Response: We have added the corresponding r values as suggested.

Line 680-682

Moreover, we observed that compounds with clear positive correlations ($r > 0.5$) to OP_m generally exhibit moderate oxidation state OS_c (-1 to 1),

Line 687-688

In contrast, the clearly positive correlated OA compounds ($r > 0.5$) fall into two groups:

6. Lines 613–619: On 22 November and 28 March, secondary inorganic aerosol (76%) and dust (47%), respectively, dominate the $PM_{2.5}$ mass, while OP_m remains comparable to the campaign average. These observations are used to conclude that secondary inorganics and dust are not the key components driving OP. If so, could the authors clarify which components or sources are thought to account for the observed OP_m on these two days? Was it still biomass burning and coal combustion?

Response: We apologize that the OP_m value cited in the original manuscript corresponded to the wrong date. The raw data we submitted with the manuscript clearly show a much lower OP_m on the days in question than on the solid-fuel-combustion-dominated days (<https://zenodo.org/records/21298413>). For the two days suggested by the reviewer, the OP_m values were 11 and 15 $pmol\ min^{-1}\ \mu g^{-1}$, significantly lower than the campaign average (24 $pmol\ min^{-1}\ \mu g^{-1}$). This supports our statement that secondary inorganic species were not the dominant contributors to OP during those periods. We have corrected the data in the revised manuscript. In addition, for the dust-dominated day (e.g., Mar 18), the OP_m value was close to the campaign average. This is likely because the influence of dust itself did not exhibit high OP activity. To correct the

erroneous data citation and clarify the discussion, we have revised the manuscript as follows:

Line 705-714

We compared the source apportionment results and the corresponding OP_m variations on several representative days: Nov 22 ($PM_{2.5}$: $122 \mu g m^{-3}$, OP_m : $11 pmol min^{-1} \mu g^{-1}$), Jan 6 ($PM_{2.5}$: $20 \mu g m^{-3}$, OP_m : $38 pmol min^{-1} \mu g^{-1}$), Jan 21 ($PM_{2.5}$: $15 \mu g m^{-3}$, OP_m : $37 pmol min^{-1} \mu g^{-1}$), and Mar 28 ($PM_{2.5}$: $73 \mu g m^{-3}$, OP_m : $15 pmol min^{-1} \mu g^{-1}$). Generally low OP_m values were observed on the days dominated by secondary inorganic aerosols and dust (11 and $15 pmol min^{-1} \mu g^{-1}$ on Nov 22 and Mar 28, and $27 pmol min^{-1} \mu g^{-1}$ on Mar 18), implying that secondary inorganic species and dust were not the key components driving OP activity in Weifang City.

7. **Line 680:** The terminology used to describe correlations should be made more consistent throughout the manuscript. For example, around lines 496–498, $r=0.81$ is described as a high correlation whereas $r=0.72$ is described as moderate, while around line 680 $r>0.4$ is used when describing compounds as “significantly correlated.” As mentioned in (1) of the Major comments, there doesn’t seem to be too strong of a difference between these two correlations. Also, Please clarify whether defined ranges are being used to classify correlation strength and apply them consistently. In addition, correlation strength (r) should be distinguished from statistical significance (p -value or confidence interval). Since correlation analysis is central to the manuscript, I suggest reporting the numerical r values where these relationships support important interpretations rather than relying only on qualitative terms. A supplementary table summarising the principal correlations used for source attribution and OP interpretation may also improve transparency.

Response: We applied different correlation coefficient thresholds for the positive and negative correlations because different variables were correlated in the two analyses. In Lines 496–498, we correlated the absolute concentrations of $PM_{2.5}$ components and the signal intensities of OA compounds and clusters from HCA. Considering that the co-

variation of different species induced by meteorological conditions (e.g., boundary layer evolution) and emission characteristics may introduce spurious correlations, a higher correlation coefficient threshold was appropriate. In contrast, in Line 680, we correlated the OA compound signals normalized to total CHO_X with the normalized OP_m, which was defined as the total OP divided by PM_{2.5} concentrations. These two normalized variables are influenced by additional factors, such as the varying fractions of secondary inorganics in PM_{2.5}. Moreover, when exploring the contribution of OA compounds to the OP of PM_{2.5}, the results may be affected by components other than organics as well as by the varying OA fractions in PM_{2.5}. Therefore, a lower correlation coefficient threshold ($r > 0.4$) was applied. To avoid potential misunderstanding, we have added the following explanations and removed the term “significant” throughout the discussion of the normalized data correlations.

Line 774-776:

Furthermore, the compounds whose signals were normalized to CHO_X were positively correlated with OP_m ($r > 0.4$; a lower threshold was applied because both the OA compound signals and OP_m were normalized).

Additionally, as suggested, we have provided the correlation coefficients and the corresponding p-values between the normalized signal intensities of the 274 high-intensity compounds used in the HCA and the OP_m of PM_{2.5}.

Table R3 (Table S3). The correlation coefficients and the corresponding p-values between the normalized signal intensities of the 274 high-intensity compounds

Compound	Correlation Coefficient	p-value	Compound	Correlation Coefficient	p-value	Compound	Correlation Coefficient	p-value
CH ₂ IO ₃	0.07	0.63	C ₈ H ₆ IO ₄	-0.45	0.00	C ₁₁ H ₁₃ NIO ₃	-0.26	0.09
C ₂ H ₂ IO ₃	-0.12	0.43	C ₅ H ₁₀ IO ₆	0.45	0.00	C ₈ H ₁₇ NIO ₅	-0.19	0.21
C ₂ H ₅ NIO ₂	-0.20	0.20	C ₉ H ₁₀ IO ₃	0.08	0.58	C ₁₁ H ₁₂ IO ₄	0.11	0.47
C ₂ H ₄ IO ₃	-0.46	0.00	C ₈ H ₉ NIO ₃	0.11	0.49	C ₁₀ H ₁₁ NIO ₄	-0.09	0.57
C ₃ H ₃ NIO ₂	-0.35	0.02	C ₈ H ₈ IO ₄	-0.16	0.28	C ₆ H ₁₀ IO ₈	-0.29	0.05
C ₃ H ₄ IO ₃	-0.11	0.46	C ₉ H ₁₂ IO ₃	0.00	1.00	C ₁₀ H ₁₀ IO ₅	0.02	0.88
C ₂ H ₄ N ₂ IO ₂	-0.21	0.17	C ₇ H ₇ NIO ₄	-0.28	0.07	C ₇ H ₁₄ IO ₇	0.08	0.62
C ₂ H ₃ NIO ₃	-0.28	0.06	C ₇ H ₆ IO ₅	-0.57	0.00	C ₉ H ₉ NIO ₅	-0.30	0.04
C ₃ H ₇ NIO ₂	0.31	0.04	C ₈ H ₁₀ IO ₄	-0.07	0.64	C ₉ H ₈ IO ₆	-0.39	0.01
C ₂ H ₂ IO ₄	-0.48	0.00	C ₉ H ₁₄ IO ₃	0.11	0.47	C ₁₃ H ₈ IO ₃	-0.15	0.32

C3H6IO3	0.49	0.00	C7H9NIO4	-0.55	0.00	C10H12IO5	-0.21	0.17
C6H6N2O7	-0.03	0.84	C7H8IO5	-0.62	0.00	C14H12IO2	-0.13	0.40
C3H8IO3	-0.02	0.88	C11H8IO2	-0.26	0.08	C11H16IO4	-0.28	0.07
C4H5NIO2	-0.29	0.05	C8H12IO4	-0.38	0.01	C9H10IO6	-0.57	0.00
C4H4IO3	0.03	0.83	C12H12IO	-0.02	0.90	C10H14IO5	-0.38	0.01
C3H4N2IO2	0.10	0.53	C9H16IO3	0.21	0.17	C11H18IO4	-0.38	0.01
C4H6IO3	0.18	0.23	C6H6IO6	-0.33	0.03	C9H13NIO5	-0.26	0.08
C3H5NIO3	-0.62	0.00	C7H10IO5	-0.57	0.00	C9H12IO6	-0.54	0.00
C3H4IO4	-0.56	0.00	C11H10IO2	-0.35	0.02	C13H12IO3	-0.36	0.01
C4H8IO3	-0.17	0.26	C8H14IO4	-0.25	0.09	C10H16IO5	-0.40	0.01
C3H6IO4	-0.63	0.00	C6H8IO6	-0.62	0.00	C8H11NIO6	-0.24	0.12
C5H4IO3	-0.07	0.67	C10H8IO3	-0.27	0.07	C12H11NIO3	0.14	0.36
C4H4N2IO2	-0.33	0.03	C7H12IO5	-0.23	0.13	C12H10IO4	-0.42	0.00
C5H7NIO2	-0.12	0.45	C11H12IO2	0.06	0.68	C9H14IO6	-0.29	0.05
C4H2IO4	0.14	0.35	C9H7NIO3	-0.18	0.24	C8H13NIO6	-0.45	0.00
C5H6IO3	0.12	0.44	C6H11NIO5	0.17	0.28	C9H17NIO5	0.01	0.96
C4H5NIO3	-0.68	0.00	C9H6IO4	-0.39	0.01	C13H17NIO2	-0.09	0.55
C4H4IO4	-0.52	0.00	C6H10IO6	-0.36	0.02	C12H12IO4	-0.25	0.10
C5H8IO3	0.03	0.83	C10H10IO3	0.10	0.52	C9H19NIO5	-0.21	0.16
C4H7NIO3	-0.62	0.00	C9H9NIO3	-0.16	0.29	C11H12IO5	0.14	0.36
C4H6IO4	-0.46	0.00	C6H13NIO5	-0.20	0.18	C12H16IO4	-0.13	0.41
C5H10IO3	-0.14	0.36	C9H8IO4	-0.26	0.08	C10H11NIO5	-0.10	0.50
C4H8IO4	-0.59	0.00	C9H11NIO3	-0.10	0.52	C10H10IO6	-0.52	0.00
C2H6N2IO4	0.28	0.06	C8H6IO5	-0.62	0.00	C7H14IO8	-0.01	0.95
C6H6N2IO	0.22	0.14	C9H10IO4	-0.07	0.66	C14H28IO2	0.36	0.01
C2H5NIO5	-0.11	0.49	C10H14IO3	0.38	0.01	C10H14IO6	-0.50	0.00
C6H5NIO2	-0.08	0.59	C7H5NIO5	-0.57	0.00	C9H13NIO6	-0.31	0.04
C2H4SIO4	-0.31	0.04	C4H9NIO7	0.03	0.83	C10H17NIO5	-0.01	0.93
C5H5NIO3	-0.56	0.00	C9H12IO4	-0.06	0.67	C9H15NIO6	-0.42	0.00
C5H4IO4	-0.48	0.00	C10H16IO3	0.14	0.36	C10H19NIO5	-0.14	0.35
C5H7NIO3	-0.39	0.01	C7H7NIO5	-0.25	0.10	C11H23NIO4	-0.16	0.30
C5H6IO4	-0.46	0.00	C8H10IO5	-0.48	0.00	C12H13NIO4	-0.51	0.00
C6H10IO3	0.05	0.73	C9H14IO4	-0.31	0.04	C12H12IO5	-0.06	0.68
C4H5NIO4	-0.59	0.00	C10H18IO3	0.13	0.40	C11H10IO6	-0.46	0.00
C5H9NIO3	-0.51	0.00	C7H9NIO5	-0.60	0.00	C12H14IO5	0.01	0.97
C5H8IO4	-0.21	0.17	C7H8IO6	-0.63	0.00	C11H12IO6	-0.01	0.95
C6H12IO3	0.00	0.98	C8H12IO5	-0.56	0.00	C10H15NIO6	-0.39	0.01
C4H6IO5	-0.63	0.00	C9H16IO4	-0.51	0.00	C14H15NIO3	-0.13	0.38
C5H10IO4	-0.27	0.07	C10H6IO4	-0.06	0.70	C11H19NIO5	-0.01	0.94
C3H5NIO5	-0.68	0.00	C7H10IO6	-0.33	0.03	C9H13NIO7	-0.52	0.00
C8H8IO2	0.28	0.07	C11H10IO3	-0.08	0.61	C10H17NIO6	-0.41	0.01
C3H6SIO4	-0.28	0.06	C8H14IO5	-0.12	0.42	C11H21NIO5	-0.19	0.20
C7H6IO3	0.07	0.65	C10H9NIO3	-0.09	0.56	C13H14IO5	0.08	0.62
C6H6N2IO2	0.33	0.03	C7H13NIO5	0.19	0.21	C13H16IO5	0.01	0.96

C6H5NIO3	-0.06	0.72	C8H17NIO4	0.36	0.01	C15H24IO3	0.27	0.07
C6H4IO4	-0.29	0.06	C9H4IO5	-0.55	0.00	C13H18IO5	-0.42	0.00
C7H8IO3	-0.17	0.26	C10H8IO4	-0.38	0.01	C18H22IO	0.01	0.97
C6H7NIO3	-0.46	0.00	C9H7NIO4	-0.37	0.01	C11H17NIO6	-0.44	0.00
C6H6IO4	-0.29	0.06	C6H11NIO6	-0.53	0.00	C10H15NIO7	-0.50	0.00
C6H9NIO3	-0.45	0.00	C10H11NIO3	-0.21	0.16	C12H23NIO5	-0.27	0.07
C6H8IO4	-0.39	0.01	C7H15NIO5	-0.19	0.22	C14H14IO5	0.48	0.00
C5H7NIO4	-0.57	0.00	C10H10IO4	-0.04	0.81	C10H17NIO7	-0.37	0.01
C5H6IO5	-0.60	0.00	C9H9NIO4	-0.12	0.44	C8H8IO10	0.52	0.00
C6H10IO4	-0.38	0.01	C10H13NIO3	0.11	0.48	C14H16IO5	-0.08	0.61
C8H5NIO2	0.08	0.60	C9H8IO5	-0.51	0.00	C10H18IO8	-0.26	0.09
C5H8IO5	-0.62	0.00	C10H12IO4	0.03	0.84	C14H18IO5	-0.26	0.09
C8H8IO3	0.14	0.37	C8H7NIO5	-0.41	0.01	C15H16IO5	-0.29	0.05
C7H7NIO3	0.06	0.68	C9H11NIO4	-0.24	0.11	C11H18IO8	-0.28	0.07
C4H11NIO5	0.13	0.39	C12H6IO3	-0.22	0.15	C15H18IO5	-0.24	0.11
C6H2IO5	-0.27	0.07	C9H10IO5	-0.33	0.03	C12H8IO8	0.56	0.00
C5H2N2IO4	-0.28	0.06	C13H10IO2	0.14	0.37	C14H16IO6	-0.39	0.01
C8H10IO3	-0.10	0.51	C10H14IO4	-0.04	0.77	C15H20IO5	-0.33	0.03
C6H5NIO4	-0.27	0.08	C5H12IO8	-0.32	0.03	C15H6IO6	0.56	0.00
C7H9NIO3	-0.44	0.00	C9H12IO5	-0.50	0.00	C13H18IO7	0.34	0.02
C6H4IO5	-0.44	0.00	C6H16IO7	-0.12	0.43	C12H16IO8	0.34	0.02
C7H8IO4	0.01	0.93	C10H16IO4	-0.40	0.01	C12H18IO8	0.12	0.43
C6H7NIO4	-0.62	0.00	C14H16IO	-0.14	0.37	C15H16IO6	-0.43	0.00
C6H6IO5	-0.57	0.00	C8H11NIO5	-0.55	0.00	C16H20IO5	-0.05	0.76
C7H10IO4	-0.32	0.03	C8H10IO6	-0.63	0.00	C15H18IO6	-0.44	0.00
C8H14IO3	0.09	0.56	C12H10IO3	-0.47	0.00	C16H22IO5	-0.22	0.14
C6H9NIO4	-0.50	0.00	C9H14IO5	-0.48	0.00	C14H20IO7	0.32	0.03
C6H8IO5	-0.35	0.02	C13H14IO2	-0.30	0.05	C13H18IO8	0.40	0.01
C10H8IO2	-0.26	0.08	C11H9NIO3	-0.10	0.50	C14H12IO8	0.42	0.00
C7H12IO4	-0.40	0.01	C8H13NIO5	-0.10	0.52	C17H24IO5	-0.16	0.29
C11H12IO	-0.01	0.95	C11H8IO4	-0.24	0.12	C15H12IO8	0.37	0.01
C6H10IO5	-0.01	0.93	C12H12IO3	0.07	0.63	C18H24IO5	-0.28	0.06
C10H10IO2	0.15	0.33	C7H11NIO6	-0.53	0.00	C15H14IO8	0.36	0.01
C5H9NIO5	0.05	0.73	C11H11NIO3	-0.15	0.32	C18H12IO6	0.37	0.01
C8H4IO4	-0.31	0.04	C8H15NIO5	0.01	0.97	C17H16IO8	0.12	0.43
C9H8IO3	0.04	0.79	C11H10IO4	-0.23	0.13	C17H18IO8	0.09	0.58
C6H12IO5	0.16	0.29	C12H14IO3	-0.01	0.93			
C8H7NIO3	-0.20	0.18	C10H9NIO4	-0.39	0.01			

8. Lines 760–762: Please report the relevant correlation coefficient(s) supporting the relationship discussed here.

Response: We have added the corresponding r values as suggested. Since normalized

signals of OA compounds were applied to CHOX and normalized OP to PM_{2.5} concentrations, a lower correlation coefficient threshold ($r > 0.4$) was applied.

Line 864-865. To evaluate the potential redox activity of the molecular formulas positively correlated ($r > 0.4$) with OP_m, such as C₁₄H₁₂O₈ ...

9. Section 3.3: The authors first discuss correlations between individual FIGAERO-CIMS compounds and the PMF-derived sources (Fig. 3), and subsequently group 274 high-abundance compounds into six clusters using HCA and again relate these clusters to the PMF sources (Fig. 4). I found this progression somewhat repetitive. Since the HCA groups compounds with similar temporal behaviour, would it provide a clearer narrative to introduce the clusters first and discuss relevant individual compounds/tracers within each cluster? Alternatively, please clarify what distinct information the individual compound analysis in Fig. 3 provides beyond the subsequent HCA analysis.

Response: The compounds discussed in Figure 3 were selected solely because of their high correlations with different source types, which helps to validate the PMF source apportionment results for PM_{2.5}. In contrast, the list of 274 high-abundance compounds applied in HCA in Figure 4 was selected based on their high signal intensities and therefore provides less indication of sources. We first present the correlations between the compounds and the source apportionment results in Figure 3 in order to validate the PMF results. This suggests that the PM_{2.5} sources identified by PMF can be independently validated by the organic compounds measured with FIGAERO-CIMS. On this basis, we can further compare the OA clusters from HCA with the PM_{2.5} sources to investigate the typical OA types and their potential sources in Figure 4. Therefore, Figures 3 and 4 are not duplicated; rather, they are logically connected within the analysis.

10. Line 100: The sentence "... when fresh anthropogenic mixed with biogenic emissions...", appears incomplete. Can be rephrased as "...when fresh anthropogenic emissions are mixed with biogenic emissions..."

Response: We have rephrased the expression as suggested.

Line 93-95

Additionally, when fresh anthropogenic are mixed with biogenic emissions, ROS generation and OP can be further enhanced...

11.Line 172: The Methods state that offline PM_{2.5} sampling was conducted from 15 November 2023 to 15 March 2024. However, the figures and later discussion appear to include measurements extending to approximately 30 March. Please check the sampling/measurement period and make the dates consistent throughout the manuscript.

Response: We have corrected the sampling period and make the date consistent.

Line 187

from Nov 15, 2023, to Mar 29, 2024, covering the whole heating season in Weifang.

Line 439-440

spring-heating season (Mar 1 – Mar 15), and the post-heating season (Mar 16 – Mar 29).

12.Lines 188–189: The text currently states that “OC was calculated as TC minus OC,” which appears to be a typographical error. The Methods state that BC was measured using an AE33 and TC using a TCA-08, while the Supporting Information indicates that OC was obtained from the difference between TC and BC. I therefore assume this should read $OC=TC-BC$. Please correct/clarify.

Response: We have corrected the expression.

Line 209-210

Organic carbon (OC) was calculated as TC minus BC and OA was calculated as 1.4 times OC.

13.Line 673: Consider replacing “whereas” with “while

Response: We have replaced the expression as suggested.

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