Atmos. Chem. Phys. Discuss., 5, S3238–S3241, 2005
www.atmos-chem-phys.org/acpd/5/S3238/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

Received and published: 17 October 2005

General Comments:

This manuscript presents observations of total carbon (TC), water soluble organic carbon (WSOC), and several trace organic species present in smoke from biomass combustion in Brazil. Included in the manuscript are attempts to elucidate fractions of low and high molecular weight material in total carbon and WSOC, an examination of diel and seasonal changes in TC and component properties, and an interesting analysis of ratios of individual organic compounds that the authors utilize to consider chemical transformations in aging smoke plumes. Overall, the manuscript is novel and worthy of publication. Several concerns, however, should be addressed before the manuscript is suitable for publication. These are outlined below.

Specific Comments:

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.

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?

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.

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 ex-

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planation 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?

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

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.

Technical corrections:

A. The authors tend to move rather quickly in several cases from speculation to conclusion stages. As a result, interesting hypotheses contained in the manuscript are sometimes asserted with more confidence than the supporting observations and arguments warrant. My impressions in this regard reflect the tendency of the authors to choose strong language, saying “would have been” rather than “might be explained by” or “cannot be explained” rather than “are not consistent with” and so forth.

B. Although the manuscript is generally well written, there are several minor errors in grammar and syntax that should be corrected. In addition some sentences are confusing/unclear, including the first sentence of the methods section.

C. The sentence beginning on line 10 of p. 8030 might give the reader the impression that the compounds that are discussed in the manuscript make up more than 10% of the TC. This is not the case.

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D. The authors need to do a better job explaining their calculation and application of various statistics. In particular the authors should: i. Define the standards used to judge significance at the bottom of p. 8038 ii. Revise their discussion of error bars and confidence intervals in the caption to Fig. 2. These are not really error bars, nor do they express confidence intervals, both terms that would reflect issues of measurement precision. They simply indicate the variability in a series of data (not replicate measurements).

E. The “-“ symbol used in Table 1 needs to be defined. Does it indicate data are unavailable? Below detection limit?

F. The introduction discusses many issues that are fairly common in publications in the wood chemistry field. The reader would benefit from a few references to key publications in this related field of study.

G. I found the title of the manuscript somewhat misleading, since no direct evidence of "chemical transformations" was presented and the focus of the manuscript discussion was broader than the title suggested.

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