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Interactive comment on "Effects of aging on organic aerosol from open biomass burning smoke in aircraft and lab studies" *by* M. J. Cubison et al.

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Overview:

R2.0) "This work is an attempt to analyze some recent and very interesting field and lab measurements, some of which are already published, and which likely constitute a major result from a major campaign. For this reason, I hope that they eventually are properly documented, with the citations that should be added as noted by other comments posted in the ACPD discussion, and of course with appropriate material on "aging" once Hecobian et al. 2011 is peer-reviewed and publicly available. The global estimate presented is too briefly presented to evaluate, and is at best (as noted) "a

first estimate" based on very limited data – but nonetheless useful if documented. If these things are done, I think this will make an important contribution to the literature on this topic. As it is, the existing focus of the paper on what 44 and 60 may or may not represent chemically, and how they co-vary, seems directed at the AMS community rather than the broader ACP audience, and really might fit better in AMT. In sum, as noted below, I cannot support publication of this aging-focused paper without access to the aging calculations in "Hecobian et al. 2011", but I may be willing to review it again once that work, and the other required revisions, are provided."

Hecobian et al. (2011) has been recently published in ACPD, between the time of the reviewer comment and this reply. Our paper and Hecobian et al. were being worked on in parallel for more than a year and neared submission at around the same time, and we had assumed that they would also appear in ACPD at about the same time, which turned out to be inaccurate. We apologize for the confusion that this caused. We also added text to our manuscript briefly summarizing the plume selection criteria used by Hecobian et al. (2011) to identify their BB plumes, as discussed in more detail in response to comment R1.3 above.

The calculation of the global estimate has been expanded as requested by both reviewers, and an uncertainty has also been provided, as discussed in detail in response to comment R1.8 above.

We have also added a citation to Hawkins and Russell (2010), which was the only one requested in the other comments.

The focus of this paper is indeed on the aging of biomass burning plumes, comparing aircraft with laboratory data, and also with data from studies with little impact of biomass burning. Although the main tool used is the Aerosol Mass Spectrometer, we strongly believe that this paper belongs in ACP and not AMT because the focus is on the chemical transformations of the aerosol, and not on the details of the AMS measurements. The AMS is hardly a specialized tool, as there are more than 100 instruments around the world and over 500 published papers using it, and the relationships between AMS tracers and composition have been well documented in the literature, as already discussed in the ACPD paper and supported by appropriate citations to the literature. In particular, what f44 represents chemically is not the subject of speculation, and was already described in the ACPD paper (P12107 L6-8) as “f44 has also been shown to be linearly correlated with the elemental oxygen/carbon ratio (O:C) of ambient OA (Aiken et al., 2008).” Thus f44 has a clear chemical meaning. To emphasize this point, we have added right axes for O:C to Figures 1, 3, 4, and 5, and emphasized this point in several instances in the text. We have also added the following text in the introduction:

“Higher f44 and O:C are also associated with increasing hygroscopicity and cloud nucleation ability of OA particles (Jimenez et al., 2009; Duplissy et al., 2010).”

See also the response to comment R2.2 below.

Another reason for the interest of these results and the usefulness of performing our analysis with unit mass-resolution data, is the recent availability of a monitoring version of the AMS (the ACSM or “mini-AMS”, Ng et al., 2011b, cited in the ACPD manuscript) which can obtain similar unit-resolution data and is rapidly expanding into continuous monitoring, e.g. with a network of $\sim$12 instruments being set up in Europe with the ACTRIX EU project, and similar networks starting to be established in Asia and Canada. We modified the text in section 3.1 to read:

“Similarly, the f44 vs. f60 plot is introduced here to map the formation and transformation of primary and secondary BBOA as BB plumes are advected from source to background regions. This analysis can be performed with data from any version of the AMS, including the newly developed monitoring version (ACSM, Ng et al., 2011b).”

Comments:

R2.1) "p.12107 Zhang et al. (2010) report poor correlation between K and fire counts in

the Southeast US, which they attribute to the influence of other K sources such as soil dust, sea salt, vegetation and meat cooking” –while this is true (and discussed in more detail in a broad range of prior publications to the one noted here), isn’t it possible to correct for or remove these influences in many cases?"

This comment refers to text in the introduction of our paper about previously-used biomass burning tracers, although potassium is not used in our study (as data for it are not available). It is sometimes possible to correct for the influences of other potassium sources, depending on which other data are available, but this is not always successful, as documented e.g. in Aiken et al. (2010).

R2.2) "p.12108 while this discussion attempts to “prove” that m/z60 is from BB sugars and m/z44 is from acids, they do a very limited job of citing the uncertainty associated with such proof, such as the lack of quantitative relationships and the lack of ambient support for these two tenets. A more balanced discussion would note both of these facts."

Firstly, we must note that the discussion does not, in fact, attempt to show that m/z 44 arises from acids, or that all m/z 60 arises from BB anhydrosugars. The fact that carboxylic acids produce m/z 44 in the AMS was actually mentioned only once in the ACPD paper (P12108 L20) and not as part of the section on the interpretation of f44, but in the context of the small background signal at m/z 60 in air masses without biomass burning impact. As discussed above in response to comment R2.0, the key point about the interpretation of f44 is that this variable is linearly correlated with the atomic O:C of OA. Thus the main use of f44 in the interpretation of the ambient data in this paper is an indicator of O:C and OA aging, and these interpretations do not rely on a correspondence between increasing f44 and increasing carboxylic acid content.

However, for the record, there is evidence that f44 does correlate with the carboxylic acid content of the OA for both for field and laboratory data, in contrast with the reviewer’s statement. For field data, see e.g. Takegawa et al. (AS&T 2007), who state in their abstract “The mass concentrations of diacids and ω-oxoacids show tight correlation with the m/z 44 signal (r2= 0.85–0.94) during the measurement period.” (see Fig. 1, 2, and 11 in that paper). For laboratory data, see e.g. Figure 8 of Duplissy et al. (ACP 2010, http://www.atmos-chem-phys.net/11/1155/2011/acp-11-1155-2011.pdf) who show a strong correlation between the acid content of laboratory standards and their f44 signals. The relationship between f44 and carboxylic acid content is also supported bythe findings of Hawkins and Russell (Atm. Env., 2010) as pointed out by L. Hawkins in her contributed comment to the public discussion of our paper. We have added text to the introduction summarizing these points as:

[Higher f44 is also associated] “with increasing carboxylic acid content (Takegawa et al., 2007; Duplissy et al., 2010; Hawkins and Russell, 2010)...”

Similarly, the interpretations in this paper are not dependent on whether most or all m/z 60 arises from BB anhydrosugars. In fact we already acknowledged as much in the text (P12108 L6-13) where we stated: “However the total signal at m/z 60 in BBOA is 3-10 times larger than would be expected from levoglucosan, mannosan, or galactosan, indicating that most of it arises from different molecules that fragment in a similar way as levoglucosan in the AMS (Aiken et al., 2009; Lee et al., 2010). [..] We define such species here as “levoglucosan-like” species.”

Our main use of m/z 60 is as a tracer for primary BBOA in the AMS, as many studies have reported that this fragment is elevated in BB plumes and at low levels for non-BB influenced air, as supported by several references already cited in this section of the manuscript (Schneider et al., 2006; Alfarra et al., 2007; DeCarlo et al., 2008; Docherty et al., 2008; Ulbrich et al., 2009a; Aiken et al., 2009; Lee et al., 2010). Although not essential for the interpretations in this paper, we do note that several studies have reported strong correlations between levoglucosan and other BB anhydrosugars and AMS m/z 60, see e.g. Figure 9 of Aiken et al. (ACP 2009) showing R2=0.79 for field data, or Figure 1c of Lee et al. (AS&T 2010) showing R2=0.93 for laboratory data.

R2.3) "p.12111 data are shown from CalNex, and the only reference describing the project is an AGU talk (Hayes et al. 2010) for which there is no peer-reviewed publication describing the location or measurement details. Provide the details in this work, or wait til that work is published, or omit CalNex data from this publication."

We have added the following text to the revised version of our manuscript to address this point:

“The CalNex-LA campaign was a ground supersite located in the Caltech campus in Pasadena, CA, during May 15 to June 15, 2010. An HR-ToF-AMS sampled ambient air during that period, with a very similar setup to the SOAR-1 measurements. More details on CalNex-LA can be found at http://tinyurl.com/CalNex.”

R2.4) "p.12116 given the central and repeated role of age in the analysis and conclusions of this paper (the words age and aging are used 85 times in the document), the method used to estimate that age, and the required assumptions, should at least be discussed here rather than simply referencing the Hecobian work, which I had initially presumed was published and/or publicly available. However, it turns out that this work is either omitted entirely from the reference list as there is no “Hecobian et al., 2011” or it is the incomplete and un-peer-reviewed (“Hecobian and Weber. . .in preparation”). Further, given that “age” is not a simple or measurable parameter and its calculation likely relies on questionable assumptions, I see no way to approve publication of this work without access to even a draft copy of that work."

This issue has been resolved, see responses to R1.3 and R2.0 above.

R2.5) "p.12117 “the two parameters are effectively independent” – what does this mean? Linearly independent, if so based on what metric?"

The authors concede that this sentence is confusing. It is meant that the contribution of the levoglucosan-like species to the total signal at m/z 44 (before or after aging) is small, implying that when these species oxidise, thus potentially creating more signal at m/z 44 in the spectrometer, this increase is overwhelmed by any changes in m/z 44 signal arising from other, more abundant, organic species present. The manuscript is thus modified to clarify this point as:

"Given that the levoglucosan-like species that give rise to f60 only contribute a small fraction of the OA mass, their contribution to the total signal m/z 44 before or after aging is also neccesarily small. The observed changes in f44 are thus driven by oxidation of the bulk OA, and not just by the oxidation of levoglucosan-like species. Given that the levoglucosan-like species that give rise to f60 are much less-abundant than the bulk oxidised OA mass and may not oxidise directly to increase f44, the two parameters are effectively independent. Thus, the relative slopes of the different plume data facilitates a comparison of the rates of oxidation of the OA as a whole to those of just the levoglucosan-like species.

R2.6) "p.12119 "cumulative probability distributions (CDFs)" why not cpds? Or include "functions"?"

A conditional probability distribution (CPD), that is, the distribution of probability of one variable given a fixed, known value of a second, jointly distributed variable, is not what is shown here. These are rather cumulative (probability) distribution functions, hence the abbreviation CDF. We have altered the text to reflect the proper nomenclature.

R2.7) "p.12121 this calculation is not clear. Please define terms and escplicitly state how to get 8 Tg/yr and 5%. Define "netOA", "delta OA", "POA", delta CO, etc."

Please see response to comment R1.8 above.

R2.8) "Fig. 4 The "inset" isn't an Inset. Try labeling panels as is appropriate for an archival publication."

The term "Inset"" has been changed to "Right panel" in both the text and figure caption.

R2.9) "Fig. 7 It would help to give the years of the cited publications, let the authors get a reputation for being sloppy in their citations; for example, the plot says "DeCarlo

et al." but there are no less than three of these in the reference list."

The years of publication have been appended to all papers in the legend of Figure 7.

R2.10) "Supp info – Five figures are provided with no text. Please discuss here, and cite in MS"

The figures provided in the Supplementary Information do have captions which explain each one of them. These figures were already discussed in the main text of the ACPD paper, Figs. S1 & S2 in p. 12110, Figs. S3 & S4 in p. 12113, and Fig. S5 on p. 12114, 12116 and 12119. This is a standard use of the supplementary information, and therefore we have not modified the manuscript in response to this comment.

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