

Interactive comment on “HULIS in emissions of fresh rice straw burning and in ambient aerosols in the pearl river delta region, China” by P. Lin et al.

P. Lin et al.

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Response to referee #2

Comment 3. EC concentrations may arise from diesel emissions and other combustion processes (biomass combustions, coal burning, etc) however they are not well associated with gasoline vehicles, thus I'm not convinced that the anti-correlation of HULIS and EC negates vehicle emissions as a source of HULIS. There are many well documented studies of SOA produced from benzene, toluene and other semi-volatile aromatics often emitted by gasoline vehicles. The SOA produced in those reactions may very well be water soluble and isolated by HLB cartridges.

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Author's Response:

We agree with the reviewer that EC is not well associated with gasoline vehicle emissions; however the anti-correlation of HULIS and EC is not the only piece of evidence for our suggestion to negate vehicular emissions as a significant primary source of HULIS. NO is primarily from vehicular emissions at urban locations. The anti-correlation of NO and HULIS at the urban location (Fig. 4a) also serves as supporting evidence for our suggestion. We also note that our discussion on vehicular emissions as a primary source of HULIS is not contradictory to what the reviewer suggests about VOC emissions from vehicles serving as precursors for secondary HULIS formation. The following sentence is added to clarify this point.

“However, it is worth noting that VOC emissions (e.g., toluene, xylenes) and semi-volatile aromatics from vehicles could have significant contributions to the precursor pool for the secondary formation of HULIS.”

Comment 4. HULIS is not thought to be comprised of polycyclic ring structures. It may indeed have aromatic properties, but it also has aliphatic properties as well. The list of functional groups should also include oxides of nitrogen and sulfur.

5. The molecular composition of isolated water soluble organic compounds has been under investigation by several groups and some interesting papers have recently been published that include molecular details. Please see Wozniak et al., ACP 2008; Altieri et al., ACP 2009; Altieri et al., ES&T 2009; and Mazzoleni et al., ES&T 2010.

Author's Response: Thanks for alerting us to these recent papers on chemical composition study of aerosol components relevant to the HULIS fraction. We have taken into consideration of the new information and revised the description on the chemical nature of HULIS.

“They are thought to be comprised of aromatic and aliphatic structures containing hydrophilic oxygenated functional groups such as hydroxyl, carboxyl, carbonyl, nitrate,

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and nitroxy organosulfate groups (Mukai and Ambe, 1986; Graber and Rudich, 2006; Reemtsma et al., 2006; Altieri et al., 2009a; Mazzoleni et al., 2010). Recent studies using ultrahigh-resolution Fourier Transform ion cyclotron resonance mass spectrometry have led progresses in identification of structural moieties and determination of chemical formula of individual compounds in HULIS (i.e., Wozniak et al., 2008; Altieri et al., 2009a; Altieri et al., 2009b; and Mazzoleni et al., 2010). However, complete molecular-level chemical characterization of the HULIS fraction remains unachieved."

Comment 6. HULIS concentrations vary of 3 orders of magnitude. Is this due to differences in operational definition? Perhaps a summary of HULIS definitions are in order here. Also, please note that some investigators chose to not use the ill defined term HULIS in their work.

Author's Response: The large variation of HULIS concentration in ambient environment is primarily due to difference in source strengths of primary emissions (e.g., biomass burning) and in abundance of precursors for secondary formation in difference ambient environment. It is not due to difference in operational definition of HULIS.

Comment 7. I found reading Lin et al., J. Aerosol Science, 2010 to be very helpful in understanding the significance of this work, perhaps more brief details with the reference to that work can be added to this paper.

Author's Response: Our previous paper (Lin et al., 2010) mainly focuses on characterization of the HULIS determination method and its size distribution. We feel that we have provided enough information about the HULIS isolation and determination method in the current manuscript (see the experimental section).

Comment 8. BB emissions and HULIS concentrations. This section is very well done; I especially like the summary of how BB emissions may contribute to HULIS on page 7196. This section and the conclusions can be strengthened even further by the inclusion of OC concentration changes with dilution. Note that the chamber studies of fresh rice straw emissions did not include substantial dilution, thus the OC concentra-

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tions may be higher due to semi-volatile compounds. As noted, there are substantial concentrations of semi-volatiles in biomass combustion. Please see Robinson et al., Science 2007.

Author's Response:

(1) We agree that with dilution, some semi-volatile VOCs could off-gas and subsequently they are oxidized in the gas-phase contributing to HULIS. The following sentence is added to the text.

"Some semi-volatile VOCs originally present on freshly emitted BB particles could off-gas as the BB particles are diluted in the atmosphere."

(2) We agree that the BB smoke may not be sufficiently diluted in the chamber studies and this could cause a bias on the HULIS/OC ratios. The following sentences are added to make note of this point.

"The HULIS/OC ratios in the chamber-generated BB smoke were in the range of 0.28-0.44. It is noted that in the chamber studies fresh rice straw emissions did not include substantial dilution, thus the OC concentrations may be biased higher and thereby the HULIS/OC may be biased lower due to presence of semi-volatile compounds on the freshly emitted particles."

Comment 9. HULIS versus oxidant concentrations (O₃ and NO₂), does point toward aerosol aging and secondary chemistries. Similar analysis was done previously SOA versus "odd oxygen" (O₃ and NO₂) in Mexico City. Please see Herndon et al., GRL, 2008.

Author's Response: We have added one sentence, citing the study by Herndon et al. (2008) to strengthen the argument on contribution of secondary chemistries to HULIS.

"Similar analysis was carried out previously on secondary organic aerosol (SOA) derived from Aerosol Mass Spectrometry measurements in Mexico City and SOA was found to highly correlate with odd oxygen (R² > 0.9) (Herndon et al., 2008)."

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