

Response to the comments of Dr. Jason Surratt:

1) Extractions and HULIS preparations:

Like Reviewer 2 and 3 stated, I still have concerns with acidifying the water extracts before SPE separation. The reason for this concern is if the acidity of the extract is too high in the presence of water you will likely induce acid-catalyzed hydrolysis of certain compounds such as hydroperoxides or even catalyze further reactions that produce lower-volatility OA than originally present in the original aerosol sample. Shouldn't the authors more clearly state that based on the current set of measurements that this can't be ruled out? Basically, at least directly acknowledge the limitations of the current work. I feel this limitation is weakly stressed in the revised text.

Response: Thanks for the comment.

The main reason for acidifying the water extracts is to make the organic poly-acids in the neutral form rather than ionic form so that they can be retained by the SPE sorbent. We acidified the water extract right before loading the sample on the SPE cartridge. That is a very short period (less than 15 min, generally). Since this is in diluted water solution rather than condensed-phase, I think the acid-catalyzed reactions won't take place significantly at this time scale (e.g. Birdsall et al., 2013). We have added this information in the revised manuscript as following.

*Line 122-125: "Since the HULIS samples were in diluted water solutions rather than condensed-phase, and were acidified right before (in general, less than 15 min) loading the sample on the SPE cartridge, we believe the acid-catalyzed reactions unlikely would take place to a significant degree as to influence their volatility (e.g. Birdsall et al., 2013)."*

*Birdsall, A. W., Zentner, C. A., and Elrod, M. J.: Study of the kinetics and equilibria of the oligomerization reactions of 2-methylglyceric acid, Atmos. Chem. Phys., 13, 3097-3109, 10.5194/acp-13-3097-2013, 2013.*

Related to this, the authors should be aware that I think the statement lines 120-122 "It should be noted here that HULIS extracted in this work refers to part of the WSOCs that

are hydrophobic" is unclear. Should one really say ".....that are partly hydrophobic in character." They wouldn't be in the water extract if they were completely hydrophobic, right? I can see potential readers of your article being confused by this wording.

Response: Agree, and have changed in the revised manuscript.

Since the extraction is very specific to water, for wording like on line 155 "HULIS samples," I would be clearer here and throughout the remainder of the text that this is the "water-soluble HULIS fraction." Please change this so readers don't get confused that you mean the entire fraction of HULIS. I agree with reviewer 3's concerns on the extraction issue.

Response: Agree, and have changed in the revised manuscript.

2) One point I want to make after re-reading this manuscript. The authors assume that ELVOCs explain the volatility behavior of the water-soluble fraction of HULIS discussed throughout the manuscript. However, it is unclear to me what chemical data exists at the molecular level to support this statement. The water-soluble fraction can include many compounds resulting from heterogeneous reactions (e.g., acid-catalyzed ring-opening reactions of epoxides, like IEPOX), or other processes. I suggest that more care be taken here. Can the authors at least add a statement clarifying this. All of the pathways you describe could tentatively explain these compounds and I don't think the chemical data are strong enough to emphasize one over any others. As of now, all are tentative proposals.

Response: Thanks for the comment.

We agree that we did not have enough molecular information for the extracted HULIS to support their volatility estimation. But in this work, our target was to evaluate the volatility of water-soluble HULIS more directly based on the VTDMA measurement, which was believed to be more reliable. One of our previous studies at another city clusters of Pearl River Delta (PRD) in east China have provided detailed molecular information of extracted HULIS (Lin et al., 2012). In that study, the detected molecular weight was in the range from 100 to 500 g/mol, and contained compounds of CHON,

CHO, CHOS and CHONS. With the method provided by Li et al. (2016) to estimate the volatility of these compounds, we can confirm that a large fraction of these compounds was LVOC or ELVOC, especially for the S-containing compounds with molecular weight higher than 200. We will investigate the molecular information of the extracted HULIS in the future study, and connect the estimated volatility to the measured results. We added the following sentences in the revised manuscript.

*Line 252-257: "Detailed molecular information of extracted HULIS was not available in this study. But a previous study at the Pearl River Delta, another polluted megacity region in China, showed the molecular weight of HULIS was in the range of 100 to 500, with a significant fraction higher than 260. Using the method provided by Li et al. (2016) to estimate the volatility of these compounds, we calculated that a large fraction of these compounds in water-soluble HULIS was LVOC or ELVOC, especially the S-containing compounds with molecular weight higher than 200. Future volatility measurement studies are suggested to investigate the S-containing compounds."*

For the issue of potential acid-catalyzed reactions, please refer to our response to comment 1. We think the acid-catalyzed reactions won't take place significantly in a time scale less than 15 minutes.

*Lin, P., Rincon, A. G., Kalberer, M., and Yu, J. Z.: Elemental Composition of HULIS in the Pearl River Delta Region, China: Results Inferred from Positive and Negative Electrospray High Resolution Mass Spectrometric Data, Environ Sci Technol, 46, 7454-7462, 10.1021/es300285d, 2012.*

*Li, Y., Pöschl, U., and Shiraiwa, M.: Molecular corridors and parameterizations of volatility in the chemical evolution of organic aerosols, Atmos. Chem. Phys., 16, 3327-3344, 10.5194/acp-16-3327-2016, 2016.*

3) Revised line 151 stating "we totally analyzer 8 samples": Dont' the authors mean to say: "we analyzed a total of 8 samples collected during both winter and summer," or do they mean to say 4 total in summer and 4 total in winter? This is unclear from the revised text added to the manuscript.

Response: Agree, and have changed to the following sentence in the revised manuscript.

*Line 154-155: "In this work, we totally analyzer 8 samples with 6 of them collected during winter and the other two during summer."*

4) Revised Lines 155-156: This is a poorly worded sentence. Can the authors revise this to something like: "Of the 8 samples analyzed, we selected only 4 of the samples representing different PM concentrations to represent the ranging types of HULIS samples collected at the SORPES station." The last part of this sentence "and made the argument clear..." seems to be an incomplete sentence. Please correct this.

Response: Agree and have changed the statement in the revised manuscript.

*Line158-160: "Of the 8 samples analyzed, we therefore selected only 4 of the samples representing different PM concentrations to represent the ranging types of HULIS samples collected at the SORPES station."*

5) Revised Line 276: Change "Organic matters, ..." to "Organic material, ...."

Response: Agree and have changed in Line 286 in revised manuscript.

6) Revised Line 153 stating "(figures not shown)": Can't the authors add the figures to the SI section? I think interested readers may want to see these details.

Response: Agree and have added the figure to the SI section.