Dear reviewer:

Thank you very much for your recommendation of our manuscript "Measurement Report: Effects of transition metal ions on the optical properties of humic-like substances revealing structural preference". It is very kind of you to give comprehensive and thoughtful advises on the present research. We have carefully addressed all of the comments and explained them as following paragraphs. We have modified the language though out the article as well. Thank you again.

For Specific Comments:

1. Lines 20-21: Why is the fourth component named as "mixing residentials" ?

Thank you for your question. We have checked the context and renamed the component as "mixing residuals" in the manuscript. They now read as follows.

Lines 19-21: The parallel factor analysis (PARAFAC) results extracted four components of HULIS, including low-oxidized humic-like substances (C1), N-containing compounds (C2), highly-oxidized humic-like substances (C3), and the mixing residuals (C4), from the fluorescence spectra in both winter and summer.

Lines 229-231: they were characterized as low-oxidized humic-like substances (C1), N-containing compounds (C2), highly-oxidized humic-like substances (C3), and the mixing residuals (C4), respectively (Chen et al., 2016).

2. Lines 21-25: The subject's adjective phrase is overly extensive in this sentence, compromising the clarity and conciseness of the sentence.

Sorry for the unconcise description. We have rewritten the sentence as follows.

Lines 21-24: The spectral characteristic of HULIS with Cu^{2+} additions under three acidity conditions indicated that electron-donating groups of HULIS mainly corresponded to C1 and C3, with Cu^{2+} binding with HULIS by replacing proton, while electron-withdrawing groups of HULIS could correspond to C2, with its connection with Cu^{2+} through electrostatic adsorption or colliding induced energy transfer.

3. Line 31: The transitional word "Besides" seems inappropriate here, because the health effect had already mentioned in the beginning.

Thank you for your advice. The word "Besides" have been deleted in the context.

Lines 30-33: HULIS and many TMs, like Fe, Cu, Mn, V, Cr, and Co, have negative impacts on human health since they can promote the generation of reactive oxygen species (ROS), which cause inflammatory response of human respiratory system (Verma et al., 2012; Gali et al., 2015; Lin and Yu 2019).

4. Line 34-26: some references should be cited here to explain the HULIS composition and its environmental effect.

Such as: Seasonal and diurnal variation of PM2.5 HULIS over Xi'an in Northwest China: Optical properties, chemical functional group, and relationship with reactive oxygen species (ROS). Atmospheric Environment, 2022, 268, 118782.

Optical properties, chemical functional group, and oxidative activity of different polarity levels of water-soluble organic matter in PM2.5 from biomass and coal combustion in rural areas in Northwest China. Atmospheric Environment, 2022, 283, 119179.

Optical properties, molecular characterizations, and oxidative potentials of different polarity levels of water-soluble organic matters in winter PM2.5 in six China's megacities. Science of The Total Environment, 2022, 853, 158600.

Thank you for your advice. The references are cited in the corresponding places.

Lines 30-35: HULIS and many TMs, like Fe, Cu, Mn, V, Cr, and Co, have negative impacts on human health since they can promote the generation of reactive oxygen species (ROS), which cause inflammatory response of human respiratory system (Verma et al., 2012; Gali et al., 2015; Lin and Yu 2019; Zhang et al., 2022a). HULIS are known as a mixture of macromolecular organic compounds, containing aromatics and aliphatic species with multiple oxygenated functional groups like carbonyls, hydroxyl, nitrate, and nitroxy-organosulfate (Win et al., 2018; Huang et al., 2022; Zhang et al., 2022b). TMs can transfer electrons and participate in chemical reactions or serve as catalyst, especially in atmospheric photochemistry (Mao et al., 2013; Guasco et al., 2014).

5. Lines 45-46: Is it a repeat statement that TMs can affect the light absorption properties of HULIS？ when lines 40-42 had firstly emphasized that TMs could mediate the formation of light absorbing SOA.

Thank you for your question. We intend to emphasize that the light absorption properties of HULIS may change directly when exposed to TMs solution. We have modified the sentence as follows.

Lines 44-45: Moreover, TMs can also bind with HULIS and directly affect the light absorption properties of HULIS (Fan et al., 2021; Wang et al., 2021).

6. Line 95: How can 5 mg HULIS sample be dissolved into 1 mg D2O solution?

Sorry for the mistake. It should be 1 mL D_2O solution here, we have corrected it in the context.

Line 94: About 5 mg HULIS samples were redissolved into 1 mL D_2O for detection.

7. Line 138: An extra line break here.

Sorry for the mistake. We have modified the mistake and checked through the whole manuscript.

8. Line 172: The phrase of "the addition of a small amount of any of the four TMs" is excessive redundant.
Thank you for your advice. We have shortened the phrase to make it concise.

Line 171: a small amount of any TMs (0–50 μM) could induce evident increase of MAE_{365} at a range of 16% to 20%

9. Lines 178-179: The sentence is hard to read.
Sorry for the unconcise description. We have rewritten the sentence as follows.

Lines 178-179: An exception was observed for Ni^{2+} because of its self-absorption between 350–400 nm, leading to the continuously reducing of $AAE_{300–400nm}$ with increasing [Ni^{2+}].

10. Line 185: Ambiguous description of "their complexes don't have structural effects on HULIS.", please clarify it.
Sorry for the unconcise description. We have rewritten the sentence as follows.

Lines 183-184: the TMs-HULIS mixtures might not compose complexations or their complexes exhibited no structural difference.

11. Line 231: An extra line break here.
Sorry for the mistake. We have modified the mistake and checked through the whole manuscript.

12. Lines 333-334: It is controversial only use "signal" in "TMs either enhance or attenuate the signal", because "spectral indices" could be part of "signal", I believe the author tends to say "signal strength" here.
Thank you for your advice. We have corrected the words as suggested.

Lines 330-331: TMs either enhance or attenuate the signal strength, contingent on the metal species, but with negligible impact on the spectral indices.

13. Lines 337-340: The sentence is too long with many comma, it's better to use proper punctuation marks, and make it easier to comprehend.
Thank you for your advice. We have tried our best to make the language terse, but it still needs many words to draw a relative precises conclusion, thus, we added ":" to break the sentence, and make it friendly to read.

Lines 334-337: The distinct tendencies of PARAFAC-separated fluorophores with increasing Cu^{2+} under three acidity conditions indicated that electron-donating groups might correspond to low and highly oxidized humic-like substances, and Cu^{2+} coupled with HULIS by substituting H atom; while electron-withdraw groups were N-containing species or protein-like species, with their fluorescence quenching likely caused by electrostatic adsorption or colliding induced energy transfer.

14. Lines 342-348: In the last paragraph, long descriptions about co-effect of TMs and HULIS on ROS generation, with a short sentence mentioned the implication of this research is somewhat a disappointing end, the authors may add some more specific implications.
Thank you for your advice. Because HULIS and TMs are both well-known ROS generative species, we intended to set connections between present research and former research on ROS. We have reorganized the last paragraph as follows.

Lines 338-345: Results from this study not only revealed that the complexations of HULIS and TMs could be fragile, but also connected the fluorescence spectra of HULIS with structural characterizations through the micro-effects of TMs on HULIS. HULIS and TMs are both well-known ROS generative species, and the combined effects of HULIS and TMs on ROS generation can be synergistic or antagonistic depending on the TMs species. The ROS generation abilities of TMs and HULIS are essentially determined by their physical and chemical properties and interactions, the complexation, electrostatic adsorption, and colliding induced energy transfer processes could enhance or prohibit ROS generation and resulted to synergistic or antagonistic effect. Our results could provide some perception from chemical analysis perspective on interactions between HULIS and TMs, however, the exact reaction mechanisms still require further research.