We deeply appreciate Reviewers for their constructive recommendation and the helpful suggestion. We have updated the manuscript following these comments and addressed all points raised. These comments are very helpful for improving our manuscript. Specific responses to each of the comments are provided below (review's comments in **black**, our responses in blue, details of the changes made to the manuscript in *blue font*). And the modifications in the revised manuscript with marks are marked in yellow. We are pleased to provide the revised manuscript and hope both Reviewers are satisfied with our responses.

Response to Reviewer #2

1) Reviewer's general comment:

In this study, different fractions of organic carbon in ambient fine particulate matter (PM2.5) in ten Chinese cities and their optical effects were investigated. Results indicated that the optical effects of extractable organic carbon are mainly contributed by relatively hydrophobic fractions (i.e., water-insoluble organic carbon and humic-like substances). Both empirical indices and the source apportionment model indicate that aromatic compounds from primary emissions tend to exhibit a stronger light-absorbing capacity. This study can provide significant information on the chemical compositions and sources of brown carbon (BrC) for further mitigating the climate effects of PM2.5. I recommend accepting this manuscript if the following comments could be addressed in the revised version.

Response: We appreciate Reviewer#2 professional review for our article. We have revised the manuscript to address the comments. Our responses to the specific comments and changes made in the manuscript are given below

2) Reviewer's comment:

1. This study cannot represent the entire China, because only samples from urban areas were analyzed. All these samples were collected during 2013-2014, a period marked by intensive coal combustion in China. Since 2017, coal has been gradually replaced by natural gas for domestic heating during the cold season. Please change

the title of the manuscript.

Response: We appreciate the constructive feedback provided by the reviewer. It is acknowledged that our sampling sites are primarily located at typical urban areas, and therefore, they may not fully represent the entirety of China. In response, we have amended the title of the manuscript to reflect this focus: *"The Wate -insoluble organic carbon in PM2.5 of typical Chinese urban areas: light-absorbing properties, potential sources, radiative forcing effects, and the possible light-absorbing continuum".*

Furthermore, we agree with the reviewer's observation regarding the significant policy shifts initiated by the Chinese government since 2017, particularly in promoting clean energy policies and prohibiting open biomass burning. It is important to note that our samples were collected during the period of 2013-2014, predating these clean energy initiatives. Consequently, our findings are reflective of a time when coal combustion and biomass burning exerted considerable influence on the sampled air quality. Additionally, during the sampling period, a substantial contribution from secondary aerosols to particulate pollution was observed in China. Given the significance of biomass burning, coal combustion, and Secondary Organic Aerosols (SOA) as sources of BrC with strong light-absorbing capabilities, WIOC emerges as a major contributor to the light absorption of BrC. The sample sets collected during this timeframe offer a unique opportunity to elucidate which sources predominantly contribute to Chinese WIOC and which exhibit the strongest light absorption capacity.

3) Reviewer's comment:

2. This manuscript only investigated the optical effects of organic aerosols. Please remove sentences regarding the health effects of organic aerosols from the Abstract and Introduction.

Response: Good suggestion! We agree with reviewer that this study mainly focus on the light-absorbing properties of WIOC. We have removed health effects of organic aerosols in the Abstract, and rewritten the second paragraph in the Introduction to emphasize the main point of this study.

The manuscript is revised as follows:

Lines 66 to 81: *"According to water solubility, OC can be classified into two main categories: water-soluble OC (WSOC) and water-insoluble OC (WIOC). While WSOC has been extensively studied over the past decades, with investigations focusing on its sources, light-absorbing properties, and atmospheric processes (Bosch et al., 2014; Dasari et al., 2019; Mo et al., 2021; Wang et al., 2020; Wozniak et al., 2014). WIOC, which makes up large fraction of OC (~up to 80%) and a substantial portion of light absorption by BrC, has received comparatively less attention. WIOC exhibits a significantly higher light-absorbing capacity compared to WSOC, attributed to the enrichment of strong light-absorbing BrC chromophores in WIOC. For instance, certain strong BrC chromophores like polycyclic aromatic hydrocarbons (PAHs) and their derivatives, as well as high-molecular-weight oligomers, are water-insoluble (Huang et al., 2020; Kalberer et al., 2006; Xie et al., 2017). Indeed, Zhang et al. (2013) reported that the light absorption by methanol-extracted OC in Los Angeles was approximately 3 and 21 times higher than that by WSOC. Moreover, field observations indicate that WIOC exhibits greater recalcitrance during long-range transport processes compared to WSOC, leading to a longer lifetime for WIOC (Fellman et al., 2015; Kirillova et al., 2014; Wozniak et al., 2012). Given that WIOC represents a relatively long-lived OC component with a higher light-absorbing capacity, a comprehensive understanding of its sources and light-absorbing properties is imperative."*

4) Reviewer's comment:

3. In this manuscript, coal combustion has been proposed as an important source. Please demonstrate the contribution of coal combustion areas without central heating during winter. Is coal combustion indeed a significant source?

Response: Thank you for your constructive comment. As suggested by the reviewer, we have conducted further analysis to investigate the spatiotemporal dynamics of WIOC sources. Despite coal combustion and biomass burning (BB) contributing comparably to the annual WIOC levels (31.1% vs. 31.0%), notable spatial and seasonal variations were evident. As illustrated in Figure R1, As showed in Figure

R1, during cold seasons, coal combustion contributed, on average, 17.4% of WIOC in areas without central heating, a proportion significantly lower than that attributed to BB (54.2%). Conversely, in areas with central heating, coal combustion exhibited a much higher contribution than BB (56.2% vs. 14.8%) during cold seasons. These observations underscore the prominence of coal combustion and BB as primary sources of WIOC in areas with and without central heating, respectively, particularly during cold seasons.

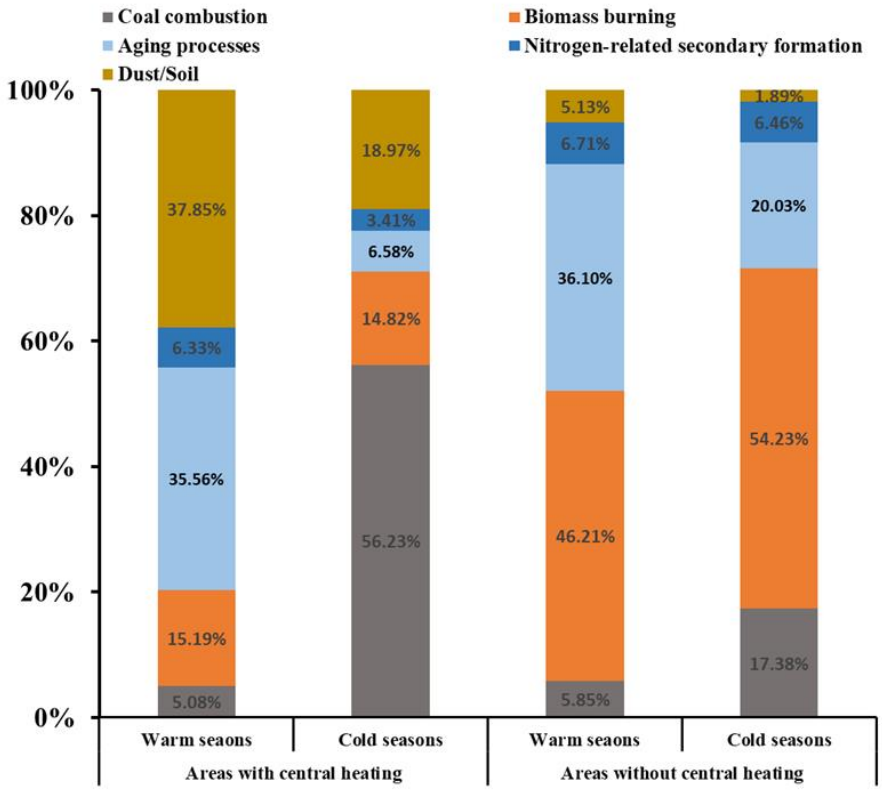

Figure R1. The spatial (Aeras with/without central heating) and seasonal (warm/cold seasons) variation of sources contribution of WIOC in China

The manuscript is revised as follows:

Lines 391 to 411: *"The primary sources of WIOC were combustion sources, with coal combustion and BB averagely account for 31.1% and 31.0% of the WIOC, respectively. Although the contribution of coal combustion to WIOC was comparable to that of BB, both exhibited distinct spatial and seasonal variations. Specifically, during winter, coal combustion emerged as the dominant source of WIOC, accounting*

for 48.4% of the total, likely driven by increased coal usage in areas with central heating. Indeed, coal combustion constituted the primary source of WIOC in areas with central heating during cold seasons (56.2%). In contrast, in areas without central heating, the contribution of BB surpassed that of coal combustion significantly (54.2% vs. 17.3%). Therefore, coal combustion and BB were identified as the predominant sources of WIOC in areas with and without central heating, respectively, during cold seasons. Compared to primary emissions sources, the contributions of the sources related to aging processes and nitrogen-induced secondary formation were relatively lower, accounting for 18.2% and 5.2% of the WIOC, respectively. That may be due to these two secondary sources are more enriched in water-soluble components (HULIS-C + non-HULIS-C). Actually, although the uncertainties of sources contribution of HULIS-C and non-HULIS-C resolved by PMF model may be high, the aging processes and nitrogen-related secondary formation contributed 10.1% and 20.2% to HULIS-C, and 18.3% and 21.6% to non-HULIS-C, respectively. In addition, during the summer, when both temperature and solar radiation intensity rise, the contributions from aging processes and BB increased to 39.3% and 41.3%, respectively. In spring, a significant fraction of WIOC was associated with dust/soil, reaching up to 28.8%. Specially, the dust/soil contribution was much higher in the aeras with central hearing than those without central heating. This is consistent with the fact that sandstorms from the Gobi desert that borders China and Mongolia ride springtime winds to affect the air quality of Northern China (Filonchyk et al., 2024).”

5) Reviewer’s comment:

4. Cl- is used as a marker of coal combustion. However, sea salt is also a significant source of Cl- in PM2.5, particularly in cities like Shanghai and Guangzhou. Please ensure that only non-sea salt Cl- is included into the model. Please refer to the equation for calculating non-sea salt Cl- as provided in Ma et al. (10.5194/acp-18-5607-2018).

Response: We appreciate the reviewer for highlighting this aspect and recommending the referenced article. We acknowledge the contribution of sea salt

aerosols maybe also a significant source of Cl- in PM2.5, particularly in coastal cities like Guangzhou and Shanghai in this study. Before conducting the PMF model, we assessed the contribution of sea salt Cl- to the total Cl- using the equation: non-sea salt Cl- ([nss-Cl-] = [Cl-] − 1.17 × [Na+]). The analysis revealed that the contribution of sea salt Cl- to the total Cl- was generally below ~7% in Guangzhou and Shanghai. Furthermore, we performed comparisons between the PMF results obtained using only non-sea salt Cl- and those using total Cl-. We found that the PMF factors and their corresponding contributions did not exhibit significant changes (within 6%). In the revised manuscript, we added more discussion to emphasize that sea salt was not a significant source of Cl- in this study.

The manuscript is revised as follows:

Lines 371 to 376: *"Factor 1 exhibited a high Cl- loading (57.0%), which a typical tracer for BB, coal combustion and sea-salt aerosols. Sea-salt derived Cl- is considered as a significant source of Cl- in PM2.5 in coastal cities. In this study, we assessed the contribution of sea-salt Cl- ([ss-Cl-] =[ss-Cl-] = 1.17 × [Na+]) to the total Cl-. We found that even in the coastal cities, such as Guangzhou and Shanghai, the contribution of sea-salt Cl- to total Cl- was generally below ~7%. Thus, the high loading of Cl- is not likely caused by the sea-salt aerosols."*

6) Reviewer's comment:

5. The authors proposed a light-absorbing carbonaceous continuum. However, it is important to note that there may be overlaps between the different carbon components. The operational definition of carbon components also varies. The compounds the authors refer to as 'char BC' most likely belong to 'brown carbon' or 'humic like substances', and are unlikely to bias optically based BC measurements in large cities. Please address this point.

Response: Good point! Indeed, the distinction between various carbonaceous components is based on a conceptual and operational definition and does not correspond in reality to a clear boundary. In this work, the WIOC, HULIS-C, and non-

HULIS-C are well-defined based on their polarity, while the definition BC, including the char- and soot-BC, is more related to the thermal and optical properties. These are two different operational definitions, so there may be overlap between these carbonaceous components. A part of char-BC may show a chemical and physical behavior similar to high-molecular-weight OC compounds (e.g., HULIS), which indeed overlap with BrC. We have added a discussion to the revised manuscript to deal with this point raised by the reviewer.

The manuscript is revised as follows:

Lines 605 to 617: *"It is important to acknowledge that carbonaceous aerosols encompass a wide array of diverse components, exhibiting a continuum of physical and chemical properties. The distinction between these carbonaceous components, as discussed above, is primarily based on conceptual and operational definitions, rather than clear boundaries in reality. In other words, the classification of carbonaceous components in aerosols is highly dependent on operational criteria. In this study, on the one hand, the WIOC, HULIS-C, and non-HULIS-C are well-defined based on their polarity. On the other hand, the definition of BC, which includes char- and soot-BC, is more closely associated with thermal and optical properties. These operational definitions may lead to overlaps between different carbonaceous components. For instance. BB and coal combustion emit large amounts of large molecular weight soluble compounds, such as HULIS (e.g., HULIS), which may char and produce false char EC signals in the TOT analysis (Yu et al., 2002). Additionally, certain portions of char-BC may exhibit chemical and physical behaviors akin to high-molecular-weight OC compounds, thereby overlapping with BrC. Therefore, there is no a clear boundary for the carbonaceous components."*

7) Reviewer's comment:

6. Please double check for grammar. There are lots of grammatic errors in this manuscript.

Response: We sorry for the grammatic errors. We have let a native speaker help polish the language.

8) Reviewer's comment:

7. Please shorten the titles of each section in Results and Discussion.

Response: Thanks for your suggestions. We have shortened the titles of each section in the Results and Discussion.

9) Reviewer's comment:

Specific comments:

Section of Materials and Methods:

Please clarify the year in which the samples were collected.

Response: Thanks for your comment. We have clarified that all the filter samples were collected during 2013 to 2014 in the revised manuscript.

The manuscript is revised as follows:

Lines 104 to 106: *"All the filter samples were collected on pre-combusted (450℃, 6h) quartz-fiber filter (Pall, England) from 2013 to 2014, use a high-volume sampler at a flow rate of ~ 1000L/min."*

10) Reviewer's comment:

Why does Figure 1 display the average aerosol optical depth at 550 nm instead of other wavelengths?

Response: Thanks for your questions. Aerosol optical depth (AOD), is indeed often measured at a wavelength of 550 nanometers (nm). This wavelength is chosen because it falls within the visible spectrum of light and is sensitive to changes in aerosol concentration in the atmosphere. Regarding the sensitivity, Aerosols, such as dust, smoke, and pollutants, have a significant impact on the scattering and absorption of sunlight. At 550 nm, the scattering and absorption properties of common aerosols are well-characterized, making it an ideal wavelength for measuring their optical thickness.

In addition, many satellite sensors designed for measuring AOD, such as the Moderate Resolution Imaging Spectroradiometer (MODIS), operate at or around 550 nm. This wavelength was chosen for its practicality in remote sensing applications. Finally, using a standard wavelength like 550 nm allows for comparability between different studies and datasets. It provides a common reference point for researchers to assess aerosol loading across different regions and times. Therefore, 550 nm is the most common wavelength used for AOD measurements.

11) Reviewer's comment:

Please describe the instrumental method of ion chromatography.

Response: We have provided the instrumental details of ion chromatography in the Supporting information of the revised manuscript (Text S1). Briefly, 3 anions (Cl^-, NO_3^- and SO_4^{2-}) and 4 cations (Na^+, K^+, Ca^{2+} and NH_4^+) were analyzed with ion-chromatography (761 Compact IC, Metrohm, Switzerland). Anions were separated on a Metrohm Metrosep A sup5-250 column with 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ as the eluent and 35 mM H_2SO_4 for a suppressor. Cations were measured using a Metrohm Metrosep C4-150 column with 2 mM sulfuric acid as the eluent. The injection loop volume for anion and cation was 100 μL. The water-soluble ions analyses were duplicated for several filter samples, and the overall relative standard deviations were generally less than 4%.

12) Reviewer's comment:

The random errors and rotational ambiguity of the source apportionment model should be estimated using the bootstrap model and the displacement model. Please provide the evaluation results.

Response: Thanks for your insightful suggestions. We have evaluated the estimate the errors associated with both random and rotational ambiguity of PMF solution by the bootstrap (BS) model and the displacement (DISP) model. The BS factors from the resampled data matrices are mapped to the base run factors to provide the reproducibility of different base run factors due to the random errors. The 4 BS factors

model showed that factor mapping higher than 85%, indicating both uncertainties and the number of factors were appropriate. DISP mainly explores rotational ambiguity in the PMF results. At 4 factor PMF model, no swaps were found in DISP model. In the revised manuscript, we have provided the uncertainty assessment of the PMF model.

The manuscript is revised as follows:

Lines 205 to 212: *"The errors associated with both random and rotational ambiguity in the PMF solution were assessed using the bootstrap (BS) model and the displacement (DISP) model. The BS model involves estimating errors by resampling data matrices, with the resulting BS factors being aligned with the base run factors to gauge the reproducibility of different factors amidst random errors. Analysis using a 4-factor BS model indicated a factor mapping exceeding 85%, suggesting both the suitability of the number of factors and the presence of uncertainties. On the other hand, DISP primarily investigates rotational ambiguity within the PMF outcomes. Notably, in the context of a 4-factor PMF model, no swaps were identified in the DISP analysis."*

2) Reviewer's comment:

Section of Results and Discussion

Please clarify whether the value after average is standard deviation or interquartile range. For instance, in Line 232-232, "The concentrations of WIOC ranged from 1.45 to 12.95 μgC/m3, with an average of 3.64 ± 2.53 μgC/m3 among the 10 cities (Figure 2a)."

Response: Thanks for pointing this out. The value after average is the one standard deviation. We have clarified this point in the revised manuscript.

2) Reviewer's comment:

BB in Line 279 and MW in Line 320 should be defined.

Response: We thank the reviewers for their meticulous work. We have defined the BB (biomass burning) in the right position the revised manuscript. The MW (molecular

weight) was defined before Line 320 in the initial manuscript, so we do not define it again in the Line 320.

2) Reviewer's comment:

p should be in italic.

Response: Corrected.

2) Reviewer's comment:

Technical corrections:

Line 20: Water-insoluble "organic" carbon

Response: Corrected.

2) Reviewer's comment:

Line 45: WIOC "is" primarily originated

Response: Corrected.

2) Reviewer's comment:

Line 157: the relative standard deviation of what?

Response: It should be *"The carbon contents of WIOC were determined by an OC/EC analyzer with standard deviation of reproducibility test less than 3%"* (**Lines 151 to 152**)

The manuscript is revised as follows:

2) Reviewer's comment:

Line 251: were higher than those of non-HULIS (Figure "2"c).

Response: Corrected

The manuscript is revised as follows:

2) Reviewer's comment:

Line 426: It is important

Response: Corrected