

Dear Editor-in-Chief and Reviewers,

We are submitting a revised version of the manuscript (No.: acp-2022-321), entitled: **“Measurement Report: Investigation of pH- and particle size-dependent chemical and optical properties of water-soluble organic carbon: implications for its sources and aging processes”**. We have carefully addressed all the comments provided by the reviewers. The details can be found in our enclosed “Response to Reviewers”. In the attachment, an item-by-item response to the comments of the reviewers is given below. All revisions are highlighted in blue in the main text of the revised manuscript.

Thank you for taking care of the review process for this paper.

Sincerely,

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The manuscript exhibited the effects of pH and particle size on optical properties and functional groups to identify the chemical structure, aging and sources of WSOC. Considering that the characteristics of WSOC are influenced by many factors and the complexity of atmospheric processes, this is an attractive study that can improve data support for climate effect of WSOC. There are several issues that need to be point out before publication (see additional comments):

Additional comments:

1. Line 38: Avoid lumping references as in (Yu et al., 2017; Park et al., 2015; Du et al., 2014) and all other. Instead summarize the main contribution of each referenced paper in a separate sentence. For example, "...derived from the biomass combustion and atmospheric oxidation reactions of organic compounds (Yu et al., 2017; Park et al., 2015; Du et al., 2014), ...".

Response: We are grateful for the suggestion. We have summarized the results of each referenced in Line 40-45 and Line 51-58 according to your suggestions, and details are as follows:

Line 40-45: "WSOC is released from anthropogenic (e.g., biomass burning and coal combustion) and natural sources, and can also be formed through complex secondary reactions (Yu et al., 2017; Wu et al., 2018). The sources of WSOC vary significantly with location and season, e.g., WSOC in PM_{2.5} was primarily derived from secondary aerosol formation and biomass burning in Korea (Park et al., 2015), and from coal combustion, biogenic emission, and secondary aerosol formation in winter and biogenic emission and secondary oxygenation of vehicle exhaust in summer in a northwest city of China (Qin et al., 2018)."

Line 51-58: "Therefore, the size-distribution of WSOC can serve as a good indicator of its sources, fate, and aging processes (Boreddy et al., 2021; Jang et al., 2019; Frka et al., 2018). For example, Frka et al. (2018) found that wood burning were the most important source of humic-like substances (HULIS) in the aerosol accumulation mode (from ~0.1 to ~2 μm) during the autumn and winter; Jang et al. (2019) reported that HULIS in smaller particles were likely derived from local sources while those in larger

particles were from secondary organic aerosols (SOA) in the atmosphere, and Qin et al. (2021a) found that the fluorescence properties of WSOC varied with the particle size, and the fluorescence characteristics of different particle sizes could be used to reveal the aging of WSOC.”

2. Line 41-42: “...air quality and human health”. Please provide references to other literature on the environmental and health effects of WSOC.

Response: Thank you for your valuable suggestion. We have cited related references in Line 39-40 as follows:

“Water-soluble organic carbon (WSOC, see Appendix A for a list of abbreviations) comprises a considerable fraction of organic aerosol mass (10%–80%) (Horník et al., 2021), and plays important roles on climate change (Chen et al., 2020; Sun et al., 2011) and air quality (Snyder et al., 2009).”

3. Line 75: Please supplement the information of the sampling location, such as what is the major impact on the surrounding environment, whether there is a residential area, etc.

Response: Thank you for your above suggestion. We have added the information of the sampling location and described them in Line 89-92 as follows:

“Particulate samples were collected on the roof of a building (~20 m above the ground) inside the campus of the University of Chinese Academy of Sciences (40°24’N, 116°40’E) in Huairou District of Beijing, China. The sampling site is in a typical urban environment surrounded by schools, research institutes, and hospitals. There were no obvious industrial sources nearby, and pollutants were mainly derived from regional transport.”

4. Line 78: In Section 2.3.2, quantitative information is required to calculate SUVA, MAE and FI/TOC. Therefore, filters need to be weighed after sampling until analysis. Please supplement the weighing details.

Response: Thank you for your comment. Quantitative calculations of SUVA, MAE and FI/TOC can be performed without weighing the filters in this study. We are mainly focused on the relative comparison of these indices at different particle sizes in the same period, rather than absolute comparison. So, quantifying SUVA, MAE, and FI/TOC in terms of WSOC concentrations may be more appropriate, and the method of WSOC concentration analysis has been described in Line 101-104. Based on your suggestion, we will present the weighing details of filters to be included in a follow-up paper. We seek for the reviewer's tolerance and understanding. Many thanks for your kind help!

5 Line 80: "...similar to previous studies (Qin et al., 2018)". Please provide more references.

Response: Thank you for your valuable suggestion. Since our description here is not clear enough, we have deleted this sentence from manuscript and modified it in Line 101 as follows:

"For each particle size, a quarter of each filter of all the collected samples in summer or winter season were mixed together, extracted twice via ultrasonication in Milli-Q water for 15 min to achieve the extensive release of solubilized WSOC,"

6. Line 83: Please provide the blank concentration of WSOC in the method section.

Response: Thanks for your kind reminder. We have added the WSOC concentration of blank filter in Line 104 as follows:

"The average WSOC concentration of the blank filter was 0.39 mg L⁻¹."

7. Line 85 and Line 95: "HCl" should be "HCl".

Response: We are grateful for the suggestion. We have replaced all "HCl" with "HCl" in the revised manuscript as follows:

Line 107: "HCl and NaOH were used to adjust the pH of the WSOC solutions."

Line 119: "a drop of 2 mol L⁻¹ HCl was added to the WSOC solution to remove the interference of inorganic carbon."

8. Line 88: Section 2.1.3: Is the pH characteristic of the sample lost after adjusting the pH value of WSOC, then it can not represent the environmental samples? Can we use the pH value of the sample?

Response: Thank you for your careful review. The point you mentioned is really important. Previous study has demonstrated that the change in fluorescence from pH 2-12 are reversible (Henderson et al., 2009). Therefore, the pH fluorescence properties of WSOC would not disappear after adjusting the pH of WSOC.

The pH of particulate matter from different sources varies widely (0-9) (Fridlind and Jacobson., 2000; Qin et al., 2021), and the pH of the same sample also varies significantly during atmospheric chemistry processes (Caig et al., 2018). In these cases, a pH range of 2-10 was selected for our study in order to comprehensively investigate the effect of pH on the fluorescence properties of WSOC. Furthermore, the effect of pH on the fluorescence properties of WSOC with different particle sizes has not been reported yet. The chemical components and structures of different particle size samples were different. Using the pH of the samples for the study may lead to difficulties in interpreting the mechanism of the effect of pH on the fluorescence properties of WSOC. But you are also right in your consideration, we will consider researching the effect of raw pH of sample on the fluorescence properties of different particle sizes in further study according to your suggestions.

Reference:

1. Henderson R K, Baker A, Murphy K R, et al. Fluorescence as a potential monitoring tool for recycled water systems: A review[J]. *Water Res*, 2009, 43(4): 863-881.
2. Fridlind, A. M.; Jacobson, M. Z. A study of gas-aerosol equilibrium and aerosol pH in the remote marine boundary layer during the first aerosol characterization experiment (ACE 1). *J. Geophys. Res.* 2000, 105(D13), 17325-17340.
3. Qin, Y., Yang, Y., Qin, J, et al. pH-responsive fluorescence EEM to titrate the interaction between fluorophores and acid/base groups in water-soluble organic compounds of PM_{2.5}. *Environ. Sci. Technol. Lett.* 2021, 8(2), 108-113.

4. Caig R L, Peterson P K, Lucy N, et al. Direct determination of aerosol pH: size-resolved measurements of submicrometer and supermicrometer aqueous particles[J]. Anal. Chem. 2018, 90(19), 11232–11239.

9. Line 89: “50 ml” should be “mL”.

Response: We are extremely grateful for pointing out this problem. We have revised it in Line 113 as follows:

“a 50 mL WSOC solution was first acidified to a pH below 3 by addition of HCl solution,”

10. Line 100: Section 2.2.2, these quality assurance and control (QA/QC) procedures for these experiments should be explained in details.

Response: Thanks for your kind reminder. We have added quality assurance and control procedures for these experiments in Section 2.4 according to your suggestion as follows:

“2.4. Quality assurance and quality control

Quality assurance and quality control (QA/QC) procedures were applied through the laboratory and instrumental analysis processes. Before sampling, all quartz fiber filters were baked at 550°C for 5.5 h. Prior to analysis, all vials were washed with Milli-Q water, dried, and preheated at 550°C for 5.5 h in a muffle furnace, and then wrapped in aluminum foil before being used. WSOC extraction and measurement were conducted in a designated laboratory. All WSOC concentrations, UV–Vis absorption spectra, EEM fluorescence spectra, and functional groups data were blank-corrected. All instruments operated in this study require regular calibration. Sterile gloves and robes were worn throughout the experimental procedure to avoid contamination and to ensure the accuracy of the test results.”

11. Line 130: In Section 2.3.3, please provide how Raman scattering and Rayleigh scattering are removed in EEM.

Response: Thank you very much for your valuable advice. In this work, we used an interpolation technique to eliminate Rayleigh and Raman scatterings from EEM fluorescence spectra. We have described it in Line 154-155 as follows:

“The interfering fluorescence signals of the Rayleigh and Raman scattering were then eliminated by an interpolation technique.”

12. Line 166-170: The author showed the difference of WSOC sources through different MAE, so please give a specific value or range in order to more intuitively express the MAE difference between biomass burning and secondary formation. In addition, the authors has only discussed biomass burning and secondary formation before, however, it points out three primary sources (biomass burning, coal combustion, and vehicle exhaust) at the end of this sentence (Line 172), please elaborate on this point.

Response: Thank you for your comment. The range of MAE₃₆₅ values for WSOC from different sources have been provided in previous studies (Geng et al., 2020; Washenfelder et al., 2015), the MAE₃₆₅ of WSOC from biomass burning was 0.76-2.47 m² g⁻¹, 0.20-1.33 m² g⁻¹ for fossil fuel combustion, and -0.11±0.20 m² g⁻¹ for biogenic SOA. Following your suggestion, we have added the range to demonstrate the difference in MAE₃₆₅ between biomass burning and secondary formation in in Line 215-216.

The MAE₃₆₅ values of < 0.26 μm, 0.44–0.77 μm, 1.40–2.50 μm, and 2.50–10.0 μm were 0.1258, 0.1321, 0.1014, and 0.1145 m² g⁻¹ in summer and 1.2615, 0.7991, 0.8206, and 0.3707 m² g⁻¹ in winter. Previous study has found that the MAE₃₆₅ of WSOC from biomass burning was 0.76-2.47 m² g⁻¹, 0.20-1.33 m² g⁻¹ for fossil fuel combustion, and -0.11±0.20 m² g⁻¹ for biogenic SOA (Geng et al., 2020). Therefore, we speculate that WSOC may be mainly derived from secondary formation in summer and from mixed sources of biomass burning and fossil fuel combustion in winter. According to your suggestion, we have carefully revised it in Line 215-219 and now described as:

“Literature reported MAE₃₆₅ from different sources showed values of 0.76–2.47 m² g⁻¹ for biomass burning smoke, 0.20–1.33 m² g⁻¹ for fossil fuel combustion, and -0.11±0.20

$\text{m}^2 \text{g}^{-1}$ for biogenic SOA (Geng et al., 2020). Our previous study also found higher MAE_{365} from combustion sources than ambient samples (Qin et al., 2022). The MAE_{365} values observed in the present study suggest that WSOC may be mainly derived from secondary formation in summer and from mixed sources of primary emissions (e.g., biomass burning and fossil fuel combustion) in winter.”

Reference:

1. Geng X, Mo Y, Li J, et al. Source apportionment of water-soluble brown carbon in aerosols over the northern South China Sea: Influence from land outflow, SOA formation and marine emission[J]. Atmospheric Environ. 2020, 229.117484.
2. Washenfelder R. A., Attwood A. R., Brock. C. A, et al. Biomass burning dominates brown carbon absorption in the rural Southeastern United States[J]. Geophys. Res. Lett. 2015, 42, 653–664.

13. Line 175: The unit of “Stokes shift” –“ um^{-1} ” should be “ μm^{-1} ”.

Response: Sorry for our mistake. The corresponding revision has been presented in Table 1 as follows:

“Stokes shift (μm^{-1})”

14. Line 186, Line 340 etc: The article has repeatedly mentioned statistical terms, such as “significant” or “significantly”. Therefore, when make the comparison of data between seasons, authors should supplement the statistical analysis in Section 2(Experimental methods) and provide the statistical results (t-test or ANOVA) in Section 3(Results and discussion).

Response: Thank you for your comment. As suggested by the reviewer, we employed independent samples *t*-tests to evaluate seasonal differences of the data. Descriptions of the statistical analysis for data are shown in Line 172. The results of the *t*-tests are presented in Line 223 and Line 390 of the revised manuscript as follows:

Line 172: “Additionally, the independent-samples *t*-test was used to evaluate the seasonal differences in light absorption and fluorescence properties of WSOC.”

Line 223: “Furthermore, there are significant seasonal variations in the optical properties (e.g., SUVA₂₅₄, MAE₃₆₅, and FI/TOC) of WSOC in smaller particles (*t*-test, *p*=0.021),”

Line 390: “The most significant seasonal differences in the optical properties (e.g., SUVA₂₅₄, MAE₃₆₅, and FI/TOC) were observed for WSOC in smallest particles (*t*-test, *p*=0.021),”

15. Line 199-200: Please supplement references.

Response: Thank you for your valuable suggestion. We have cited the related reference in Line 234 as follows:

“A peak at 1641 cm⁻¹ was also previously reported, which was attributed to conjugated carbonyl (C=O) groups and aromatic rings (C=C) (Zhang et al., 2022).”

Reference:

Zhang T, Huang S, Wang D, et al. Seasonal and diurnal variation of PM_{2.5} HULIS over Xi'an in Northwest China: Optical properties, chemical functional group, and relationship with reactive oxygen species (ROS)[J]. Atmos. Environ, 2022, 268: 118782.

16. Line 205: The title showed the identification of structure by pH value and particle sizes, but author only reflects the influence of particle sizes on functional groups in Section 3.1.2. Please provide the pH value of Figure 1. Additionally, please provide the effect of different pH values on functional groups (Figure and text description).

Response: Thank you for the above suggestion. Indeed, we have discussed the effect of different pH on the functional groups via the variation of EEM fluorescence and UV-Vis absorption spectra properties in Sections 3.2 and 3.3. The variation of UV-Vis absorption spectra with pH showed the presence of at least two distinct chromophores (carboxyl and phenolic groups) deprotonated for particle sizes of >2.50 μm in pH 3-6, while phenolic groups should predominate at pH>8.0. The change of EEM fluorescence revealed that the hydroxyl groups play a leading role in pH-responsive fluorescence in

summer samples, while carboxylic and nitro groups play a dominant role in winter samples. It will be more profound if we get the effect of pH on FTIR spectra results, as you said. We previously investigated the effect of pH on the functional groups of WSOC in PM_{2.5} using FTIR spectroscopy (Wang et al., 2021). However, the determination of FTIR spectra of different pH requires a large mass of samples. Therefore, after considering the large sample requirement or other parameters, the effect of pH on FTIR spectral analysis weren't conducted in this study. The referee's concern is of importance for our further study.

We have added the pH of Figure 1 in Section 2.1.3 (Line 109-111) and modified the title of Figure 1 in Line 246 as follows:

Line 109-111: “The raw pH of WSOC with particle sizes of < 0.26 μm, 0.44–0.77 μm, 1.40–2.50 μm, and 2.50–10.0 μm was 5.61, 5.75, 5.89, and 6.19, respectively, in summer, and 6.19, 6.49, 6.64, and 6.83, respectively, in winter.”

Line 246: “**Figure 1.** FTIR spectra of WSOC in particles of different sizes in summer and winter at raw pH.”

Reference:

Wang X, Qin Y, Qin J, et al. Spectroscopic insight into the pH-dependent interactions between atmospheric heavy metals (Cu and Zn) and water-soluble organic compounds in PM_{2.5}[J]. Science of The Total Environment, 2021, 767:145261.

17. Line 209-210: “pH titration enables qualitative and quantitative analyses of functional groups on the surface of substances (Zhang et al., 2011; Xiao et al., 2014).” Suggest put it in Section 2 (Experimental methods). “However, measurements of such type have not yet been performed for particles with different sizes.” Suggest put it in Section 1(Introduction) and supplement it appropriately.

Response: We are appreciative of the reviewer's suggestion. According to your suggestion, we have moved the sentence “However, measurements of such type have not yet been performed for particles with different sizes.” to Line 78 of Section 1 (Introduction), and have revised and supplemented it carefully. Additionally, Reviewer

#2 also pointed out this problem. However, they suggested “pH titration enables qualitative and quantitative analyses of functional groups on the surface of substances (Zhang et al., 2011; Xiao et al., 2014).” is better placed in Section 1 (Introduction). After careful consideration, we have made the following modifications in Line 69-78. Thank you for input on these changes.

“The commonly used analytical methods to characterize the optical properties of WSOC are three-dimensional excitation-emission matrix (EEM) spectroscopy and ultraviolet–visible (UV–Vis) absorption spectroscopy (Zhang et al., 2021; Yang et al., 2020). The EEM spectroscopy is a rapid as well as informative method to identify chromophores that may not be distinguished by UV–Vis absorption spectroscopy (Chen et al., 2019; Xiao et al., 2020). Therefore, EEM spectroscopy has been widely applied in atmospheric WSOC characterization (Fu et al., 2015; Qin et al., 2018). However, such a technique has not been widely applied to investigate the fluorescence properties of WSOC in different particle sizes. Fourier transform infrared (FTIR) spectroscopy has been frequently used for the identification of WSOC functional groups (Chen et al., 2016a), although this analysis is difficult to perform quantitatively. pH titration enables qualitative and quantitative analyses of functional groups on the surface of substances (Zhang et al., 2011; Xiao et al., 2014), and this approach has recently been successfully applied to the characterization of WSOC in ambient PM_{2.5} (Qin et al., 2021b), but not yet on size-resolved WSOCs.”

18. Line 223-255: Although phenols account for a high proportion in winter, it seems that the proportion of carboxylic acids cannot be ignored in the particle size range of 1.40-2.50 μm . In addition, although the proportion of carboxylic acid groups in summer is higher than that in winter, the proportion of phenolic groups is greater than 50% in both winter and summer, except for 1.40-2.50 μm in winter. The explanation in Line 223-225 is insufficient, and it is suggested to revise this sentence.

Response: Thank you for your careful review. We apologize for not describing it clearly. We have added the description of the proportion of carboxylic and phenolic groups in Line 261-264 as follows:

“Overall, the contribution of strong phenolic groups (>54%) was higher than that of carboxyl groups in all samples except particle sizes of 1.40–2.50 μm . This result indicates that phenolic groups were more abundant than carboxylic groups in WSOC. Meanwhile, except for particle sizes of 1.40–2.50 μm , the contribution of carboxyl was higher and the phenolic group was lower in summer than winter.”

19. Line 281: A redshift of fluorescence peak positions with increasing pH can be observed in summer. The phenomenon could not be seen in Figure 7. Is it Figure 6?

Response: Sorry for causing such confusion. As you said, a redshift of fluorescence peak with increasing pH for the summer samples can be observed in Figure 6, rather than in Figure 7. We have corrected it in Line 324 as follows:

“a redshift of fluorescence peak positions with increasing pH was observed in summer (Fig. 6),”

20. Line 290: It is advised to choose the unified color represents each size. For example, Figure 5 and Figure 7.

Response: Thanks for your kind reminder. We have re-plotted Figure 4 and Figure 7 to make the color representing the different particle size samples uniform, and details are as follows:

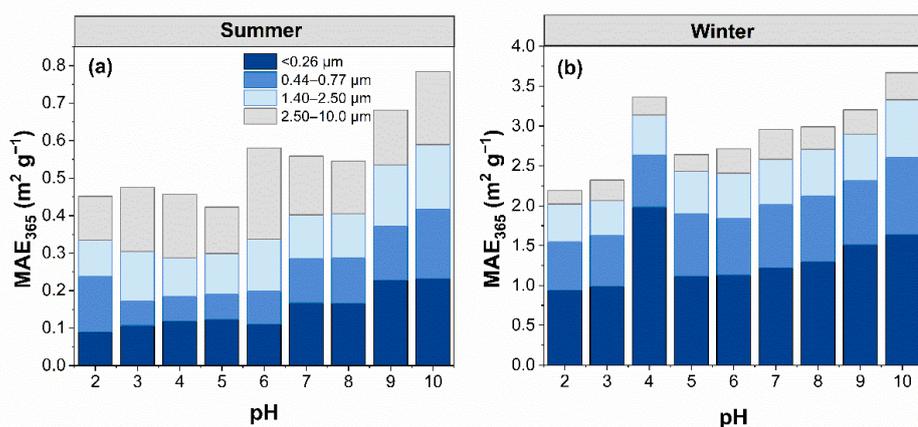


Figure 4. pH dependence of mass absorption efficiency (MAE₃₆₅) for WSOC in particles of different sizes in (a) summer and (b) winter in the pH range of 2–10.

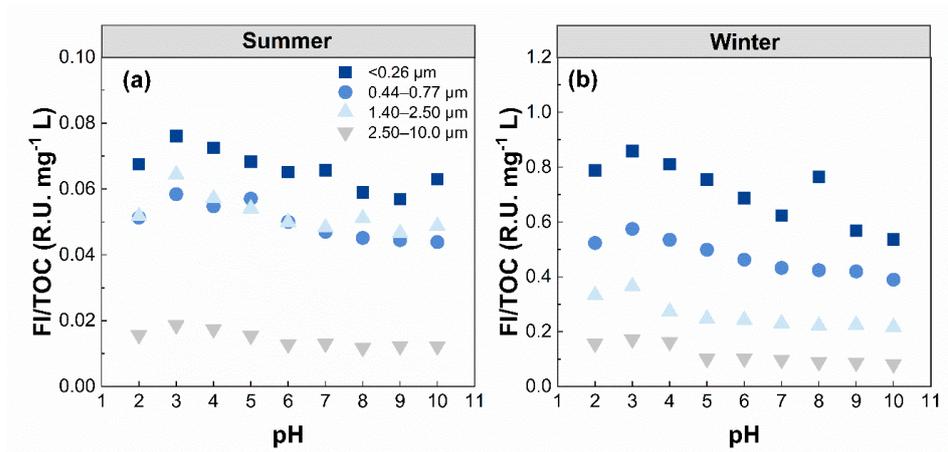


Figure 7. pH dependence of the FI/TOC for WSOC in particles of different sizes in (a) summer and (b) winter in the pH range of 2–10.

21. Line 312: Please provide references.

Response: Thanks for your kind reminder. We have revised it and cited related references in Line 365 as follows:

“Additionally, a high AQY of a substance means that only a small portion of the absorbed radiative energy will be converted into heat, thus reducing its heating effect (Aiona et al., 2018).”

22. Line 371: Some newly references should be cited in this paper, such as: Light absorption properties and molecular profiles of HULIS in PM_{2.5} emitted from biomass burning in traditional "Heated Kang" in Northwest China. *Science of the Total Environment*, 2021, 776, 146014-146022. Seasonal and diurnal variation of PM_{2.5} HULIS over Xi'an in Northwest China: Optical properties, chemical functional group, and relationship with reactive oxygen species (ROS). *Atmospheric Environment* 268. Optical properties, chemical functional group, and oxidative activity of different polarity levels of water-soluble organic matter in PM_{2.5} from biomass and coal combustion in rural areas in Northwest China. *Atmospheric Environment*, 283, (2022)119179

Response: Thanks for your reminder. These references have been included in the revised manuscript. Specific references are listed as follows:

Line 70: “The commonly used analytical methods to characterize the optical properties of WSOC are three-dimensional excitation-emission matrix (EEM) spectroscopy and ultraviolet–visible (UV–Vis) absorption spectroscopy (Zhang et al., 2021; Yang et al., 2020).”

Line 192: “The average MAE₃₆₅ values of particles in the size range of <0.26 μm, 0.44–0.77 μm, 1.40–2.50 μm, and 2.50–10.0 μm were 0.6937, 0.4656, 0.4610, 0.2426 m² g⁻¹, respectively, indicating that WSOC in smaller particles had stronger light absorption capabilities (Huang et al., 2022).”

Line 234: “A peak at 1641 cm⁻¹ was also previously reported, which was attributed to conjugated carbonyl (C=O) groups and aromatic rings (C=C) (Zhang et al., 2022).”

Reference:

1. Zhang T, Shen Z, Zeng Y, et al. Light absorption properties and molecular profiles of HULIS in PM_{2.5} emitted from biomass burning in traditional “Heated Kang” in Northwest China[J]. Science of The Total Environment. 2021, 776: 146014.
2. Huang S, Luo Y, Wang X, et al. Optical properties, chemical functional group, and oxidative activity of different polarity levels of water-soluble organic matter in PM_{2.5} from biomass and coal combustion in rural areas in Northwest China[J]. Atmospheric Environment, 2022, 283: 119179.
3. Zhang T, Huang S, Wang D, et al. Seasonal and diurnal variation of PM_{2.5} HULIS over Xi'an in Northwest China: Optical properties, chemical functional group, and relationship with reactive oxygen species (ROS)[J]. Atmospheric Environment, 2022, 268: 118782.

23. References: Please check the references and unified format. For example, “Effect of the Urban Heat Island on Aerosol pH” in Line 378.

Response: We are very sorry for our careless mistake. We have checked all references and revised the format to make them uniform. Some of the references that were modified are as follows:

“Battaglia, M. A., Douglas, S., and Hennigan, C. J.: Effect of the urban heat island on

aerosol pH, *Environ. Sci. Technol.*, 51, 13095–13103,

<http://dx.doi.org/10.1021/acs.est.7b02786>, 2017

Snyder, D. C., Rutter, A. P., Collins, R., Worley, C., and Schauer, J. J.: Insights into the origin of water soluble organic carbon in atmospheric fine particulate matter, *Aerosol Sci. Technol.*, 43, 1099–1107, <http://dx.doi.org/10.1080/02786820903188701>, 2009.”