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Atmospheric
Chemistry
and Physics
Discussions

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 #1

Comment on whether K+ is a suitable biomass burning tracer in our study region

Overview – Peng et al. examine the HULIS content in aerosols emitted directly from rice straw burning. They also investigate the HULIS contained in atmospheric aerosols collected from the Pearl River Delta Region (PRD), China.

Generally speaking, HULIS in aerosols is a timely research topic relevant to the ACP journal. Furthermore, the HULIS measurements Peng et al. are providing are unavailable currently for the PRD; thus, these results are potentially useful to the atmospheric aerosol research community.

In this reviewer's opinion, the major drawback of the study is that the vehicular and biomass burning source assignments are arbitrary and uncertain. Although K is sometimes used as a biomass combustion marker, it is known to be somewhat unreliable. The source testing for this study seems to also confirm this conclusion. It would be very interesting to compare levoglucosan and HULIS concentration values for the source and atmospheric aerosols. Such a comparison may allow the authors to be less anecdotal about the biomass burning source contributions to HULIS. As it stands currently there is limited direct evidence in the present study for linking biomass burning aerosols to HULIS in the PRD atmosphere, although this link is strongly implied throughout (especially for rice straw burning). At least a statement should be made about specifically when the agricultural or biomass fires typically occur in this region, and the data should be examined for concomitant increases in HULIS. So, a revised paper should include less speculative discussion about what the combustion sources of HULIS are without more evidence. More specific comments for revision are provided below.

Author's Response: We agree with the reviewer that levoglucosan is a more robust tracer compound for biomass burning than water soluble potassium. Almost all of the biomass activities emit levoglucosan. However, burning of only some biomass emit K+, while others such as wood burning emit little K+.

We show below that both K+ and levoglucosan are good biomass burning tracers in PRD region. In this region, the dominant type of biomass burning is burning of crop residues either in field or in household cooking stoves. The dominant crop residues in this region are rice straw and sugarcane leaves. Potash fertilizer is a fertilizer widely used in the rural areas of south China. In the year 2007, 989200 tons of potash fertilizer was consumed in Guangdong Province. On average, 31.4 kg potash fertilizer was applied per mu of cultivated land (Guangdong statistical yearbook 2008, http://www.gdstats.gov.cn/tjnj/ml_e.htm). Although the element content of rice straw

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and sugarcane leaves was not measured, potassium is expected to be one important element enriched by the agricultural vegetation.

We measured K+ content in PM2.5 collected from simulated field burning of rice straw and sugarcane leaves and found that K+ accounted for 13±3% and 14±2% of PM2.5 mass in rice straw and sugarcane leaves smoke aerosols (PM2.5) (Lin et al., 2010). These results suggested that the volatilization of potassium was significant in both type of burning activities.

In one of our earlier study (Wan and Yu, 2007), we measured concentrations of levoglucosan and major ions in 30 ambient PM2.5 samples taken in Hong Kong from August 2004 to May 2005. In these 30 samples, the concentration of levoglucosan is positively correlated with K+ (R2 = 0.56, n = 30). We classify these 30 samples into three subgroups according to the air mass back trajectories on the sampling days, using the same method as the one used in the current study. Among the 30 samples, 11 samples were influenced by continental air masses, 10 samples were in the category of under the influence of transition air masses, and 9 samples were influenced by marine air masses. The levoglucosan and K+ concentrations were nearly 10 times lower the samples influenced by the marine air masses than those samples under the influence of the continental air masses (Figure R1). These results suggest that (1) the aerosol samples taken in the continental air masses were significantly influenced by the biomass burning emissions and (2) In the PRD region, both levoglucosan and K+ are good tracers for biomass burning. It is not a trivial task to obtain levoglucosan concentration for 120 samples. At the moment we do not have levoglucosan data and it is uncertain whether we will have resources to carry out levoglucosan chemical analyses for these 120 samples.

Comment on Introduction section Introduction – Although the objectives of the study are clearly stated in the Introduction, information about the main hypothesis being tested is missing. In other words, the authors may want to provide more about what they set out to do. It seems that the attempt was to show that primary and secondary

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aerosols from biomass burning were the main sources of HULIS in the PRD atmosphere. This should be explicit at the outset.

Author's Response: We revise the last sentence in the introduction part of our manuscript as follows:

"One objective was to determine abundance, temporal, and spatial variation of HULIS in this region. Results derived from the small set of measurements in our previous study (Lin et al, 2010) also suggest that secondary formation and primary emissions from biomass burning are important sources of HULIS in rural PRD area. The second objective of the current study was to assess the contribution of primary BB emissions to ambient HULIS in the region and to examine whether there is evidence to indicate secondary formation of HULIS is promoted by BB particles or gaseous components in BB emissions."

Comment on the experimental section

Experimental – Are there other means to measure HULIS in aerosols? Isn't the definition of HULIS somewhat operational at the moment? If so, this should be briefly discussed in the text.

A coarse and fine ambient aerosol fraction was collected. Yet only data for the fine fraction are presented. The different size fractions can sometimes help with the apportionment exercise. For example, the marine aerosol may show more NaCl in the coarse fraction. Should these data be presented?

Author's Response: (1) Yes, HULIS at the moment is operationally defined by the isolation and detection protocol used for its determination. There are a number of methods reported for the determination of HULIS. The following text is added to section 2.3 to briefly discuss the current status of HULIS determination in the literature.

"HULIS is operationally defined by the isolation and detection protocol used for its determination. A number of methods, differing in either the isolation step or the detection

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means, have been reported for the determination of HULIS. The atmospheric community has not yet agreed on a standard analytical method for HULIS. Techniques applied to isolate HULIS from bulk aerosol materials include solid phase extraction (e.g., Varga et al., 2001), ultrafiltration (e.g., Havers et al., 1998a), capillary electrophoresis (e.g., Havers et al., 1998b), ion-exchange chromatography (e.g. Decesari et al., 2000), size-exclusion chromatography (e.g., Krivacsy et al., 2000; Samburova, et al., 2005), and reversed-phase chromatography (e.g. Hutta et al., 2003). Limbeck et al (2005) developed a more complex two-step isolation procedure, the first step using polar interactions on a C-18 SPE cartridge and the second one utilizing the acidic nature of HULIS to isolate them on SAX resin, a strong anion exchanger. Quantification methods for HULIS include TOC analyzer (e.g., Krivacsy et al., 2000), UV-VIS detector (e.g., Samburova, et al., 2005), evaporative light scattering detector (ELSD) (e.g., Emmenegger et al., 2007), and gravimetric measurements (Salma et al., 2010). One recent study (Baduel et al., 2009) compared two HULIS determination procedures and found that a one-step DEAE (a weak anion exchanger) isolation procedure leads to higher recoveries and better reproducibility than Limbeck et al's two-step C18-SAX procedure. However, the high ionic strength used in the final elution step in the DEAE isolation procedure makes it difficult to characterize the chemical and physical properties of HULIS due to interferences with the abundant inorganic ions.

In this work, HULIS in aerosol filter samples was first isolated from the other constituents in water extracts using solid phase extraction (SPE), followed by quantification with ELSD. This method is adopted with modifications from the isolation procedure developed by Varga et al. (2001) and quantification using ELSD proposed by Emmenegger et al. (2007)…"

(2) The samplers used in our study collect aerosols into two size bins. Particles less than 2.5 μm were collected on 10×25 cm quatz filters and particles of 2.5-10 μm in diameter were collected on slotted quartz filter substrates. Only PM2.5 samples were analyzed for HULIS for two reasons. First, our previous study of the size distributions of

HULIS in this region (Lin et al., 2010) showed that HULIS in ambient aerosols is dominated by droplet mode with a MMAD in the range of 0.63-0.87μm. The coarse mode (MMAD: 4.0-5.7 μm) only accounted for about 7% of the PM10 HULIS mass. There is little to be gained to analyze HULIS in the PM2.5-10 in related to the objectives of our study. Second, the amount of PM2.5-10 filter material in each sample is much smaller than PM2.5 material and we have reserved the limited PM2.5-10 aerosol materials for other types of analyses (e.g., bioaerosol tracer analysis) in our overall project. The following sentence is added to the manuscript to explain this.

“PM2.5-10 filters were not analyzed for HULIS because our previous study indicated that more than 90% of HULIS in ambient aerosols in this region reside in fine particles (Lin et al., 2010) and this portion of filter materials have been reserved for other analyses.”

Comment on volatilization of potassium during biomass burning P 7192, lines 1-7: Check the boiling points of the potassium salts because smoldering fire burns at lower temperatures than flaming fire. This may explain why the K doesn’t volatilize during smoldering fire. This observation can be checked for validity by burning rice straw from the same growing location under varying fire conditions. In addition, the discussion here is focused on an enrichment factor, which is not necessarily an emission factor.

Author’s Response: We agree with the reviewer that the potassium emission from biomass burning is related to the burning temperature. The follow sentence is added to the manuscript to clearly indicate this.

“Higher fire temperatures favor the volatilization of potassium salts (e.g., KCl with a boiling point of 1420oC).”

We also agree that “enrichment factor” is more appropriate than “emission factor”. Revision is made to the manuscript on this.

Comment P 7193, lines 14-16: please clearly explain why these samples are considered to be BB-influenced samples. What about the time of their collection with respect to local fire activity?

Author's Response:

The continental area of Mainland China, which is north to our sampling sites, is the BB source region. BB takes place in the form of crop residue burning or cooking fuel burning in the countryside year around. Open burning of crop residues is more prevalent in the harvest season (i.e., October-December). The field burning is usually scattered and does not form large scale BB activities to allow detection by satellite. Domestic biofuel burning is present year around and no seasonal variation is expected of this category of BB activities. The text from Lines 250-253 is revised to better explain why the samples under influence of continental air masses are considered to be BB-influenced samples.

"When the sampled air masses had passed over the continental area of Mainland China, which is north to our sampling sites and the BB source region, in the past 96 hrs before their collection at TW and NS, the samples were considered to be BB-influenced samples. In South China, BB takes place in the form of crop residue burning or cooking fuel burning in the countryside year around."

Comment on HULIS in BB-affected ambient samples

P 7195, lines 1-8: Many of the organic species being given here (e.g., benzoic acids, alkanes, -oic acids etc.) are emitted from anthropogenic sources including fossil fuel combustion. Why wouldn't these also be combined to form HULIS in this case? It may be fundamentally incorrect to isolate this discussion to biomass burning since identical pollutants emitted from different sources can just as easily be present and interact in the atmosphere. As suggested, the same is true for the NOx, CO, and VOC compounds being described, many of these are not unique to biomass burning. Furthermore, is there need for such speculative discussion? Why not mention that many of these compounds that potentially react to form HULIS are potentially contributed from many combustion sources. The bottom line is that with so many unknowns with regard to HULIS formation, the discussion is over-focused on BB as a source of atmospheric HULIS.

Author's Response: In this section, we discuss HULIS concentrations and its relative abundance to OC in air masses that are impacted by biomass burning. Both the mass concentrations of HULIS and HULIS/OC ratios were much higher in BB-affected ambient samples than the samples under influence of marine air masses. The BB-affected samples were identified through air mass back trajectory analysis and confirmed by K+ data. We then provide supporting evidence for the hypothesis that secondary formation of HULIS involving BB particles or gaseous components in BB emissions is plausible and could explain the enhanced HULIS content in BB-affected ambient aerosol samples. We feel this is a reasonable analysis and useful in providing guidance to future work in identifying molecular identities of the major precursors to secondary HULIS. However, we agree with the review that on the basis of our ambient observations alone we can not exclude the contributions of precursors from other combustion sources. This point is acknowledged by the statement in our original manuscript (Lines 310-312): "The elevated oxidant level could in turn speed up secondary formation of HULIS from both BB-derived VOCs and VOCs already in the atmosphere from other emission sources."

Comment on whether HULIS can be called as unresolved POM

P 7196, lines 20-22: How do we know that HULIS comprises unresolved POM? Isn't the definition for HULIS in this study operational and couldn't some compounds resolved by certain GC-MS or LC-MS methods elute as HULIS in the current study? Please explain.

Author's Response: While it is true that some well-defined organic compounds (e.g., phthalic acid, trimesic acid and azelaic acid) partially end up in the HULIS fraction after the isolation step (Lin et al., 2010), the majority of HULIS mass have not been identified and typically not fully re-solved on HPLC columns. We agree that strictly speaking calling HULIS "unresolved POM" may not be correct. The word "unresolved" is removed in the revised manuscript.

Comment on EC sources P7197, lines 21-23: Please clarify this statement bearing in mind that EC is not specific to any individual combustion source and that EC emissions can vary substantially with combustion conditions.

P7197 and 7198, lines 24-end and lines 1-2: Again, it is not possible to ascribe pyrogenic EC to a single source, and the similar concentrations observed for the continental, marine, and transient atmospheric aerosols is more likely due to a regional effect as opposed to assuming "local" emissions sources (i.e., how is local really being defined here?). It's hard to fathom a marine aerosol that contains 20% EC without some contribution from ship emissions or other pollution source. Clearly, this is a polluted marine aerosol not a pristine one as the term "marine" otherwise suggests.

Author's Response:

We would like to clarify two points. (1)We agree that EC can not be ascribed to a single source. What we try to convey in the manuscript is that in Hong Kong vehicular exhaust is the dominant source for EC. Source apportionment using positive matrix factorization (PMF) analysis of PM10 chemical composition data indicates that EC in Hong Kong is mainly from vehicular emissions (Yuan et al., 2006). Other field measurements in Hong Kong also support this conclusion (e.g., Hagler et al., 2006). Ship emissions also make somewhat important contributions to EC to the degree of accounting for the weak and variable seasonality of EC among different air quality monitoring stations in Hong Kong (Yu et al., 2004). Contributions from other combustion sources (e.g., biomass burning, coal combustion, cooking) are minor to ambient EC loadings in Hong Kong. We failed to mention ship emissions as one important local sources of EC. The following text is added to explain that vehicular exhaust is the dominate source for EC among various combustion sources in Hong Kong.

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“Source apportionment using positive matrix factorization (PMF) analysis of PM10 chemical composition data indicates that EC in Hong Kong is mainly from vehicular emissions (Yuan et al., 2006). Other field measurements in Hong Kong also support this conclusion (e.g., Hagler et al., 2006). Ship emissions also make somewhat important contributions to EC to the degree of accounting for the weak and variable seasonality of EC among different air quality monitoring stations in Hong Kong (Yu et al., 2004). Contributions from other combustion sources (e.g., biomass burning, coal combustion, cooking) are minor to ambient EC loadings in Hong Kong.”

(2) In this work we categorize air mass back trajectories into three groups: continental, marine and transitional. These names are used to indicate the origins of air masses influencing Hong Kong and should not be interpreted to indicate that aerosols are mainly continental or marine aerosols during the respective periods. For example, when we say Hong Kong is under influence of marine air masses, it does not mean marine aerosols are the dominant source of aerosols. Hong Kong is highly urbanized, with vehicle emissions as a major primary aerosol source, just like all the big cities around the world. When the wind is from the ocean (i.e., under influence of marine air masses), pollution in Hong Kong is dominated by local emissions (i.e., emissions from the city) since the pollutant levels from the marine air outside Hong Kong are much lower.

We do not think the similar EC concentrations observed for the continental, marine and transient atmospheric aerosols is due to a regional effects. Sulfate, as a secondary pollutant, is strongly influenced by regional pollutants. Sulfate has a clear variation pattern among the three groups of samples, highest in the samples influenced by continental air masses and lowest in the samples influenced by marine air masses.

Comment on NOx, O3 measurements, correlation between NO and EC P7198, lines 3-15: How does r = 0.36 indicate “significant correlation”. Although the NO and EC are positively correlated, I would argue just the opposite.

Also, how are the ozone and NOx species being measured? There is nothing mentioned in the Experimental section.

Author's Response: In our manuscript, it is R2=0.36 not R as the reviewer said in the comment. The word 'significantly' is replaced with 'positively' to better reflect the degree of correlation.

The urban site is an air quality monitoring site of the Hong Kong Environmental Protection Department (HKEPD). The ozone was monitored by an UV absorption ozone analyzer (API 400) and NOx was monitored by a Chemiluminescence NOx analyzer (API 200A). The details of the O3 and NOx monitoring are provided in HKEPD's annual air quality report (e.g., HKEPD, Air Quality in Hong Kong 2008, available at http://www.epd-asg.gov.hk/english/report/files/aqr08e.pdf). The following sentences are added to the manuscript to describe the O3 and NOx measurements.

"Nitrogen oxides and ozone data at TW are available from the HKEPD's air quality monitoring program. The measurement details of these criteria air pollutants are described in HKEPD's annual air quality reports (e.g., (e.g., HKEPD, Air Quality in Hong Kong 2008, available at http://www.epd-asg.gov.hk/english/report/files/aqr08e.pdf)."

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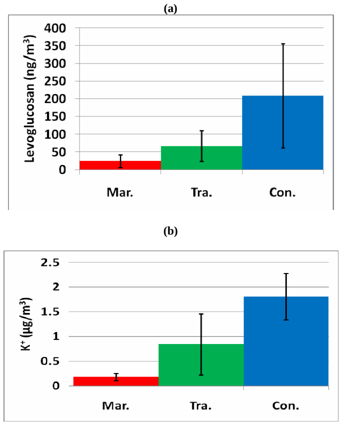

Figure R1. Comparison of (a) levoglucosan and (b) water soluble potassium (K^+) in three groups of $PM_{2.5}$ samples influenced by air masses of marine, transition, and continental origin.

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Fig. 1. Figure R1. Comparison of (a) levoglucosan and (b) water soluble potassium (K+) in three groups of PM2.5 samples influenced by air masses of marine, transition, and continental origin.

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