

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

A. Hoffer et al.

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1. The authors divide their thermograms at 280 C and assert that carbonaceous material evolved below this temperature is low molecular weight (LMW) material, while material evolved at higher temperatures is high molecular weight (HMW). As far as I can tell, this division has been tested only by analysis of two standards: LMW levoglucosan and a HMW humic standard. The authors do not indicate to the reader what they consider “low” and “high” molecular weight ranges. Further, in order to assert such a simple division exists, the authors need to test the evolution of many more specific compounds alone and in realistic aerosol matrices. Finally, the authors actually point out that some charring of (presumably LMW) material ends up being measured as HMW carbon.

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). Since similar compounds present in the samples, choosing one temperature threshold might be appropriate to compare the change in the thermochemical properties and in the relative amount of the different MW compounds. 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.

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

2. Insufficient explanation is provided for the THM-GC/MS methodology. More detail should be provided about the procedure and its limitations. Are previous publications utilizing this technique available to cite?

The THM-GC/MS is a widely used technique in the chemical characterisation of higher molecular weight polymers. This methodology was also successfully used in the investigation of the chemical composition of aerosol samples (Gelencsér et al., 2000, Blazsó et al., 2003). Beside the individually present compounds, the technique is able to measure the building blocks of the polymeric matter. The hydroxyl and carboxyl groups of the released compounds are converted to the corresponding methyl esters and ethers with TMAH and measured after separation on a GC-column with a mass-spectrometer. Although the technique provides mainly qualitative information due to the slightly reproducible processes in the pyrolizer, quantitative information can be also gained on a relative basis comparing the signal ratios in a sample.

3. The authors rely on a single internal standard to quantify concentrations of a variety of organic compounds in their GC/MS analyses. Commonly, labs working in the area of organic aerosol speciation employ several standards that are chosen to mimic the extraction and derivatization efficiencies experienced by their suite of organic analytes. Often, isotopically labeled versions of the analyte compounds are used for this purpose. It is unclear that the dimethylglutaric acid internal standard used by the authors appropriately captures the extraction efficiencies of the suite of sugar anhydrides, methoxy phenols, and other compounds considered here.

During our work we used one internal injection standard. 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.

4. In several parts of the manuscript, the authors imply that changes in aerosol properties between the biomass burning and cleaner periods are associated with changes in the atmospheric residence times of the particles sampled. If I understand their argument correctly, a decrease in local burning means the sampled aerosol must have originated farther away. This assertion is not entirely obvious and deserves further explanation and justification. Do the authors have other study information (e.g., satellite photos of smoke plumes and fire locations combined with trajectories) to more clearly justify their assumption?

A decrease in local burning means that the relative amount of the freshly formed smoke decreases at the expense of haze.

5. At the bottom of p. 8040 the authors suggest that because both levoglucosan and methoxyphenols are emitted in the smoldering temperature range from 300-500 degrees C, no drastic changes in combustion product ratios of methoxyphenols to levoglucosan are expected with changing combustion conditions. This is a bold conclusion to draw. Is evidence to support their claim available from source characterization

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studies of appropriate fuel types burned over an appropriate range of conditions?

Due to lack of literature data we assumed that ratio of the emission factors of the methoxyphenols and levoglucosan is constant in the temperature range between 300 and 500 degrees C. The manuscript indicates this assumption more clearly.

6. The authors choose to only present small portions of their data set. The reader would benefit from inclusion of more data. In particular, it would be helpful to add a figure illustrating changes in TC throughout the measurement period, including the sample-by-sample division of TC into LMW and HMW fractions.

The manuscript focus on the diel and seasonal variation of the chemical properties of the biomass burning aerosol, therefore we have chosen samples which were collected on consecutive days and nights in a longer period of time. During the campaign not only day and night samples were collected, but samples with 24 hours sampling time as well, which are not considered in the manuscript. For the purpose of the manuscript the figure presented might be more useful, than the figure (see below) illustrating the changes in TC including the sample-by-sample division of TC into LMW and HMW fractions.

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