**Atmospheric Chemistry and Physics Discussions**

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# *Interactive comment on* "Laboratory investigation of photochemical oxidation of organic aerosol from wood fires – Part 1: Measurement and simulation of organic aerosol evolution" *by* A. P. Grieshop et al.

**A. P. Grieshop et al.**

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The authors offer our sincere thanks for the encouragement and the insightful and constructive comments of the three anonymous reviewers. We have endeavored to address all reviewers8217; points below. Reviewer comments are included in italics and author responses are in plain text

Response to Referee 1:

*However, the lack of dilution in the experiments raises some doubts to what extent the results can be adapted in chemical transport models in spite of the fact that their*

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*currently applied simplified approach is also not valid. The authors found a significant increase (by a factor of 1.8 to 2.7) in OA mass after 4 to 6 hours of photochemical aging. Atmospheric dilution would be expected to reduce this effect significantly due to a combination of several factors: 1) depletion of the pool of semi-volatile organic compounds by volatilization, as observed in other source dilution experiments (page 15715 line 1); 2) reduction of the reaction rates due to reduced concentrations of precursors; 3) depletion of the pool of freshly formed SOA by volatilization (although the authors found that SOA is substantially less volatile than POA, it still had a significant volatile fraction of 20-40 percent by mass, page 15713 line 12). Taken together, it might well be that the atmospheric dilution effects would override the experimentally observed increase in OA in smoke plumes, leading to a net decrease in OA as the plume ages in the atmosphere. It may also mean that the oversimplified approach taken by chemical transport models (POA non-volatile, SOA semi-volatile) may not be as bad as indicated: the loss of POA is compensated by non-volatile SOA to an unknown extent. What may happen there is a chemical transformation of POA into a combination of POA+SOA, with a highly uncertain net effect on the mass concentration of OA. Therefore without considering the effects of dilution experimentally the direct comparison of experimental results with field observations (such as on page 15719-15720) may not be justified. Clearly, the paper represents a self-consistent and very important contribution to our understanding of basic processes undergoing during plume aging, but clearly further studies are need before this knowledge can be adapted in chemical transport models.*

This is an important point and inspired us to do additional modeling work in an effort to quantitatively assess the influence of these competing processes; we have added text and a figure to the revised manuscript which we think address the reviewers concern. First of all, we agree (and have added text saying so) that an important next step in this work is to conduct additional (difficult) experiments which include both aging and dilution and thus more fully simulate aerosol processing in a biomass-burning plume. However, our modeling suggests that including such dilution in these experiments would have a relatively small impact on the observed enhancement of OA levels

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and thus gives us added confidence in comparing our laboratory measurements to field observations of in-plume OA enhancement.

A critical distinction must be drawn between absolute and relative aerosol concentrations; absolute concentrations will be reduced by dilution in a plume. The behavior of relative concentrations 8211; both the particle-phase concentrations relative to an inert tracer and the relative concentrations of particle- and gas-phase SVOCs- is more complex when both partitioning and photochemical aging are at play. Applying plume-like dilution to our aging/partitioning box model shows that starting from the 8216;near-fire8217; level of dilution which was simulated in the chamber ( 100 $\mu$g m-3), that further dilution does little to counteract the production of OA on a relative (dilution-corrected) basis. For example, relative to a non-volatile plume tracer (such as BC or CO), our model predicts a roughly two-fold enhancement of OA with around 4 hours of aging whether dilution is included or not (Figures 8a and 7a, respectively). Particle mass will evaporate with dilution as suggested by the reviewer, but this gas-phase material is thus available for aging and forms less-volatile material. Reaction rates in the gas phase will remain constant as OH concentrations throughout the plume are roughly constant and there is a constantly replenished pool of SVOC vapors to react.

It is certainly true that dilution-driven evaporation and aging-driven condensation in a plume will push the partitioning of SVOCs in opposing directions. This fact may be the reason that current emission inventories and chemical transport models may not do as bad as they might. However, the findings of our work show clearly that these processes are indeed occurring and that the model of SVOC partitioning and gas-phase oxidation does a pretty good job of recreating these processes. We do not present them as an end point in our understanding of organic aerosols, but as an important evolutionary step forward.

*Minor comments: BC is considered as a conservative tracer in the experiments and used to compensate for wall losses in the experimental chamber. However, given that it was measured with an aethalometer and the optical properties of soot may change*

*upon acquiring an organic coating or simply by physical aging, this may introduce some uncertainty into the correction approach which needs to be discussed.*

There is doubtless uncertainty in the BC measurements from the aethalometer due to evolution of the optical properties of the aerosol. This was minimized by using aethalometer data from the longer wavelengths in our 7-channel instrument. Kirchstetter et al. [2004] found these associated more strongly with black versus brown carbon and thus more stable with age. This data showed first-order exponential decay with no affect of the commencement of photo-oxidation. More importantly, a variety of calculations yielded similar estimates for OA enhancement. The following text was inserted to highlight this fact:

8220;There is good agreement between the BC- and SMPS-based approaches and also the (not shown) spectral decomposition method, the results of which are presented in the companion manuscript [Grieshop et al., 2008]. This suggests that, while the aerosol is undergoing significant evolution which may influence the aethalometer response to BC loading, the aethalometer data provides a consistent measure of POA. Aethelometer data will thus be the basis upon which OA enhancement levels are presented in this paper.8220;

Response to Referee 2:

*... consider the size distributions in figure 2. In all of my years of biomass burning research, I have never seen a size distribution this small. Currently, the record for smallest VMD for fresh smoke is on the order of 0.22 um, whereas here you have 0.06 and 0.16 um. Such a small size will result in massive coagulation and wall loss. Hence with time an issue is that the smaller particles will quickly go to the walls and result in a bias in measurements. I think this bias is small, but it is likely there. Given the experiment design, this small size is no doubt to the use of a wood stove-considerably more efficient than a real fire. This coupled by the very quick dilution, results in the abnormally small size.*

Small particle size is a concern as far as our data being representative of field measurements biomass-burning emissions, but we agree with the reviewer that it does not offer a serious challenge to the general findings or conclusions of the paper. Smaller sizes are likely partially due to the quick dilution (with air at high temperatures) that takes place in the ejector dilutor. Our fresh organic size distributions (vacuum-aerodynamic diameter measured with the AMS) had mode diameters between 100 and 190 nm, which match well with dilution tunnel measurements collected of wood burning in a fireplace which had VMD values in this range [Kleeman et al., 1999]. Therefore, combustion mode also likely influences the size distribution relative to the 8216;fresh8217; smoke the reviewer refers to. Such smoke is likely still in a plume, and thus substantial condensation and coagulation have already occurred. As the reviewer indicates, the slightly smaller size distribution in our experiments will lead to higher coagulation rates and potentially larger wall-loss rates. However, because most of our measurements are done on a particle mass basis (via AMS measurements) and are wall-loss-corrected (using BC and other methods), we argue that this doesn8217;t affect out interpretation of the data. Finally, particle size might be expected to impact the kinetics of evaporation and condensation, but would likely not affect the equilibrium partitioning of SVOCs as they age, which we hypothesize to be the critical process in the observed aerosol processing.

*This also makes me wonder about the particle emission factors. Are they much less than what is normally reported in the literature? These criticisms said, I do not think that this weakens the paper. You have given considerable evidence regarding the mechanisms of particle mass growth. I do not think it is necessary that you show an exact match to the environment, but as the reviewers point out this point of view must be clearly expressed. In fact, some effort should be taken to look at air pollution wood stove emissions papers which technically are closer in line with the measurements here than any actual biomass wild fire.*

As noted in the text (on page 15712, line 3), the OC:CO2 ratio (a rough proxy for OC

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emission factor) in these experiments was slightly lower than those measured in field measurements, suggesting that our PM emission rates are lower than measured in the field. Issues of inconsistent artifact correction and the bias in OC measurements conducted at high concentrations [Lipsky and Robinson, 2006; Shrivastava et al., 2006] complicate comparison of our results with conventional source tests.

*Second (in the emphasize category) is the issue of measuring 8216;black carbon8217; with an aethalometer. To be clear one cannot measure black carbon optically, especially given the massive change in size experienced during growth (Reid et al., 1998 on BC). Single scattering albedo and absorption cross-section will undoubtedly change rapidly with size growth as these particles are moving out of the near Rayleigh into the Mie regime. This should be on the order of 20-50 percent -relatively small compared to the mass changes. Again, as long as this is treated only semi-quantitative to show the likely chemical mechanism, I am ok. Given that an AMS is available, you should consider more traditional tracers. Perhaps potassium, or leviglucosan.*

This point was largely addressed in our response to the second point from Referee 1, above. The good agreement between the different estimates of OA production based on the BC measurements, SMPS measurements, and the AMS spectral decomposition indicate that the BC approach is a reasonable tracer for the primary emissions. Levoglucosan and potassium cannot be directly quantified in wood-smoke using the AMS due to interference at important mass fragments. An approach to quantify secondary production by decomposing AMS spectra is presented in the companion manuscript [Grieshop et al., 2008]and some text was added to this paper to emphasize that this alternative approach yields similar estimates for OA enhancement.

*Another fundamental issue not discussed is that of the control run. The assumption here is that mass growth only occurs photo-chemically. Because the authors assumed that a dark case can be used to subtract out wall loss and such, we don8217;t know anything about what dark reactions are occurring. Indeed, there are a few limited data sets I have seen that suggest mass growth even without photons. I would really like*

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*to see more data on their dark control runs. Even if no data is really easily available (because it was a blank), you can say you are looking at only the photochemical part. But, again, this needs to be made clear. I was also fairly impressed about the rapid increase in particle mass growth followed by the fast roll off after an hour or so. This matches very well what was observed in Hobbs8217;s 1996 paper in Levine8217;s book.*

Data from separate dark experiments were not presented or discussed in this paper. The beginning (injection and initial mixing) and end of each experiment were conducted with no lights. We saw no evidence of initial mass growth under dark conditions (both OA and BC measurements decayed as mass was deposited to the chamber walls) but did see some evidence of particle growth after lights-off as was discussed on page 15710, lines 2-4.

*Other minor comments: 15708 line 5: To compare to more real data the authors may want to took at Blake8217;s and Ferek8217;s data in the literature.*

The paper contained some comparisons with literature data and we have expanded and consolidated these comparisons into the discussion section.

*15710 line 4: The authors should also consider that with the small particle size in this experiment, heterogeneous ozone loss to the particles is also likely more limited.*

These experiments focus on gas-phase oxidation of evaporated wood-burning emissions, we believe primarily by OH radicals. If any processes are changing the ozone concentrations this will, in turn, influence OH concentrations. However, we don8217;t believe this is a first-order concern here.

*15710 line 21: That8217;s what Reid et al., 1998 and Trentmann et al., 2003 said*

We are not sure what the reviewer8217;s concern is here.

*15711 line 14: This definition holds for large wildfires that have both flaming and smoldering combustion and is for 8216;predominately flaming8217; or 8216;predominately*

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*smoldering8217;. I do no think that is the issue here. Next time perhaps the combustion state should be logged on film to help separate things.*

Film logging of the flame is an interesting suggestion, we will consider this in future experiments.

*15712 line 18: Yep-and it is almost certainly NOx limited.*

Our findings suggest that the chemistry is likely NOx-limited under most plume conditions and was in most of our experiments though either NOxň- or VOC-limited conditions are possible in the ambient atmosphere. More work is certainly called for.

*15715 line 26+: I understand the point that is being made, but the way it is said, 8221;which are based on diesel exhaust data, to represent wood smoke8221; is a total non-sequitor. That is like saying, 8220;which are based on a car to represent a boat.8221; You may want to rephrase this.*

We have clarified this text.

*15720 line 7: Reid et al., 1998 included this hypothesis, as well as many others. Besides, I do not think the case has been made that it is photochemistry that is the most active in the first 30 minutes. You guys see the mass growth (e.g., figure 3), but you don8217;t account for dark reactions.*

The fact that the emissions8217; initial residence in the chamber was under dark conditions precludes a large contribution from dark reactions on the initial rapid growth.

Response to Referee 3:

*I believe it is very important that the authors indicate early in the paper (eg, possibly in the abstract) how representative these experiments are compared to the various forms in which biomass is burned naturally or as a fuel. For example, adding a line describing that these experiments involved burning wood in a wood stove would clarify at the very beginning what type of fire smoke was investigated. The paper tends to*

*imply that the results are widely representative, including being applicable to burning in natural environments. Considerable and very worthwhile discussion is given to the comparison of concentrations of a number of smoke compounds (eg, OC etc) between these experiments and ambient observations. However these experiments involved burning various varieties of small pieces of wood in a small stove (page 15703 lines 58211; 10), which seems highly unlikely to represent ambient biomass burning where fuel mixtures (wood, duff, canopy leaves or needles etc), range of moisture contents, etc. are much more complex. Furthermore, in natural fires heating of non-combusting material (e.g. forest litter and canopy) by the fire could produce an additional variety of VOCs along with those generated in the burning. Along with noting early in the paper the specific burning method used, a larger discussion later in the paper on the limitations of broadly applying these results to biomass-burning in general would also be of value. For example, can the results of the OA formation observed in this paper be applied broadly to natural fires, and under what conditions would the results be applicable. In the Discussion and Conclusions, the OA production in the experiments are in some ways contrasted to ambient results, three studies being cited. Here again, the comparison between ambient and these experimental results should by qualified by including why there could be significant differences and what the implications are. For example, it is noted that Lee et al suggested isoprenoid species generated from heating (canopy etc) as a possible source for OA production, but not surprisingly, considering the burning method, these experiments observed that they were too low by 2 order of magnitude.*

This is an important and helpful point. In response, we have added a brief mention of the burning method used to the abstract, and reorganized the paper to more clearly compare and contrast our experimental conditions to those in the literature. The 8216;Discussion and Conclusions8217; section now has several paragraphs devoted to the comparison of our experimental conditions to those encountered in field measurements. We have added mention to the differences in burning conditions between a wood stove and general biomass burning in the field. We have also added a men-

tion of the important point that VOC emissions from a wild fire (from things like canopy heating and different fuel mixtures) will be very different from those of a wood-only fire in a stove.

*It would also be worthy discussing that little O3 was generated in these experiments, whereas in ambient studies O3 production can be substantial in biomass-burning plumes (eg, Lee et al.)*

Substantial O3ň was generated in all experiments and is noted in a figure (Figure 1d) and in the text in several locations (page 15709 line 29 to page 15710 line 5; page 15710 line 29 to page 15711 line 2).

*In the section on Basis Set Modeling, pg 15715 lines 20 to 25. If I understand this correctly the distribution of measured OC on the front and back quartz filters are used to infer the partitioning of SVOC between the particle and gas phases (i.e. front filter equals particle concentration, back filter equals SVOC concentration). This should be explained more clearly in the text, although I may have it wrong. If this is what is used what is the justification for assuming that OC volatility relative to air flowing through a baked quartz filter is the same relative to smoke particles?*

Filters alone are not used to determine SVOC phase-partitioning. In short, gas-particle partitioning was determined by simultaneously measuring emissions (using multiple dilution samplers and quartz filters) at different levels of iso-thermal dilution. A full explanation of this is contained in the Robinson et al. paper [2007] and references therein. We have added a more clear reference to this paper, which has a more detailed exposition of the generation of volatility distributions from dilution data. We8217;ve elected not to add a more detailed description to this paper for the sake of simplicity.

*On page 15720, lines 3 to 6 it is suggested that the results here of SOA production in smoke may explain the modern carbon observed in urban areas by other investigators. Do these cited papers report that biomass burning was a significant source of the urban OC? This must be the case for this statement to be justified. More details are need if*

*this point is to remain in the paper.*

Source apportionment studies have been unable effectively apportion the large quantity of 8216;modern8217; carbon found in urban areas carbon-isotope studies. This suggestion is indicating that the unaccounted-for (in emission inventories, chemical transport models and source-apportionment studies) source of OA that we have demonstrated in this work may make a substantial contribution to the modern carbon detected in urban aerosols.

*Minor comments. Page 15701 line 16: 8221;SOA is formed when8230;8221;. This statement should be qualified noting that this is the 8216;traditional8217; SOA model, see Volkamer et al. 2008 (Atmos. Chem. Phys. Dis, 8, 14841-14892) for an alternative theory.*

We have added text emphasizing that there are other models for the formation of SOA.

*Page 15705, lines 3 to 10. The use of wavelengths 880 and 590nm as indicators of brown carbon seems highly suspect since many references show little light absorption by brown carbon at these wavelengths, see for example Fig 1 in Sun et al, Geophys Res Lett, VOL. 34, L17813, doi:10.1029/2007GL029797, 2007. This would explain why no wavelength dependence was observed with SOA formation; it may not be detectable at these wavelengths.*

We are using the aethalometer data as an indicator of primary material and thus chose wavelengths that detect black versus brown carbon. Shorter wavelengths showed some evidence of secondary production of light-absorbing carbon which would bias our estimates of primary aerosol.

*Page 15705 line 17, what about the AMS vs filter OC magnitude (slope) comparison, only r2 is given, whereas both slope and correlation is given for BC vs EC.*

We have added slope.

*Page 15711 line 5, I do not believe this sentence should be referring to Table 1, maybe*

*Figure 1.*

This was changed to refer to Table 2.

*Table 1. Define MCE somewhere on the table (footnote?).*

Footnote added to table.

*Fig 7, no letter labels on individual plots.*

Added

*Also, in Fig 7 caption, change they to the in second last line.*

Fixed

REFERENCES:

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Kleeman, M.J., J.J. Schauer, and G.R. Cass (1999), Size and composition distribution of fine particulate matter emitted from wood burning, meat charbroiling, and cigarettes, Environmental Science Technology, 33 (20), 3516-3523.

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Aerosols: Semivolatile Emissions and Photochemical Aging, Science, 315, 1259-1262.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 15699, 2008.

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