Dear reviewer:

We are very grateful for your careful review and insightful comments and suggestions, which have greatly helped to improve the quality and readability of our manuscript. We have addressed all of your concerns and made specific changes to the manuscript as follows.

1. Why only four transition metals were considered for the study? Since the objective is to have better understanding of atmospheric processes of transition metals with HULIS. So, why Fe^{+3} was not considered in this study? As Fe^{+3} is involved in the Fenton's reaction and it is one of major reaction known to take place in atmosphere. Then for health risk, Why Cr^{+6} was not considered?

Thank you very much for your insightful comments and questions. We agree that it would be ideal if including some more additional heavy metal species, but limited by the sample amount (it requires a lot $PM_{2.5}$ filter samples to extract HULIS), only four transition metals were selected.

Cu^{2+}, Zn^{2+}, Mn^{2+}, and Ni^{2+} were chosen because of their prevalence in atmospheric environment or significant health risks. Fe^{+3} has been reported to be ROS-generative and photoactive, and the Fe^{3+} chemistry is complex and important that deserves to carry out a separate experiment, thus it is considered in our future research.

Cr^{6+} was not considered because our previous research and recent research on the pollution profile of trace metals in Beijing $PM_{2.5}$ found that Zn, Mn, and Cu were relatively abundant, and Ni posed the highest health risk, so that we choose them as representative metal ions (Zhou et al., 2017; Lei et al., 2021, Hua et al., 2024).

References:

Zhou X, Zeng N, Li Y et al. Chemical Characteristics and Sources of Heavy Metals in Fine Particles in Beijing in 2011-2012. Environmental Science (China). 2017, 38: 4054-4060.

Hua C, Ma W, Zheng F, et al. Health risks and sources of trace elements and black carbon in PM2.5 from 2019 to 2021 in Beijing. Journal of Environmental Sciences, 2024, 142: 69-82.

Lei W, Zhang L, Xu J, et al. Spatiotemporal variations and source apportionment of metals in atmospheric particulate matter in Beijing and its surrounding areas. Atmospheric Pollution Research, 2021, 12: 101213.

2. The authors give details of the sample collected. Since it is written that samples were collected in winter and summer month. But, did the sample collected covers the whole variation of the seasons or this is only few days sample collection? Please provide details.

Thank you very much for your question. The $PM_{2.5}$ samples were collected over a one-month period each during the winter and summer seasons, and HULIS were subsequently isolated from a combination of 30 mixed samples. We have added some additional information in section 2.1 to provide a more detailed description, they are shown as follows.

Lines 57-59: In the present research, two concentrated HULIS solutions were extracted from $PM_{2.5}$ samples collected in a winter and summer month **(30 samples in each season)** in Beijing, and the detailed sample information can be found elsewhere (Qin et al., 2022).

3. Firstly, what is the HULIS spectral reproducibility? Add few sentences on uncertainty in the measurements.
Thank you very much for your question. The UV-Vis and fluorescence measurements in this research exhibit excellent spectral reproducibility and low uncertainties. We have added details regarding these aspects in the Methods section. They are read as follows in the manuscript.

Lines 90-92: The limit of detection for UV-Vis and fluorescence analysis were estimated as 2 times of their respective standard deviation of blanks, which were 0.005 and 0.01 absorption unit, respectively.

4. In the current research, 200-500 nm used to calculate AAE values. Will it make a difference if you choose a high wavelength range to calculate AAE vales? Different groups used different wavelength ranges used to calculate AAE values. Please add the wavelength range used in different studies in the main manuscript.
Thank you very much for your suggestions. Sorry that some of our descriptions are not prominent enough in the manuscript. We used the wavelength range of 300-400 nm to calculate $AAE_{300\text{-}400}$, which were commonly used range in previous research, the calculation was in section 2.3.1 (Lines 102-106). We also added some relating references in the context. They are now read as follows.

Line 104-108:

$$\mathrm{MAE} = (\mathrm{A}_{\lambda} - \mathrm{A}_{700}) \times \frac{\ln(10)}{\mathrm{C}_{\mathrm{spcies}} \times \mathrm{L}} \quad (1)$$

$$\mathrm{A}_{\lambda} = K\lambda^{-\mathrm{AAE}} \quad (2)$$

Where A_λ is light absorbance at wavelength λ, $C_{species}$ is the chemical concentration of organic compounds (WSOC and HULIS in the present research), L is the light path length (1 cm), *K* is a scaling constant, and the fitting wavelength of AAE is 300–400 nm.

Lines 141-146: The MAE and AAE of HULIS under three acidity levels in both seasons were consistent with those reported in our previous research, with the average MAE_{365} at 0.011±0.00 in winter and 0.005±0.001 in summer, and the corresponding average $AAE_{300\text{–}400nm}$ at 6.46±0.86 and 6.97± 0.83, respectively (Qin et al., 2022), which were comparable with those of Gosan Korea (Kirillova et al., 2014), Hongkong China (Ma et al., 2019), and Tibet China (Wu et al., 2019), but lower than those of biomass burning sources (Park et al., 2016).

5. The authors have concluded that Cu2+ will have strong influence on HULIS optical properties. But they have not exactly concluded the light absorption properties of HULIS in presence of Cu2+ under different acidic conditions. Please elaborate on this.

Thank you very much for your suggestion. We have carefully reviewed the conclusion section of our manuscript and agree with your assessment that it was lacking information about the effect of Cu^{2+} under different pH conditions. We have now added the following text to the conclusion.

Lines 342-343: Cu^{2+} could promote light absorption ability of HULIS at weakly acidic to neutral environment, but the effect was negligible under acidic environment.