

Dear reviewer:

Thank again for your comprehensive review and thoughtful advises on the present research. We have carefully addressed all of the comments and explained them as following paragraphs, and hoping that the new version of this manuscript will meet your satisfaction.

1. Since this study has only focused on the HULIS and optical properties measurements in China, thus the title should state that the study is for China. Otherwise, the authors should also consider other studies on HULIS or optical properties around the globe or at least in Asian Countries.

**Thank you for your advice.** As our samples were only collected in Beijing, we have amended the title to clarify that this is a case study conducted in Beijing. The revised manuscript title reads as follows.

**Lines 1-3: “Measurement Report: Effects of transition metal ions on the optical properties of humic-like substances (HULIS) revealing structural preference-A case study of PM<sub>2.5</sub> in Beijing, China”.**

2. I do not find authors response to first question i.e "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<sup>+3</sup> was not considered in this study? As Fe<sup>+3</sup> 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<sup>+6</sup> was not considered?" satisfactory. They should provide proper reasoning in the response as well as in the manuscript.

**Thank you for your advice.** Thank you for your feedback. We apologize for the previous unsatisfactory response. Our current research primarily focuses on the effects of metal ions on the optical properties of HULIS. Therefore, we selected Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, and Ni<sup>2+</sup> due to their abundance in Beijing PM<sub>2.5</sub> and their previously confirmed quenching effects on water-soluble organic compounds in our prior studies. Upon reflection, we acknowledge that our previous description, stating "Four transition metal ions including Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, and Ni<sup>2+</sup> were chosen as representative metal ions that might be reactive to HULIS, considering their richness in the atmospheric environment or significant health risks (Fan et al., 2021; Wang et al., 2021)," was inaccurate. Indeed, the significance of these four metals is lower than that of Fe<sup>3+</sup>/Fe<sup>2+</sup> and Cr<sup>6+</sup> concerning both their abundance in PM<sub>2.5</sub> and associated health risks. Therefore, we have revised this sentence in the manuscript.

**Lines 73-74: “Four transition metals ions that are relatively rich in Beijing PM<sub>2.5</sub> and can complex with HULIS were considered including Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, and Ni<sup>2+</sup> (Wang et al., 2021).”**

While Fe<sup>3+</sup> and Cr<sup>6+</sup> were not considered in our current study, their importance in atmospheric research cannot be overlooked. Therefore, we have also emphasized their significance in the "Conclusions and Implications" section at the end of the manuscript.

**Lines 361-364: “Our results provide perceptions from chemical analysis perspective on interactions between HULIS and TMs, however, due to the intricate nature of PM<sub>2.5</sub>, many crucial transition metals, such as Fe<sup>2+</sup>/Fe<sup>3+</sup> and Cr<sup>6+</sup>, which play pivotal roles in the chemical transformation of PM<sub>2.5</sub> or pose high risks to human health, are not addressed in the current study. Furthermore, comprehensive research on worldwide HULIS samples is also imperative for future investigations.”**

3. They have said that they have done one month of sampling during both the winter and summer season. So, they should also mention this in the manuscript on line 57-59.

**Thank you for your advice.** We included "(30 samples in each season)" in line 58 of the previous version of the manuscript. However, it appears that this addition may still lead to confusion. Therefore, we have revised this sentence again as follows.

**Lines 57-59:** "In the present research, two concentrated HULIS solutions were extracted from daily PM<sub>2.5</sub> samples collected in summer and winter of 2016 (30 samples in each season) in Beijing, and the detailed sample information can be found elsewhere (Qin et al., 2022)."

4. The quality of the manuscript can be further improved by incorporating the comparison with previous studies done around the globe.

**Thank you for your advice.** We have added some comparison in the "Results and Discussion" section as follows.

**Lines 174-178:** "For winter HULIS, under acidic environment, the addition of Mn<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup> at low concentrations (< 50 μM) could induce a decrease of 14%–16% in MAE<sub>365</sub>, and further increasing TM concentrations had little effects on MAE<sub>365</sub>, whereas Cu<sup>2+</sup> showed minimal effects on MAE<sub>365</sub>, which only decreased MAE<sub>365</sub> by 5% with increasing TM concentrations; **these results were consisted with former study who found that the light absorption capacity of the atmospheric HULIS solution in the Cu<sup>2+</sup>/Al<sup>3+</sup>/Zn<sup>2+</sup>-coupled system can be enhanced to 5 – 35% (mean: 19%) (Li et al., 2022).**"

**Lines 283-286:** "The <sup>1</sup>H-NMR results showed that HULIS were rich with protons of H-C, H-C=C-, Ar-H, and H-C-O and functional groups of -OH or -NH, Ar-C=O, Ar-C-O-C, and C-O in both seasons, **which were similar to the results of former researches (Fan et al., 2013; Hawkins et al., 2016; Kumar et al., 2017).**"

**Lines 290-293:** "Meanwhile, the functional groups of HULIS, revealed by FT-IR spectra, mainly included -OH/-NH, -CH, Ph-C=O, C=O, Ph-C-O-C, and -C-O in both seasons, and the summer HULIS contained more oxygen-containing functional groups than winter HULIS **because of the high atmospheric oxidization capacity (Chen, et al. 2016; Haynes et al., 2019).**"

**Lines 335-339:** "Besides, although very few studies can explicit the interaction mechanisms between HULIS and heavy metals, the hypotheses of present study are aligned with a recent soil study, exploring the retention of heavy metals by humic acid using atomic force microscopy who found that some metals (Pb<sup>2+</sup> and Cd<sup>2+</sup>) formed strong adhesion stems from the synergistic metal-humic acid complexation and cation-π interaction at pH 5.8, leading to significant retention, while other metals (As<sup>5+</sup> and Cr<sup>6+</sup>) only bound weakly through hydrogen bonds (Wang et al., 2024)"