

***Interactive comment on* “Chemical, physical, and optical evolution of biomass burning aerosols: a case study” by G. Adler et al.**

G. Adler et al.

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We thank the Reviewer for the thoughtful review and comments. We seriously examined each of them. Detailed replies to all issues raised are given below

...over half of the paper involves detailed analysis of AMS spectra that mimics then compare results to other AMS studies. Although this may be of interest to the AMS community, this approach does little toward advancing new insights on smoke evolution and, in my opinion, makes the paper of less interest than it could be. ...

Reply: This is the first time an AMS was used in this area, and one of the few AMS studies on biomass burning aerosols. As such we feel that using and comparing AMS

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accepted analysis provides a good anchor for comparison. In addition, this study provides insightful interplay between the chemical, physical and optical properties of these aerosols, combining the AMS mass spectra with ozone, aerosol concentration, particle distribution measurements and optical measurements. This is the first time such a comparison is made.

...measurements and interpretations are being based on data from one fixed sampling site, whereas the fires are widely distributed and possibly involve burning a range of fuels under varying conditions (small smoldering vs hot flaming, etc), it is not clear that meaningful interpretations can be made on the smoke aerosol chemical and physical evolution using this data set without first providing evidence that the approach is sound. Presumably, the analysis is based on the assumption that the smoke from many fires is well mixed throughout the night and persists throughout the following day so that the daytime evolution represents a regional average of all the emissions? This may be reasonable, but is there evidence to support this, for example, similar mass loadings throughout the region from network type monitors, satellite data (fire maps or smoke), etc. At the very least, it seems all data should be presented as ratios.

Reply: 1. Please see section 2: a table and a map showing different monitoring stations around the measurement site (Rehovot) and the corresponding PM_{2.5} before, during and after the burning event. It can be seen in the table a substantial increase in the PM_{2.5} concentration during the burning, substantiating our claim for widely distributed biomass burning smoke around the measurement site. 2. The fuel used for this burning event is roughly the same in all bonfire sites: local wood, wood from construction sites and old wood furniture. The mixed stages of the small smoldering vs. hot flaming is relevant only at the time period of the event itself (very few bonfires last until 4:00AM) and not for the morning-noon following the burning event itself. In addition, the amount of bonfires is very large (thousands) and widely distributed over Israel. As can be seen in fig 1, the wind speed is very slow along the whole event and after, and the barometric pressure is very stable. Additionally, the wind changed its direction in the day after

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the event bringing back the same population of aerosols to the measurement site. 3. Please see a comparison between the night of the event and a normal night (mass spectra)-figure A below. showing the different mass spectra for the event itself. 4. The authors have changed all figures to normalized mass spectra. 5. The authors have added a discussion about the possibility of mixing with other aerosol types possibly from transportation or other sources: p.24385 L15 p.24389 L5 Also see original text p.24387 L24

Assuming that the smoke is regional and well mixed, the premise that the authors were able to record the evolution of the smoke plume from night time emissions to later daytime measurements, and that temporal changes later in the day were all due to smoke chemical and physical evolution should be verified.

Reply: 1. The authors have added a discussion of mixing with oather aerosol possibility from transportation or other sources: p.24385 L15 p.24389 L5 Also see original text p.24387 L24. 2. Please see figure D below that shows the organics and ozone concentration as measured in the morning-noon of a normal day, few days after the burning event. (15.5.09). It can be seen in the graph that the ozone concentration increases with the increase in the organics (the same phenomena seen in the day after the event, but with much lower concentrations), this can provide an evidence of the capability to follow the aerosols evolution with time. In addition the m/z 57 which is a typical fragment of saturated hydrocarbons (C_4H_9) or long alkyl chains ($C_3H_5O^+$), can indicate either transportation-emitted aerosols (large amount of (C_4H_9)) or oxidized organic compounds-one of the common fragments of Levoglucosan($C_3H_5O^+$).At the day following the burning event around 60% of the m/z57 was oxidized organic compounds ($C_3H_5O^+$), compared to a normal day in only 28% of the m/z57 is oriented from oxidized organic compounds.(72% of transportation emitted aerosols C_4H_9), this shows that most of the aerosols are not from transportation in the day after the event

Can the nighttime emissions be more directly linked to the daytime measurements by

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a back-trajectory analysis, or if the assumption is that the region is uniformly impacted by the smoke, can this be justified by showing that species emitted exclusively by the fires, and largely unreactive on these time scales, remain invariant throughout the time period of interest. It is not clear that the argument made by the authors, that the PAHs and the AMS mass spectra measured in both periods (night vs day) are sufficiently unique to identify that the emissions measured at night are from the same source as those measured next day.

Reply: 1. Back trajectory analysis is not possible on this small geographical scale. The authors believe that Figure 1 gives a better understanding of the behavior of the air mass during the measurement period. Figure1 shows the very slow wind speed, and a very stable barometric pressure. Also the wind changed its direction, back to the original site at the day after the burning event, bringing back the same population of aerosols to the measurement site. 2. Please see figure B below, showing two main tracers for biomass burning $m/z60$ and $m/z 137$ which clearly show elevated levels at noon after the event, compared to the normal days (a few days after the event). This is seen as an evidence for the existence of biomass burning aerosols in the measurement site at the day after the event. 3. Please look at the Reply to the following comment (regarding PAHs)

It is curious that the idea of a uniformly impacted region does not appear to be consistent with the decrease in smoke in the morning and than increase again around noon. General consistency with expectations (ie, smoke becomes more oxidized, etc) is not sufficient to justify the analysis approach. Could it be shown that ratios of primary smoke components are constant throughout the period (eg, ratios of PAHs ? etc).

Reply: 1.Please see figure C , which presents the normalized PAHs in 4 different periods (normalized to the sum of total organics of all 4 periods). The 4 periods are: the burning event, the noon after the event, a normal night and a normal noon. It can be seen from the graph that there is a significant fraction of PAHs present on the day after the burning event at noon, compared to both normal days and nights. The amount of

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PAHs decreases from the burning event as expected. The reason the authors choose to present this normalization rather than normalizing each period to the relevant organics is that we believe that both the organics and the PAHs vary with the oxidation process, hence we do not expect to see the same ratio. The graph, however, demonstrates the large fraction of PAHs which remained in the sampling site after the event. 2 .Please see figure B below showing two main tracers for biomass burning m/z60 and m/z 137 which clearly show elevated levels in the noon time after the event compared to a normal day few days after the event.

Specific comments: Pg 24373 line 1: nitrate and ammonium are generally more significant products of biomass burning than sulfate. Not clear why sulfate is mentioned over other more prevalent species

Reply: This sentence was rephrased: "Biomass burning aerosols contain, among other compounds, nitrate, ammonium, sulfur, organic components and black carbon".

Pg. 24373 line 17, "quantitative data". What comparison substantiates this statement? In the past, the AMS was not considered quantitative as a stand alone instrument. For example, consider the assumptions made on page 24377. Give an estimated measurement uncertainty and what it is based on?

Reply: 1.All the figures are now presented in ratios,. The focus of this paper is on the aging process rather than on the absolute concentration. 2.The authors have added the following reference: De Carlo 2006 3.Please see also additional references dealing with "quantitative data" : 1. Quantitative sampling using an Aerodyne aerosol mass spectrometer Techniques of data interpretation and error analysis, James D. Allan,1 Jose L. Jimenez,2,3 Paul I. Williams,1 M. Rami Alfarra Keith N. Bower,1 John T. Jayne,5 Hugh Coe,1 and Douglas R. Worsnop JGR 2003 2. DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, Anal. Chem., 78, 8281–

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8289,2006. 3. CHEMICAL AND MICROPHYSICAL CHARACTERIZATION OF AMBIENT AEROSOLS WITH THE AERODYNE AEROSOL MASS SPECTROMETER, M.R. Canagaratna,^{1*} J.T. Jayne,¹ J.L. Jimenez,² J.D. Allan,³ M.R. Alfarra,⁴ Q. Zhang,⁵ T.B. Onasch,¹ F. Drewnick,⁶ H. Coe,³ A. Middlebrook,⁷ A. Delia,⁸ L.R. Williams,¹ A.M. Trimborn,¹ M.J. Northway,¹ P.F. DeCarlo,² C.E. Kolb,¹ P. Davidovits,⁹ and D.R. Worsnop¹ *Mass Spectrometry Reviews*, 2007, 26, 185– 222 4. Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer Jose L. Jimenez,^{1,2,3} John T. Jayne,¹ Quan Shi,¹ Charles E. Kolb,¹ Douglas R. Worsnop,¹ Ivan Yourshaw,⁴ John H. Seinfeld,⁴ Richard C. Flagan,⁴ Xuefeng Zhang,² Kenneth A. Smith,² James W. Morris,⁵ and Paul Davidovits *JGR* 2003

Pg 24374, The first paragraph is very specific and is likely of little value to researchers not familiar with AMS data analysis. Can it be clarified?

Reply: This paragraph was rewritten. "In this study we focus on the evolution of few significant ions the m/z 43, 44, 57,60 and 73. In order to identify biomass-burning aerosols and follow their evolution during the burning event and after. The m/z 43, 44, and 57 ions were used to follow the aging process and estimate the degree of oxidation, while m/z 60 and 73 were used as markers for wood burning aerosols (Alfarra et al., 2007). Specifically, In this study, the m/z 43 fragment ion corresponds mainly to $C_2H_3O^+$ and $C_3H_7^+$, while the m/z 57 was found to be correlated with $C_4H_9^+$ and $C_3H_5O^+$. In previous studies, the m/z 44 was shown to be related to the CO_2^+ ion (Alfarra et al., 2004). An increase in the f_{44} and a decrease in the f_{43} can indicate oxidation. For biomass burning indication, fragment ions m/z 60 ($C_2H_4O_2^+$) and m/z 73 ($C_3H_5O_2^+$) were used, since m/z 60, 73 and 137 have been suggested as marker fragments for wood burning emissions (Alfarra et al., 2007)."

Pg 24376. Considerable detail is given to the sampling efficiency of the inlet/tubing as a function of particle size, and the size ranges sampled by various instruments, except for the AMS. Details are needed.

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Reply: The reason the authors performed detailed sampling efficiency of the inlet/tubing as function of particle size is that the WELAS was located far from the SMPS sampling inlet. The optical properties (EIRI) are largely dependent on the size distribution. The AMS is described in details in the quoted references. (e.g DeCarlo et al. (2006))

How are the organic mass errors, stated in Fig 1 caption, determined?

Reply: The authors followed the procedures described in following reference: Quantitative sampling using an Aerodyne aerosol mass spectrometer: Techniques of data interpretation and error analysis, James D. Allan,¹ Jose L. Jimenez,^{2,3} Paul I. Williams,¹ M. Rami Alfarra, Keith N. Bower,¹ John T. Jayne,⁵ Hugh Coe,¹ and Douglas R. Worsnop JGR 2003

It seems somewhat questionable that time period B is really associated with the fires (discussed above)? Why did the concentrations from the fires drop (eg, a minimum at 9:00), then increase? Is there any CO or other tracer data available? This would suggest that there is the potential for mixing with other air not impacted by smoke during the sampling period. Or is the assumption that the whole region is uniform and the changes in concentration are just due to changes in fire emissions.

Reply: 1. Please see figure B below showing two main tracers for biomass burning m/z 60 and m/z 137 which clearly shows elevated levels in the noon time after the event compared to a normal day few days after the event, The entire area is well mixed. 2. Please see figure C below, which presents the normalized PAHs in 4 different periods (normalized to the sum of total organics of all 4 periods). The 4 periods are: the burning event, the noon after the event, a normal night and a normal noon. It can be seen from the graph that there is a significant fraction of PAHs present on the day after the burning event at noontime, compared to both normal day and night. The amount of PAHs decreases from the burning event as expected. The reason the authors choose to present this normalization rather than normalizing each period to the relevant organ-

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ics is that, we believe that both the organics and the PAHs varies with the oxidation process, hence we do not expect to see the same ratio. The presented graph, however, demonstrates the large fraction of PAHs that remained in the sampling site after the event. 3. The metrological conditions (including low wind speed, change of the wind direction back to the measurement site and very stable barometric pressure) support the claim that the same aerosol population is present at the day after. 4. The authors added a discussion of a mixed aerosol possibility from transportation or other sources: p.24385 L15 p.24389 L5. Also, please see original text p.24387L24 5. Unfortunately there is no CO data available. In this study we try to explain the change in concentration by aging process which is demonstrated in f44,f43 f57, ozone correlated to aerosol concentration variation and a change in the optical properties. 6. Additional support for the claim that the aerosol is well-mixed is found in section :, showing different monitoring stations around Rehovot (the measurement site).

Pg 24380, what is the uncertainty relating to the PAH masses stated. Comparisons are made to other AMS data, but this provides no insight on actual masses. If statements are to be made on the health effects of these species, the accuracy of the masses stated must be known; otherwise it is speculation that these masses are of any consequence.

Reply: The measurements were conducted according to the procedure described in Dzepina et al.,(2007), and the error for each measured number is presented in the paper. The errors were calculated in the same way mentioned above. Figure 3 which presents the change in the PAHs was modified to be normalized to the sum of the total PAH of both measured periods (A and C). The focus of this graph is to show the relative elevation in the PAHs during the burning event compared to a normal day. It is important to perform such a measurement to compare biomass burning to the PAH concentrations on a normal day. Obviously the PAH concentrations are substantially higher than during a regular day. Hence the claim on health impacts is substantiated even if the exact concentration has error. Also, this measurement were conducted in

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the exact same way as Dzepina et al., 2007, hence can be compared to their measurement to see the extent of this massive burning event compared to a Mega city which is dominated by traffic-emitted PAHs

Pg 24382, (discussion relating to figure 6). One might wish to comment why the intercepts are vastly different and positive (m/z 44 is greater than zero when organic mass is zero)?

Reply: The authors agree with the reviewer: the x-axis (organics) did not start from zero. Figure 6 has been changed and it now begin at zero and added minor ticks.

Pg 24383 Line 8. State here again what the significance of m/s 57 is.

Reply: The significance of m/s 57 is stated again in this line 24383 Line 8

Pg 24384: Temporal changes in concentrations during period B are taken as chemical evolution of the aerosol, however, this assumes there are no other processes that could influence the temporal trend, such as transport (even if wind speed is low), change in BL height, all of which can change concentrations by mixing in air masses of differing chemical characteristics (discussed above).It is never shown that the aerosol is regionally uniform. Comparisons involving ratios, ie relative to some conservative co-emitted species, or OA (as is done in some cases) are likely more reliable. This concern applies to all of section 7.1.

Reply: The authors added to the discussion and to the conclusions the possibility of mixing with other aerosol types from transportation or other sources and the possible effect of the ambient temperature (causing changes in the partitioning of semi volatiles) Added p.24384 L 7, p.24384 L24,(as mentioned above added: p.24385 L15) In addition, please see the Replies to the general comments above

Fig 7. More discussion is needed on why the data of period B falls out of the triangular Region thought to represent most atmospheric observations.

Reply: The triangle shown in Ng et al is for mostly urban aerosols and SOA in urban en-

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vironments. We suspect that here the SOA forms from a slightly different VOC mix. Our results are also consistent with observations of Jimenez et al who also studied aging of smoke (AGU 2010 fall meeting, private communication). Generally m/z 43 in this study is composed of two ion: $C_3H_7^+$ and $C_2H_3O^+$. The $C_2H_3O^+$ indicates oxidized organics. In the day following the burning event 72% of the m/z 43 was $C_2H_3O^+$ compared to 38% during the burning event itself. This is clearly an indication of oxidation; However, oxidation can proceed further to form carboxylic groups which are indicated in the AMS by CO_2 ion (m/z 44). The values presented in the Ng upper triangular graph are a demonstration of a complete oxidation process indicated by dominance of carboxylic groups (high f_{44}) and low $C_3H_7^+$. The case presented in this paper is a non-complete oxidation process which is indicated by high amount of carboxylic groups (high f_{44}) but also a not fully oxidized aerosols indicated by high f_{43} which mainly composed of $C_2H_3O^+$.

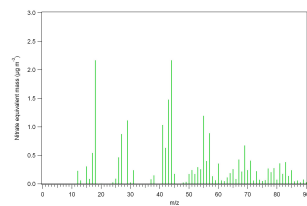
Fig 10 the trace for the organic mass is incomplete. No data during event B is shown making the discussion on pg 24385 difficult to follow.

Reply: Organic data was added to figure 10

Section 7.1 It is not clear how temporal changes in number concentration relative to OA mass indicates new particle formation. Could it not be related to growth of particles into or out of each instruments measurement size range?

Reply: The temporal changes in number concentration relative to OA mass can indicate new particle formation but not necessarily. However, combining few instruments for aerosol number concentration and size and the elevated ozone concentration combined with the change in the optical properties and chemical indication for oxidation led the authors to this explanation. The authors do not rule out the possibly of mixed population. Regarding the instrumentation, the CPC measures particles ranging from 7nm as mentioned in the paper, and all instrument showed the same trend.

The night of the event (a):



A normal night a few days after the event (b):

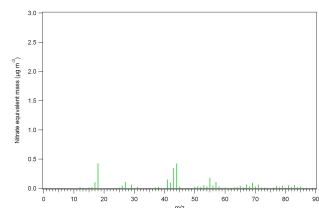


Figure A: A comparison between the two mass spectra: during the BB event (a) and during a normal night (b) (same hours of the day), this graph is presented in nitrate equivalent mass. The mass spectrum during the event shows the fundamental difference between the organic mass spectrum during burning compared to a normal day.

Fig. 1.

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Figure B:

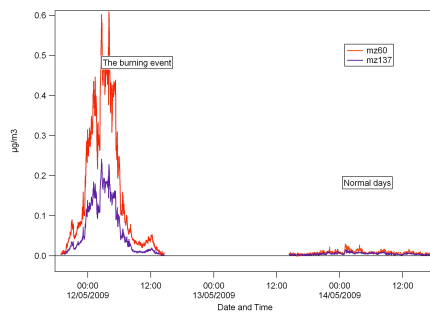


Figure B: showing two main tracers for biomass burning $m/z60$ (red line) and $m/z137$ (purple line) which clearly show elevated levels at noon after the event, compared to the normal days (few days after the event). This provides an evidence for the existence of biomass burning aerosols in the measurement site at the day after the event.

Fig. 2.

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Figure C

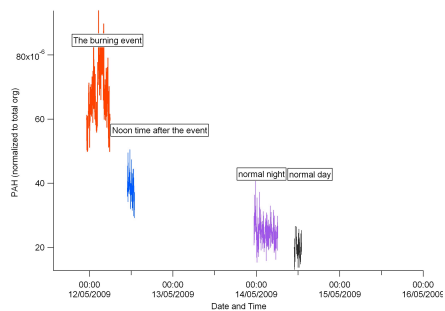


Figure C presents the total PAHs in 4 different periods normalized to the sum of total organics of all 4 periods. The 4 periods are: the burning event (red line), the noon after the event (blue line), a normal night (purple line) and a normal noon (black line). It can be seen from the graph that there is a significant fraction of PAHs present on the day after the burning event at noon, compared to both normal day and night. The amount of PAHs decreases from the burning event as expected. The reason the authors choose to present this normalization rather than normalizing each period to the relevant organics is that we believe that both the organics and the PAHs varies with the oxidation process, hence we do not expect to see the same ratio. The graph, however, demonstrates the large fraction of PAHs that remained in the sampling site after the event.

Fig. 3.

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Figure D:

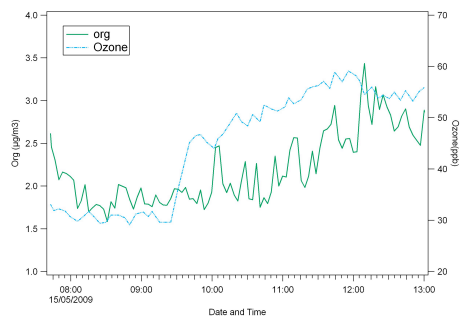


Figure D presents the organics and ozone concentration as measured in the morning-noon of a normal day, few days after the burning event. (15.5.09). It can be seen in the graph that the ozone concentration increases with the increase in the organics (the same phenomena seen in the day after the event, but with much lower concentrations), this can provide an evidence of the capability to follow the aerosols evolution with time.

Fig. 4.

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Section 2:

PM2.5 Data from nearby monitoring stations showing the widespread pollution

| Station | Distance from the measurement station | PM2.5 a day before the event (11.5.09-15:00) [$\mu\text{g}/\text{m}^3$] | PM2.5 during the peak of the event (11.5.05-22:30-00:00) [$\mu\text{g}/\text{m}^3$] | PM2.5 after the event (12.5.05-16:00) [$\mu\text{g}/\text{m}^3$] |
|----------------|---------------------------------------|---|---|--|
| Kiryat Malachi | 30.3 Km South | 29 | 193 | 10 |
| Askelon | 34.3 Km South West | 30 | 296 | 40 |
| Sderot | 45.5 Km South West | 21 | 122 | 12 |
| Holon | 13.5 Km North | 17 | 248 | 7 |

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Fig. 5.