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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Significant Seasonal Change in Optical Properties by atmospheric humic-like substances (HULIS) in Water-Soluble Organic Carbon Aerosols" *by* Heejun Han and Guebuem Kim

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Comments:

This study investigated the chemical and optical properties of water soluble organic carbon (WSOC) in TSP from urban Seoul in South Korea, including the WSOC concentration, bulk ion composition of water extracts, stable carbon isotope ratio and EEM spectroscopy of WSOC. In general, this paper is well written, however, due to the lack of novelty and other issues listed below, this manuscript is not recommended for acceptance by ACP.

1. The optical properties of WSOC in urban aerosols have been intensively studied in previous work (Baduel and Jaffrezo, 2010; Hecobian et al., 2010; Mladnov et al., 2011a). The other related studies cited in this work (Mladenov et al., 2011b; Fu et al., 2015; Xie et al., 2016) investigated the sources and optical properties of WSOC in alpine and artic areas, respectively, which are of general interest. The measurement techniques applied in this work are similar as those in Fu et al. (2015) and Xie et al. (2016). However, due to the lack of source tracers, the explanation of WSOC sources is ambiguous.

2. This paper focused on the seasonal change in optical properties of WSOC based on EEM analysis. So I would suggest the title to be changed to "Significant seasonal change in optical properties (and/or sources) of water soluble organic aerosol in urban Seoul", or something else similar. In this work, the separation of atmospheric humic-like substance (HULIS) is mainly based on EEM results, but not chemical separation after extraction. In some previous studies (e.g., Baduel and Jaffrezo, 2010; Lin et al., 2010), HULIS in aerosols were extracted from other organic components using column separation.

3. Page 6, lines 25-28. "The WSOC concentration showed seasonal variation from . . ..This result is consistent with seasonal trends observed by Xie et al. at high elevation remote site (Xie et al., 2016)." In Xie et al. (2016), the WSOC concentration exhibited maxima in the summer and minima in winter, in contrast to the results reported in the current work. The higher WSOC concentration in summer in Xie et al. (2016) is primarily due to SOA formation. Please explain the differences.

4. Page 7 lines 25-30. The authors inferred that the decrease of HULIS fluorescence should be attributed to the increase in UV radiation in summer, supported by the negative correlation shown in Figure 4b. It is well known that the UV radiation always reaches the maxima in warm season and the minima in cold season, and the increase in UV radiation can play a role in the degradation of HULIS in summer. However, the author might ignore the source type or source region changes from cold to warm season,

which might impact the HULIS fluorescence more than the photo-oxidation process. As shown in Figure 1, air masses are mainly from ocean area in summer, and from continental areas (China and Mongolia) in other seasons. It is probably that the continental aerosols contain more WSOC and HULIS components than ocean aerosols. The seasonal changes in HULIS and WSOC might be more associated with the variation in source type or region. To identify which factor (photo-oxidation vs. source variation) is the primary reason for the seasonal changes in optical properties of WSOC, the authors need to do more work on source apportionment of WSOC for the sampling period. For example, the 13C fraction of WSOC has been analyzed in this work, so the authors should be able to analyze the relative contribution of continental and marine WSOC based on the method applied in Fu et al. (2015). Then the major WSOC source in cold and warm periods could be known.

5. The photochemical degradation experiment can only demonstrate that HULIS could be photoxidized by UV lights, which has already been reported in previous work (Kieber et al., 2007; Zhang et al., 2013). While the oxidation of HULIS in the ambient samples could hardly be reflected. As such, section 3.4 cannot help to rule out the effect of source type and/or region change on the seasonal variations of HULIS in WSOC.

Minor comments: 1. In supporting information, Figures S1 and S2 are mistakenly labelled as Figures 1 and 2.

References

Baduel, C., Voisin, D. and Jaffrezo, J.L., 2010. Seasonal variations of concentrations and optical properties of water soluble HULIS collected in urban environments. Atmospheric Chemistry and Physics, 10(9), pp.4085-4095.

Fu, P., Kawamura, K., Chen, J., Qin, M., Ren, L., Sun, Y., Wang, Z., Barrie, L.A., Tachibana, E., Ding, A. and Yamashita, Y., 2015. Fluorescent water-soluble organic aerosols in the High Arctic atmosphere. Scientific reports, 5, p.9845.

Hecobian, A., Zhang, X., Zheng, M., Frank, N., Edgerton, E.S. and Weber, R.J., 2010. Water-Soluble Organic Aerosol material and the light-absorption characteristics of aqueous extracts measured over the Southeastern United States. Atmospheric Chemistry and Physics, 10(13), pp.5965-5977.

Kieber, R.J., Willey, J.D., Whitehead, R.F. and Reid, S.N., 2007. Photobleaching of chromophoric dissolved organic matter (CDOM) in rainwater. Journal of Atmospheric Chemistry, 58(3), pp.219-235.

Lin, P., Huang, X.F., He, L.Y. and Yu, J.Z., 2010. Abundance and size distribution of HULIS in ambient aerosols at a rural site in South China. Journal of Aerosol Science, 41(1), pp.74-87.

Mladenov, N., Alados-Arboledas, L., Olmo, F.J., Lyamani, H., Delgado, A., Molina, A. and Reche, I., 2011a. Applications of optical spectroscopy and stable isotope analyses to organic aerosol source discrimination in an urban area. Atmospheric environment, 45(11), pp.1960-1969.

Mladenov, N., Sommaruga, R., Morales-Baquero, R., Laurion, I., Camarero, L., Dieguez, M.C., Camacho, A., Delgado, A., Torres, O., Chen, Z. and Felip, M., 2011b. Dust inputs and bacteria influence dissolved organic matter in clear alpine lakes. Nature Communications, 2, p.405.

Xie, M., Mladenov, N., Williams, M.W., Neff, J.C., Wasswa, J. and Hannigan, M.P., 2016. Water soluble organic aerosols in the Colorado Rocky Mountains, USA: composition, sources and optical properties. Scientific reports, 6.

Zhang, Y., Liu, X., Osburn, C.L., Wang, M., Qin, B. and Zhou, Y., 2013. Photobleaching response of different sources of chromophoric dissolved organic matter exposed to natural solar radiation using absorption and excitation–emission matrix spectra. Plos one, 8(10), p.e77515.

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