**Atmospheric
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Discussions**

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Comment

Interactive comment on "Chemical transformations in organic aerosol from biomass burning" by A. Hoffer et al.

A. Hoffer et al.

Comment by reviewer: Major Comments Page 8034, lines 18-21. The authors assume that CO_2 generated at temperatures above 280 C came from high molecular weight (HMW) organics, but no justification is provided and the size of "HMW" is not described. Given the importance of the 280 C HMW "cutoff" in this paper, there should be more experimental exploration of how different MW organics behave in the EGA and an explanation of the approximate size of "HMW" organics. It seems feasible that the EGA behaviour depends not just on MW but also on chemical composition (e.g., degree of oxygenation) and perhaps on differences in the chemical matrices of the particles. In addition, does elemental carbon (e.g., soot) appear as a HMW organic (especially in aged samples)? These issues should be examined and discussed. Similarly, the possibility of LMW organics appearing as HMW compounds because of charring (page

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8035, line 2) should be examined. While I don't expect that the authors will provide an exhaustive exploration of these issues for the present paper, using only one species (levoglucosan) to choose 280 C as the transition to "HMW" compounds is an unjustified assumption and the technique overall is poorly characterized. Note that although the term "refractory", as used more in the second half of the paper, is a better (less specific) term than HMW, it still begs for experimental verification.

Reply: The EGA method has long been used to study the thermochemical properties of the carbonaceous aerosol. Due to the operating principle of the instrument in the first part of the thermogram the peaks of the more volatile and/or easier oxidisable compounds appear, whereas at higher temperatures the more refractory compounds evolve. We have studied the molecular weight and the thermochemical properties of the HULIS formed from an aromatic precursor in model cloud water (Hoffer et al., 2004). It has been shown that in the reaction higher molecular weight compounds are formed. This was shown by mass spectrometric measurements. The peak of the precursor compounds in the thermal profile evolved at lower integration time (lower temperature), whereas that of the higher molecular weight compounds formed in the reaction evolved at higher integration time (higher temperature). Consequently there is an obvious relationship between the molecular weight and position of the evolved peak. Of course the chemical composition (degree of oxygenation, polarity) affects the EGA behaviour of the compounds, but in a sample, where similar compounds might be present, choosing one temperature threshold may be appropriate to compare the relative change in the thermochemical properties and in the relative amount of the different MW compounds. The EGA method is not able to measure the MW of the analytes, so we did not give any MW range for the LMW and HMW compounds, but showed, that in the first peak of the thermogram LMW compounds might appear, and this peak is not an artefact of the last peaks (due to e.g. decarboxylation). Of course the soot appears in the thermogram as HMW compound, since it oxidizes above 280°C, but since soot are not soluble in water, it is not expected that it contributes to the water soluble HMW fraction. In aged samples however a small fraction of soot can be

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dispersed in the aqueous phase, but the estimation of the amount of this fraction is very difficult, since the measurement of soot is also loaded with high uncertainties.

The charring during the measurement is an artefact for the EGA methods, however for lack of optical correction we are unable to account for it.

It should be noted that there is a diel variation in the relative amount of the water soluble carbon, which is not consistent with the different fire types between day and night. The variation of the relative amount of the WSOC also indicates the importance of the photochemical processes, which affect the composition of the biomass burning aerosol. It should be noted, that since large amount of the carbonaceous compounds were removed during the extraction the charring is less abundant in these measurements. (Gelencsér, A.: Carbonaceous Aerosol. Springer, Dordrecht, 2004.)

In the revised manuscript we use the term refractory compounds instead of higher molecular weight compounds.

Comment by reviewer: Page 8040 - 8041. This is an interesting discussion of PM reactivity and the resulting change in concentrations of marker compounds. One missing point, however, is the potential (photo)chemical production of the phenolic acids from precursors. For example, the oxidation of vanillin (a common component in wood combustion PM) should be a source of vanillic acid, and this is probably more rapid during the day than at night. This complicates the day/night differences in the ratios of phenolic acid/levoglucosan, since (photo)chemistry could be both a source as well as a sink of the phenolic acids. Perhaps this is a reason for the less clear diel pattern of vanillic acid? While I agree that the data suggests photochemical processing of less refractory material leads to more refractory compounds, there is no good evidence in the current manuscript that the products are necessarily "HULIS" (as described in the introduction). In addition, at the same time that there is formation of more refractory material, it's likely that there is formation of low molecular weight compounds (e.g., formaldehyde) that evaporate from the particles.

Reply: The corresponding aromatic aldehydes (vanillin, syringaldehyde, 4-hydroxybenzaldehyde) were also measured together with the aromatic acids, but those were not included in the manuscript, since the vapour pressure of these aldehydes are much higher than that of the acidic compounds, consequently during the sample preparation (in the drying step), these compounds may evaporate from the sample (and from the particles in ambient conditions as well). The estimated volatility of the 4-hydroxybenzoic aldehyde and the vanillin are in the same order in magnitude, that of the syringaldehyde is one order of magnitude lower.

If a substance undergoes photochemical processes in heterogeneous phase its oxidation state will increase, which leads to the formation of less volatile compounds. On the other hand low molecular weight compounds can be also formed, but this reaction path is more characteristic for the photochemical reactions in the gas phase.

Comment by reviewer: Minor Comments Page 8032, top paragraph. The "day" and "night" times for sampling should be more explicitly defined. They appear to be 12-hour windows, but what were the times and were they consistent for each sample? Given the time of year, it seems the "night" window in fact contained some daylight hours.

Reply: The daytime samples were collected from ˜7:45 to ˜17:45 (local time), whereas the sampling times for the daytime samples were ˜10.5 hours (18.30 - 07:00) in the biomass burning period. In the transition and semi clean period the daytime samples were collected between ˜08:00 and ˜18:00, the nighttime ones between ˜19:00 and 07:00 (local time).

Comment by reviewer: Pages 8032-33. What are the errors or uncertainties for the WSOC measurements? Since the values are determined by difference, the uncertainties could be large.

Reply: We wrote in the manuscript, that "In some cases the water fraction was analyzed by a Shimadzu TOC 500A instrument. The amount of the WSOC (DOC) measured

from the liquid fraction agreed well with the amount of WSOC deter mined from the filter measurements (R2=0.9769, the equation of the regression line is DOC(μg m-3)=1.029xWSOC (μg m-3) - 1.1745 μg m-3)." The difference between the WSOC and DOC values relative to the WSOC concentration varied between -14% and 35%, on average 19%.

Comment by reviewer: Page 8033. The internal standard (IS) was added to the filtered solution made from extracting the sample filter, but it seems that a more representative technique would have been to add the IS to the sample filter prior to extraction. Have the authors tried this? Does it make a difference? It seems that chemisorption of the oxygenated compounds to the filter could be significant.

Reply: To test the chemisorption and the extraction efficiency we spiked blank filters with the standard solution, and extracted and measured them similarly to the real samples. The recoveries were above 88% for the compounds considered in the manuscript.

Comment by reviewer: Page 8033, end: It would be useful to add another sentence or two about how the hydrolysis methylation works (e.g., the types of bonds that are hydrolyzed and the efficiency of hydrolysis).

Reply: The TMAH is widely used to study the composition of humic matter. During the pyrolysis the ester bonds are hydrolised and the formed compounds are methylated. This technique yields structural information on 12-22% of the TC.

Comment by reviewer: Page 8035, lines 19-20. From my reading of Fig. 2, the day-night difference in HMW/TC is certainly not statistically significant for the transition period (given the large overlap in error bars) and probably not significant for the biomass burning period (although this depends on what the error bars actually represent; see comment for Fig. 2 below). What p-value is considered significant?

Reply: The P value is 0.001 at the biomass burning period, and 0.019 for the transition period. If P less than 0.050 we considered that the difference between the 2 data set

is significant. (The P value is the probability of being wrong in concluding that there is a true difference in the two groups. The smaller the P value, the greater the probability, that the samples are drawn from different populations.)

Comment by reviewer: Page 8037, section 4.3. No speciation data is presented for the semi-clean period. This is probably because the PM mass, and amounts of tracers, were very low during this period, but regardless of the reason it should be addressed.

Reply: In the semi clean period we collected day and night samples separately, but due to the lower concentration of PM, the sampling was continued for 4 days, and therefore a sample from this period can be considered as a 4 day average sample, consequently the diurnal variation of the tracers are not so pronounced than in the transition or biomass burning period. That is why we did not report the results from this period.

Comment by reviewer: Table 1. It would be useful to include the TC mass concentrations for each sample (even though the average values for each period are in Fig. 2).

Reply: Done. In the revised manuscript the TC concentrations are corrected for uncertainties in volume measurements by comparing TC concentrations of samples collected by different samplers operated parallel during the sampling.

Comment by reviewer: Figure 2. The meaning of the error bars needs to be better described since the term "variability (confidence interval)" is too vague. Do they represent 's 1σ? 90% confidence intervals?

Reply: Figure 2 has been changed. Regarding the TC concentrations the average value and the relative standard deviation are given, the error bars represent the standard deviation of the data.

Comment by reviewer: Figure 4. The figure would be better (i.e., it would offer truer comparisons) if the two y-axes both had the same zero point.

Reply: The figure has been changed.

Comment by reviewer: Statistics. The statistics in the paper need some attention. For example, the interpretation f p-values appears to be inverted (e.g., pages 8037, line 3 and 8038, line 27). In these instances the p-value, roughly speaking, should be the probability of obtaining the two sets of sample data if the two populations are the same. For example, in the case of two sample means, $p<0.05$ indicates that there is less than a 5% chance of obtaining these sample means if the population means are the same (i.e., it's unlikely that there is not an actual difference). $P>95\%$ (p. 8037) would mean that the population means are almost certainly the same, not that they are different.

Reply: The text has been changed.

Comment by reviewer: Although it has been stated in previous papers, it is worth repeating in this manuscript that the very high WSOC content of these particles has important implications for their ability to act as CCN and influence cloudiness, climate, etc.

Reply: A sentence is added to the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 8027, 2005.

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