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

Response to Anonymous Referee #1

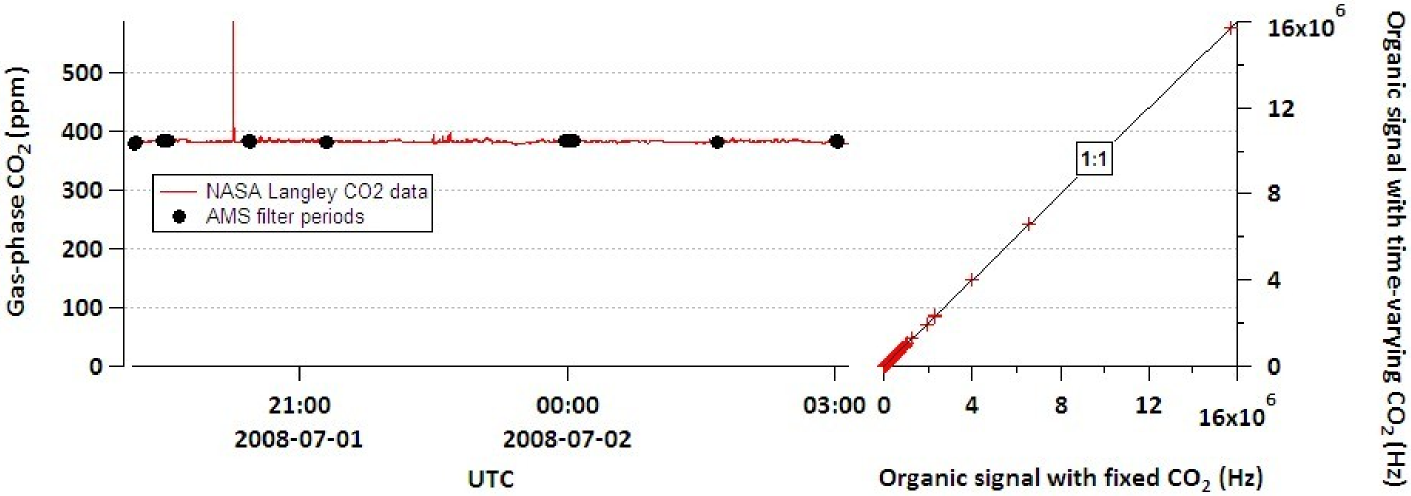
Overview
This paper presents interesting data on the aging of biomass burning aerosol in the atmosphere. The subject is certainly well within the scope of ACP. However, to my feeling the authors draw conclusions that are not backed up by their data, or at least the reader can not follow the interpretation because not enough information is given. I have three major comments related to the data analysis and interpretation:

Major Comments
R1.1) A lot of the data analysis is based on the f44 value (ratio of m/z 44 to total organics). To calculate the aerosol contribution to the peak at m/z 44, the gas-phase background of CO2 has to be subtracted. In general this background is determined by filter measurements, sampling only the gas phase. In biomass burning plumes, the gas-phase CO2 concentration is enhanced. Thus, it necessary to make this correction time-dependent, either by measuring with a particle filter several times during the plume measurement, or to take measured gas-phase CO2 data to estimate the enhanced gas phase CO2 contribution. In the paper such a procedure is not described, so I conclude this has not been done. Thus, the f44 data may be biased towards high values in the BB plumes

This is a very minor effect for this study, but it can be important under some special circumstances, and it is often a point of confusion in AMS studies. We have added the following text to the revised paper to clarify this point and to serve as a reference for future studies:

"While gas-phase CO_2 also produces a signal at *m/z* 44, the effect of this interference in aerosol variables such as f_{44} is minor for the AMS, and can be corrected for. The AMS samples particles more efficiently than gases by a factor of about 10^7. Therefore the equivalent particle-phase signal from typical ambient concentrations of gas-phase CO_2 (~380 ppm) corresponds to an equivalent organic aerosol concentration of ~40 ng m^{-3}. This average is always subtracted from the reported OA concentrations using the fragmentation table approach of Allan et al. (2004). Therefore it is only increases above the background CO_2 concentration that would produce a positive bias on the aerosol concentration and f_{44}. If only the average subtraction is used, and for typical gas-phase CO_2 enhancements during ARCTAS of the order of 10 ppm or less, the false aerosol concentration will be ~ 1 ng m^{-3}, and the error in f_{44} will be less than 1% of its value (assuming a typical background concentration of OA of 1 ug m-3 and f_{44} = 15%). For the large forest fire plumes observed in this study, CO_2 is typically 390 ppm (i.e. an enhancement of 10 ppm above background values) while OA is 100 ug m-3 and f_{44} is 10%, and using the same method we estimate that the positive bias in OA due to this effect is ~1 ng m^{-3}, thus the positive bias in f_{44} is 0.01% percent of its value. We do note that in some situations with low OA concentrations, and large CO_2 variations due to ecosystem uptake and respiration, the constant correction discussed here is not sufficient (Chen et al., 2009). During ARCTAS the *m/z* 44 correction was applied using the time-series gas-phase CO_2 measurements alongside the standard filter interpolation method; the two methods produced corrections values consistent to within 0.5%."

A figure showing the CO_2 ambient concentrations during the sampling of intense forest fire plumes (Lake McKay fire, discussed in the paper) and the comparison of both correction methods is shown below for reference.



R1.2) One of the major conclusions of the paper is that the f60 value of the aged Arctic background data "lie elevated in f60 with respect to the 0.3% of OA background level" (Section 3.5) The way the authors present their data, it appears to be clear that the answer is "yes". However, if they would not use a constant mean value for the non-BB f60 (0.3%), but fit a line to the data in Figure 1, or would use only non-BB data with f44 > 0.15 for the comparison with the Arctic background f60 data, then the non-BB f60 background value would be markedly larger. Especially looking at Figure 4, a fitted line through the grey points appears to match the Arctic-background data very well. Thus I doubt that the data support the conclusion the authors draw.

The key piece of supporting evidence for the stated conclusion "that BBOA represented a significant fraction of the total OA burden during the 2008 Arctic spring, even outside of the clear BB plumes" is that the cumulative distribution functions (CDFs) of the Arctic background dataset are different from the BB-free data at a statistically significant level. It is clear that, as the reviewer points out, the <u>mean</u> f_{60} values of the ARCTAS-A background data for flights 7-10 lie within the expected <u>range</u> of values from the BB-free campaigns. However, their distributions are not identical: the Arctic-background data has a mean whose value and standard error is sufficiently separated from that of the BB-free data so as to discern a statistically-significant difference. To address the reviewer's concerns that the more oxidised BB-free data is more elevated in f_{60}, we take their suggestion of applying a linear fit to these data. At the mean f_{44} value of the Arctic background data of 0.20, there is, unfortunately, not enough data around f_{44} ~0.2 in the BB-free datasets to compose a meaningful CDF of f_{60} for comparison. However, if linear fits are applied to the individual BB-free datasets, the slopes for the two campaigns with f_{44} closest to the range of the Arctic data would imply f_{60}~0.33% for f_{44}=0.2, more than two standard errors below the mean of the Arctic background data.

The question pertinent here is then whether a vertical line at f_{60} =0.3% is an appropriate background level. We do not believe there is enough evidence to support the existence of a <u>consistent</u> increase in f_{60} with f_{44}

and thus use the phrase “broad vertical line at f_{60}=0.3%”, which is indeed evident in the CDFs shown in Figure 6. Depending on the interpretation of background f_{60} employed, the Arctic-background data is then elevated at the 85% confidence level. We contend this is enough to support our conclusion that BBOA represents a statistically significant (but not necessarily dominant) fraction of the total OA burden during the Arctic spring of 2008. In the summary we also caveat that f_{60} is not an inert tracer and that only qualitative relationships should be sought using this analysis technique. We did not suggest that the Arctic-data were BBOA-dominated, nor assigned a quantitative conclusion as to its mass fraction. For these reasons, we believe our carefully-worded conclusion is indeed appropriate to the data presented.

R1.3) For such an analysis, it is crucial to name the criteria that were used to define a “plume”. However, the authors only refer to a publication by Hecobian and Weber, “in preparation”, which makes it impossible for the reader (and the referee) to find out how the plumes were defined. I suggest either to wait with the present paper until the Hecobian paper is published or to include a description of the criteria that were used in the present manuscript (I recommend the latter).

Hecobian et al. (2011) is now available in ACPD (11, 18589-18631, doi:10.5194/acpd-11-18589-2011, 2011; http://www.atmos-chem-phys-discuss.net/11/18589/2011/acpd-11-18589-2011.html) since 30-Jun-11, and the references in our paper have been updated. As suggested, we have also added a short description of the criteria used by Hecobian et al. in section 3.3 (line 6, p12116)

“These plumes were identified by coincident CO and CO_2 enhancements of greater than twice the experimental uncertainty and longer than 4 seconds in length. Identified plumes were only classified as BB if the R^2 of correlation between CO and both CH_3CN and HCN was greater than 0.6. An estimate of plume age was obtained from wind-vector analysis using aircraft GPS position and fire locations determined visually and through the Fire Information for Resource Management System (FIRMS). The uncertainty in plume age was estimated at 40%. The reader is referred to Hecobian et al. (2011) for further details.”

Minor comments

R1.4) Section 3.1,Page 12114, lines 20-22. What were the altitudes of the flyovers? It makes a large difference whether they were in the PBL or in the free troposphere. Mention acronym LAX here (or explain acronym in the caption of Fig 1). Also, flight dates would be useful.

The manuscript has been modified as follows to address this comment:

… “representing flyovers at or below 1000ft above ground level and within the mixed layer, during periods without forest fires, of Los Angeles and Los Angeles International Airport (LAX) (both on 12/6/2008), Sacramento and the California Central Valley (both on 14/6/2008).”

R1.6) Section 3.2, Page 12115, lines 2-11. Again, flight dates are missing in the main text. It should be mentioned that in Figure 2 also the time trace of total organics is shown.

Flight dates have been inserted into the manuscript. The text has been modified in response to the second part of the comment:

"Figure 2 shows the time-series of f_{60}, total OA and co-located gas-phase measurements across these plumes."

R1.7) Section 3.3, Page 12117, line 11. "Lake McKay plume" is mentioned here for the first time. Please give necessary information (where, when, what kind of fire, what altitude?). The flight date is given later, but only in section 3.6. In general, a table with flight numbers, campaign names and flight dates would be very helpful.

Text has been added to the manuscript to provide the requested details, as follows:

… "and the lowest values for the near-field data in the Lake MacKay plume observed on 01/07/2008. The Lake MacKay fire burned in north-western Saskatchewan province, and was classified at the time of sampling as a surface-to-torching fire with a flame front traveling over 15 km per day at an intensity along the front of 9000 kW m^{-1}, producing a very large plume that was intersected by the DC-8 between 3000 and 6000 ft altitude. The plume was followed"...

R1.8) Section 3.6, Page 12121, lines 5-12. First, I don't understand how the global source is calculated, second, I don't understand the range given for the values. If the range of OA/delta_CO ranges between -0.01 and 0.07, then the range of the global OA source should reflect this uncertainty. Why has the delta_OA/POA no uncertainty? Isn't that inferred from the same data?

We have expanded and clarified the text where the global source is estimated, and also provided a quantitative estimate of the uncertainties. We have also used updated data for one of the studies, and corrected a small numerical error which did not affect the conclusions. The revised text reads:

"We can provide a first estimate of the global source of OA due to aging of open BB plumes by two complementary methods. We define ∆OA as the net enhancement of OA, with respect to the amount that would be present in the absence of physical and chemical aging. This net enhancement combines the effects of POA evaporation and SOA formation. For the first method, we calculate the average net enhancement of OA due to aging, normalized by excess CO (above its regional background level, to remove the effect of dilution) for the six field studies summarized in Figure 7. ∆OA/∆CO during field aging ranges from −0.01 to 0.05 g/g, with an average of 0.013 ± 0.011 (std. error of the mean) g/g. We then multiply this net enhancement by the IPCC CO emissions for biomass burning (508 Tg CO yr^{-1}) to obtain an estimate of the global net source of OA due to aging of biomass burning plumes, as 7 ± 6 Tg yr^{-1}. A second estimate can be obtained in a similar way, but using the POA emissions from biomass burning as the normalizing variable, instead of gas-phase CO. The average ratio of the net OA enhancement to POA, ∆OA/POA is 0.19 ± 0.18 for the combined six sets of aircraft measurements. Combining the average increase in ∆OA/POA with the global emission inventory of BB POA (41 Tg yr^{-1}, de Gouw and Jimenez, 2009), we obtain an alternative estimate of the global net source of OA from BB aging as 8 ± 7 Tg yr^{-1}. With respect to the overall global OA budget, estimated at ~150–300 Tg yr^{-1} (Hallquist et al., 2009;

Spracklen et al., 2011), the estimated OA source from BB smoke aging of ~7-8 Tg yr^{-1} is of the order of 5% of the total global OA source. Thus secondary OA production in BB plumes could represent an important global source of OA. However, more field measurements are required to better constrain the magnitude, frequency of occurrence, and controlling parameters of net SOA production in BB plumes."

R1.9) Figure 2: The two different time scales are confusing. Either show both plots (the AOD curtain and the measured data) on the same scale. Or indicate the plume time-frames also in the measured data plot. At the end of the flight on 17/04/2008, does the smoothed curve for f60 really represent the measured data?

The plume time frames (Flight 9, 17/04/2008 from 0010 to 0045, and Flight 21, 08/07/2008 from 0920 to 1015) are indicated in a revised version of Figure 2.

The variation in the smoothed data trace noted by the reviewer at the end of flight 21 arises from the reduced signal-to-noise encountered during 1 vs. 10 sec. sampling. The increase in noise is evident from the large spread in the f_{60} time series data during this period, where some points are sufficiently negative so as to be off-scale. The black line is indeed the average, but the smoothing is applied on a point-by-point, and not time, basis, and thus the difference in variation is a true reflection of the measured signal-to-noise ratios.

R1.10) Figure 3: Why are the Arctic background data not shown here?

1) Figure 3 is introduced two sections before the discussion involving the Arctic background data, and we do not wish to detract from the discussion about the Hecobian et al. plumes pertinent to Fig 3.

2) A statistical analysis showing much more detail than could be afforded with the vertical scale in Fig 3. was already presented in Figure 6. In this figure the statistical difference between the datasets with negligible BB-influence and the Arctic background is presented.

Thus, We do not feel that the addition of the Arctic background data to Figure 3 would particularly add weight to the content of this part of the paper, but has the chance to disrupt the flow of the discussion.

R1.11) Figure 4: I suggest including the lines shown in the inset into the main figure and skip the small inset graph

The format suggested by the reviewer was the original format of the plot, but there was some confusion when discussing this graph with coauthors and collaborators, which was solved when we added the inset to schematically show the key trends that the graph is illustrating. The purpose of the inset is not to propose an exact range of slopes of BBOA progression in the f_{44} vs f_{60} space, but rather to indicate a direction and qualitative range of progression. We feel that, by overlaying the cartoon lines on the main plot, the reader could be misdirected into believing we are suggesting our data shows the exact slope, rather than general trend, that would be observed from AMS measurements of BB plumes in the f44 vs f60 space. Thus we prefer to keep the schematic inset.