Referee #1

This manuscript presents the first study to my knowledge of the volatility of humiclike substances (HULIS) in atmospheric aerosols. The results ultimately link HULIS, which has been observed ubiquitously in atmospheric aerosols using filter collection and extraction, with low and extremely low volatility organic material (ELVOC), which has been observed to be similarly common using AMS and thermal denuder-type techniques. The authors also demonstrate that interactions between HULIS and inorganic salts such as sulfate can greatly decrease the already low volatility of the HULIS. This is a very significant contribution to the field, and should be published after a few issues are addressed.

- Another reviewer commented on the relatively few filter samples that were used in this study. Can the authors make an argument to justify this, for example, were the properties of the HULIS on these filters representative of other samples taken at the same location?

Response: Thanks for the comment and suggestion.

Please refer to the response of comment A of referee 3. We actually analyzed 8 HULIS samples, which were collected during both winter and summer. The volatility of all these 8 samples behaved in quite a similar way. We thus selected 4 samples (the PM concentrations of 2 of them were high, and the other 2 were low) to make the arguments clearer.

- My main concern is the extensive chemical processing of the HULIS during isolation before analysis. Is there a way for us to know how this may have impacted the volatility or other properties of the material as compared to the real state in ambient aerosols? A discussion of this point in the manuscript is needed.

Response: Thanks for the comment.

We agree the isolation processes would influence the properties of HULIS as compared to those in real ambient aerosols, especially when inorganic ions were mostly removed. In this work, the sampling site was in Yangtze River Delta, the aerosol of which was dominated by inorganic salts, especially ammonium sulfate which accounted for about 30%

of PM$_{2.5}$ (Xie et al., 2015). This was one of the reason to investigate the possible interaction between ammonium sulfate and HULIS in the manuscript. We will add some discussion on this into the revised manuscript.

What we want to emphasize here is that the volatility (as well as some other physical properties like hygroscopicity) is an overall property/nature of an aerosol that is related not only to the volatility of each individual compounds but also to interactions between these compounds. In case of thousands of compounds in a real atmospheric aerosol, its volatility, especially for organic aerosol, behaves in a very complicated way. Currently, volatility studies on OA have mostly focused on laboratory-generated organic particles or ambient particles. Laboratory-generated organic particles are very far from the real ambient particles, whereas ambient particles are too complex to be understood. Therefore, as we stated in the introduction, one possible way is to isolate some classes of organic compounds of the aerosol and analyze their volatility separately. Here, in this work, the volatility analysis of extracted HULIS from real ambient aerosol was one of such attempts.

- Related to my last point, since the HULIS extraction process removes inorganic ions from the sample, are we to understand that the samples in which salts have been re-introduced are more representative of the true volatility of HULIS in atmospheric aerosols? If so, this should be emphasized.

Response: Thanks for the comment.

We agree with referee's viewpoint and will add some discussion into the revised manuscript.

- Some language editing is necessary in places, for example, lines 42-43

Response: Thanks. We will re-edit the language in the revised manuscript.

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:

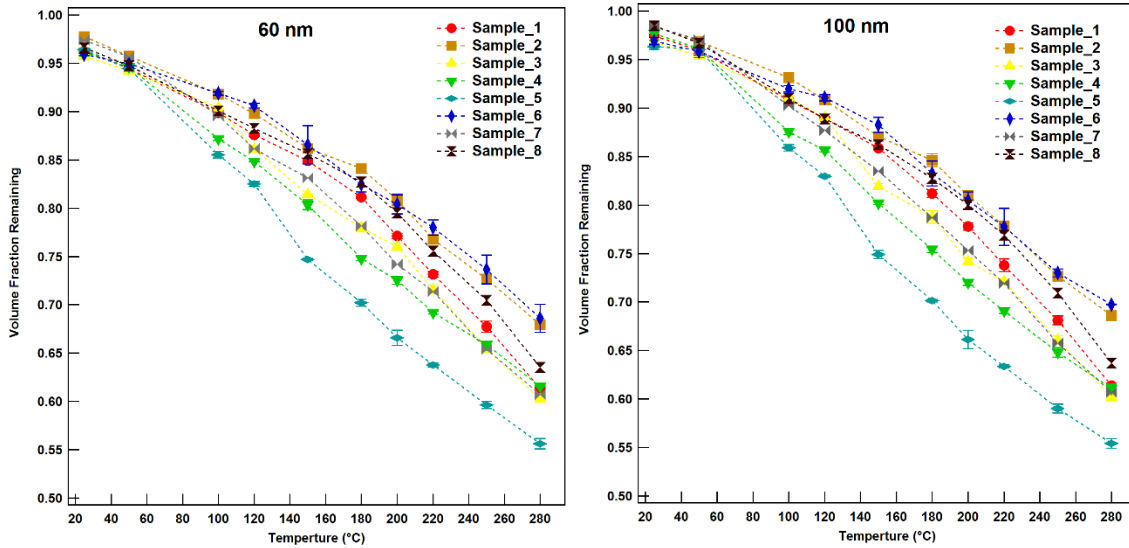**A) Limited number of ambient samples**

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.
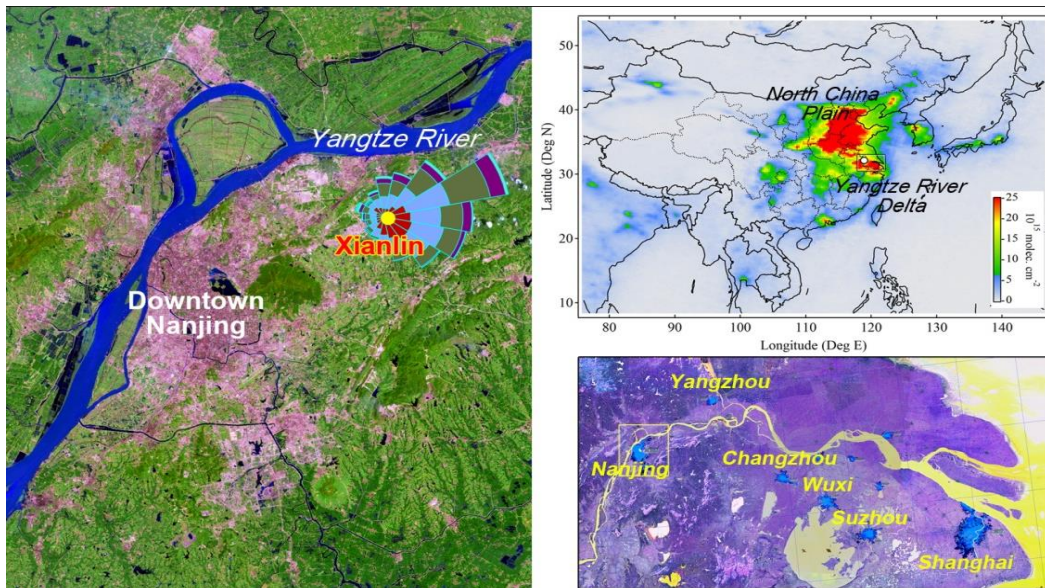
Firstly, we agree that HULIS are a very complex mixture that contains a large number of compounds with different molecular structures. However, based on our results, their overall volatility of different HULIS samples behaved in quite a similar way (which is reasonable as volatility is mostly controlled 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 figures), 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.

Referee #4

General Comments

Here the authors report results of a laboratory study of the volatility of HULIS extracted from aerosol samples collected at a rural site in eastern China. Samples were atomized, four different sizes were selected with a DMA, and then aerosol was passes through a thermal denuder to measure changes in size with increasing temperature. Extracts were also mixed with ammonium sulfate prior to atomization to investigate the effects of salt-organic interactions on volatility. The volatility profiles were analyzed using a model in which various parameters (heat of vaporization, molecular weight, etc.) were assigned based on previous studies and the aerosol was distributed among three volatility bins (SVOC, LVOC, ELVOC) using the model-measurement comparison. The results of AMS measurements indicate that HULIS is highly oxidized (O/C _ 1 or greater) and the volatility measurements show that most of the HULIS is low and extremely low volatility material, consistent with the high degree of oxidation. Small decreases in volatility were also observed when ammonium sulfate was added that indicate chemical interactions between the organic and inorganic materials. The explanations for the general trends observed in the data and model results are reasonable, and overall there are no real surprises. This is a pretty straightforward study, the experimental and modeling components are well done, and the data interpretation is reasonable. The paper is a useful contribution to the literature and is worthy of publication in ACP. I have only a few minor comments that should be addressed.

Specific Comments

1. Line 194–197: What is the fraction of HULIS in the organic component of the samples?

Response: The HULIS-C made about 30% of the total organic carbon (OC). We will add this information into the revised manuscript.

2. Line 199–201: Is auto-oxidation a potential source for these HOMs?

Response: Yes, it is possible.

Aromatics have been demonstrated to form HOMs via auto-oxidation, which would be one possible source of HULIS (Molteni et al., 2016).

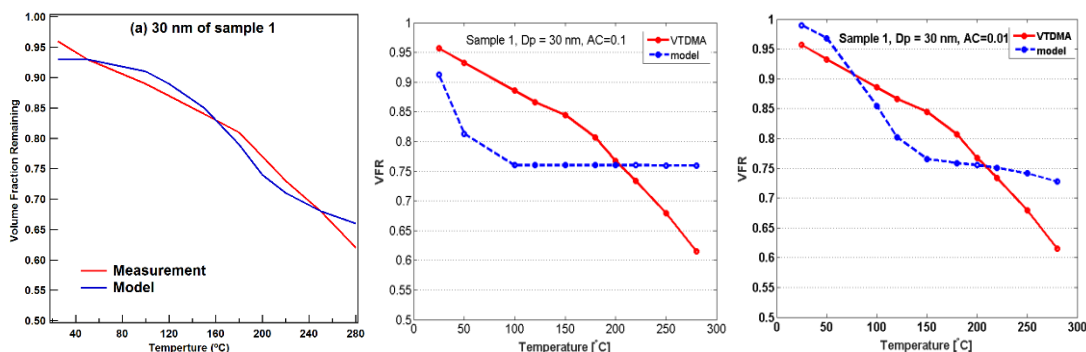We will add some discussion on this into the revised manuscript.

Molteni, U., Bianchi, F., Klein, F., El Haddad, I., Frege, C., Rossi, M. J., Dommen, J., and Baltensperger, U.: Formation of highly oxygenated organic molecules from aromatic compounds, Atmos. Chem. Phys. Discuss., 2016, 1-39, 10.5194/acp-2016-1126, 2016.
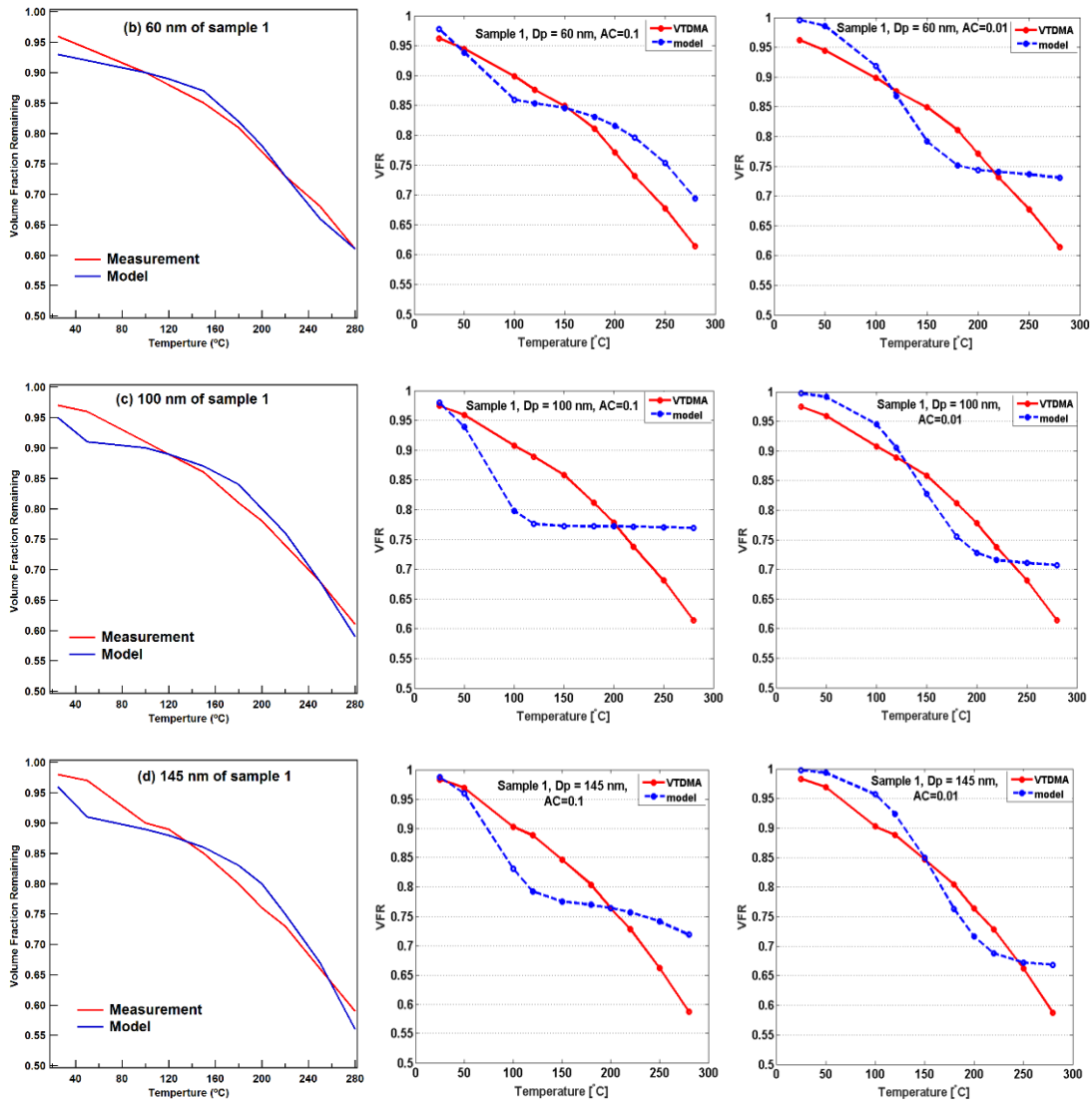
3. What are the effects of assumed model parameters on the interpretation of experimental results? Were sensitivity studies conducted? For example, there is ongoing debate about the appropriate value of the mass accommodation coefficient, which may range from about 1 to 0.001. Couldn't changes in these parameters with organic and inorganic composition be responsible for the observations rather than changes in the SVOC, LVOC, and ELVOC fractions? Some discussion of these issues is needed.
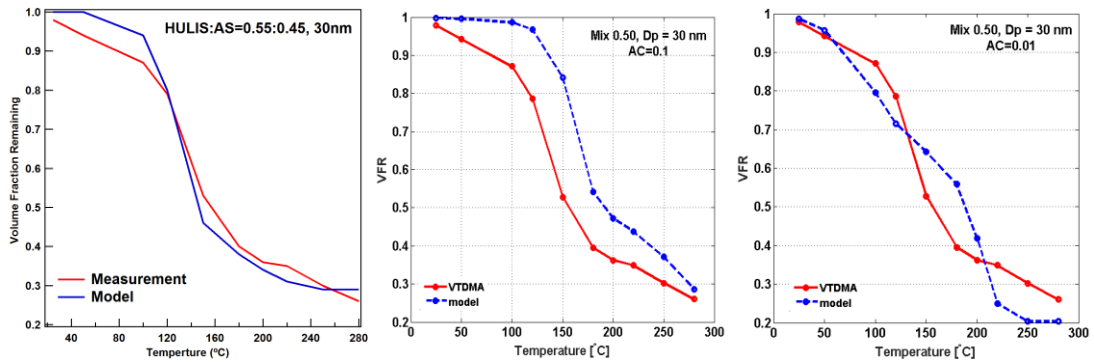
Response: Thanks for the comment.

This is actually a good question. The value of mass accommodation coefficient (MAC) did influence the simulated distribution of SVOC, LVOC and ELVOC. What we need is to choose a MCA value that the model can best reproduce the measured evaporation behavior. As showed in the following figures, sensitivity of the kinetic evaporation model was tested towards different MAC values (i.e. MAC=1, 0.1, 0.01) for both pure HULIS sample and mixed samples. It was obviously that only when MAC was set to 1, the simulated thermogram showed the best agreement with the observation. This is the reason we chose 1 as the MAC value in the MS.
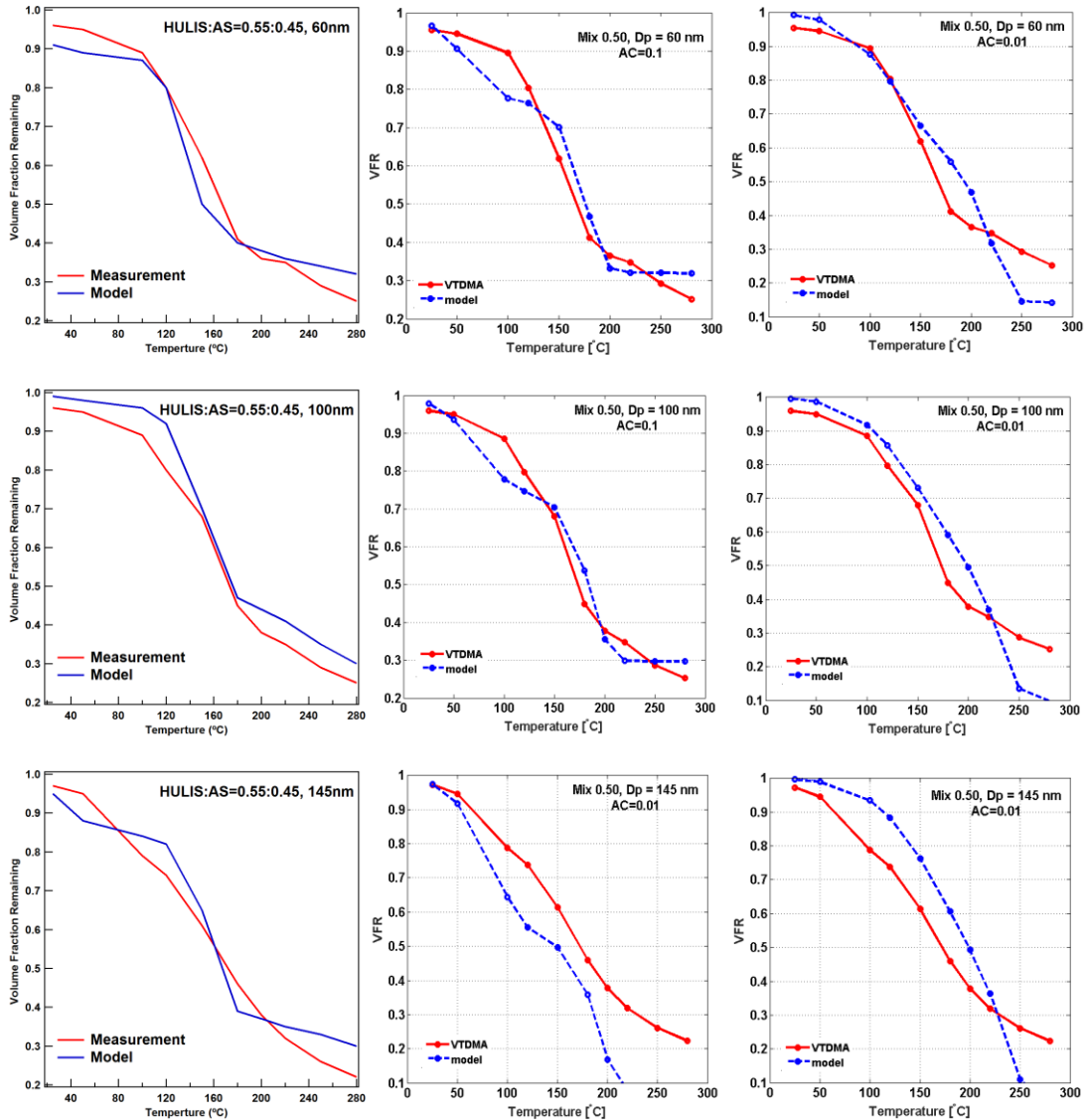
We will add some discussion on this in the revised manuscript.

Comparison of measured VFR with modeled VFR for HULIS of sample 1, with accommodation coefficient of 1 in left panel, 0.1 middle panel, and 0.01 in right panel.

Comparison of measured VFR with modeled VFR for 1:1 mixed sample of HULIS and AS, with accommodation coefficient of 1 in left panel, 0.1 middle panel, and 0.01 in right panel.

Technical Comments

Line 61: "Abortion" should be "absorption".

Response: Thanks. We will correct it in the revised manuscript.

Line 128: "An- alyzer" should be "Analyzer".

Response: Thanks. We will correct it in the revised manuscript.