Referee 3

In my opinion the submitted manuscript addresses an interesting scientific issue, i.e., the study on the volatility of HULIS aerosol compounds. The text is understandable for the reader. The objectives are clearly defined and raised conclusions are coherent. However, I would opt to likely consider moving the manuscript first to the ACPD full review process. This is because I have a few remarks as stated below:

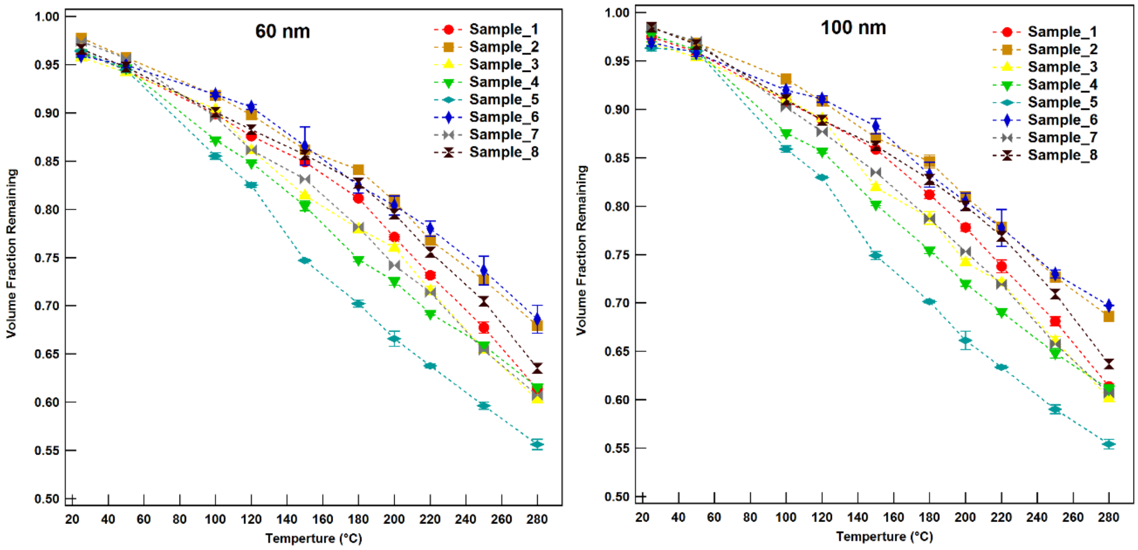
A) Limited number of ambient samples

The authors made their research based only on 4 filter samples. No justification was provided as to the choice of such a limited number of samples. Certainly, during the full ACPD review phase the authors would be requested to build up their scientific story on the results obtained from the analysis of more ambient samples, say 10 or larger due to the increased complexity of HULIS (e.g., *Environ. Sci. Technol*., 2016, 50 (4), 1721).

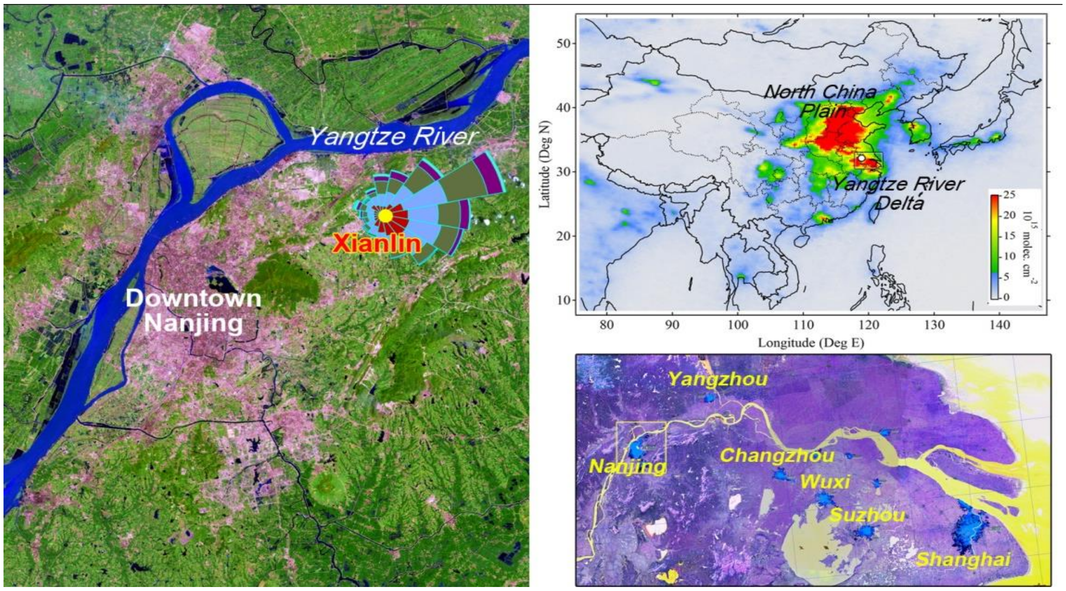
Response: Thanks for the comment, which mainly focused on the representative of our samples.

Firstly, we agree that HULIS are a very complex mixture that contains a large number of compounds with different molecular structures. However, based on our results, their overall volatility of different HULIS samples behaved in quite a similar way (which is reasonable as volatility is mostly controlled by molecule weight and oxidation state). In this work, we actually analyzed 8 samples collected during both winter and summer, and covering a wide range of PM concentration from less than 40 μg/m^3 to higher than 150 μg/m^3. All these 8 samples showed similar evaporation behavior (as showed in the following figure), with some small differences in details. Therefore, in terms of volatility, we believe that there were no large differences between the collected HULIS samples. We finally selected 4 samples with different PM concentrations to represent the HULIS samples at the SORPES station and made the argument simple and clear that ambient HULIS overall showed a low volatility. We will add some statements on this into the revised manuscript.

Secondly, our sampling site, named SORPES, has been demonstrated to be a regional background site of Yangtze River Delta. As showed in the followed 2nd figure (Ding et al., 2013), SORPES station located in the downwind region of YRD, and is about 20 km east of the downtown Najing city. Compared to the typical urban measurement station, air masses arriving at this site are more aged and well-mixed. Secondary formed aerosol, e.g. sulfate, nitrate and SOA, was dominated the mass of $PM_{2.5}$. The samples collected at this site were thus believed to be regional representation of Yangtze River Delta (Ding et al., 2013 & 2016).



Volume fraction remaining (VFR)as a function of heating temperature for 8 samples



A map showing the location of the SORPES site (Ding et al., 2013). The prevailing wind was from northeast during winter, and from southeast during summer.

Ding, A. J., Fu, C. B., Yang, X. Q., Sun, J. N., Zheng, L. F., Xie, Y. N., Herrmann, E., Nie, W., Petäjä, T., Kerminen, V. M., and Kulmala, M.: Ozone and fine particle in the western Yangtze River Delta: an overview of 1 yr data at the SORPES station, Atmos. Chem. Phys., 13, 5813-5830, 10.5194/acp-13-5813-2013, 2013.

Ding, A., Nie, W., Huang, X., Chi, X., Sun, J., Kerminen, V.-M., Xu, Z., Guo, W., Petäjä, T., Yang, X., Kulmala, M., and Fu, C.: Long-term observation of air pollution-weather/climate interactions at the SORPES station: a review and outlook, Front. Environ. Sci. Eng., 10, 15, 10.1007/s11783-016-0877-3, 2016.

B) Analytical procedure for the preparation of HULIS extracts

The authors blindly believe that a whole fraction of HULIS is greatly soluble in the aqueous phase. However, in the light of recent papers dealing with the chemical composition HULIS (e.g., *Environ. Sci. Technol*., 2016, 50 (4), 1721; *Atmos. Chem*., 2015, 72, 65), aerosol-derived HUmic LIke Substances represent a complex chemical mixtures, including high-molecular-weight aliphatics (primarily C27–C32) with small proportions of $-CH3$, $-OH$, and $C{=}O$ groups. These are poorly soluble in water, thus the extraction with pure water only may lead to the substantial loss of analyte to be further subjected to the H-TDMA analysis. I am highly surprised that the authors did not take it into account despite it is a basic approach in the analytical atmospheric chemistry: a sample preparation is the most crucial factor. I would suggest broadening a result discussion with providing additional data obtained for samples extracted with less polar solvents, say acetonitrile and water acetonitrile (50/50v). The same could be applied for another solvent couple: methanol and methanol-water (50/50), as recently have been suggested by Lin (*Environ. Sci. Technol*., 2014, 48(20), 12012). Moreover, I am a bit concern of the selection of SPE method for HULIS water extracts since it may result in a dramatic loss of highly oxidized and water soluble products, such as organosulfates (nitroxyorganosulfates).

Response: Thanks for the comment.

It is an issue of definition about HULIS. HULIS is operationally defined by the procedure that is used for its isolation. HULIS used in this work refers to water-soluble part of humic-like substance (or the part of water-soluble organic compounds that are hydrophobic). The referee's definition of HULIS is broader, including both the water-soluble and water-insoluble parts. We will add some statements in the revised manuscript.

Actually, the referee provided a good suggestion. Volatility tests of HULIS with a broader definition (both water-soluble and water-insoluble parts) have been planned in the further work.