**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Aged organic aerosol in the Eastern Mediterranean: the Finokalia aerosol measurement experiment-2008" *by* L. Hildebrandt et al.

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GENERAL COMMENTS

The authors would like to thank the two anonymous reviewers for their helpful comments and suggestions. All comments are addressed below. Reviewers' comments are included in italics and author responses are in plain text.

Response to Referee 1:

1. Page 1849 line 9

It should be explicit that you are referring to fine mode inorganic material.

This has been made explicit in the revised manuscript. The updated sentence reads: "In contrast to fine-mode inorganic aerosol, which is mostly composed of a few well-characterized components such as sulfates, nitrates and ammonium . . . ."

2. Page 1850 line 4

"Ageing and," should read "Ageing, and"

It now reads "Aging and transport can result in elevated organic PM concentrations . . . ."

3. Page 1850 line 12

It should be stressed that these classifications are typical.

This has been changed in the revised manuscript. The revised sentence reads: "Typical resulting classes include a reduced component . . ."

4. Page 1850

It seems strange that after quoting Ng et al 2009 earlier the authors don't reference it at this point as it, and the partner paper Morgan et al 2009, describe the dynamic ageing of OA in a consistent framework.

References to the Ng et al. (2009) and Morgan et al. (2009) manuscripts have been added.

5. Page 1851 lines 12-17

Given the premise of the paper it would be good to state what criteria were used by Koulouri et al 2008 for identifying the sources of aerosol.

The reference to the factor analysis by Koulouri et al. has been updated to:
"Factor analysis showed that $PM_{1.3}$ could be explained by five factors, identified based on the loadings of various chemical components. Two factors were natural . . . ."
It would be difficult to include more detailed information (i.e. the identity of the chemical components used to identify the different factors) without repeating the full description of the factor analysis performed by Koulouri et al.

6. Page 1852 line 22

It may be worth a brief synopsis of the detailed published work on the prevailing meteorology simply to provide a context for the field study presented in this paper.

We prefer not to include such a synopsis of the prevailing meteorology since the meteorological conditions during this specific study have been described in detail by Pikridas et al. (2010). A reference to this publication has been added.

7. Page 1853 line 6

". . .is presented in companion publications" should be ". . .are presented in companion publications"

Corrected.

8. Page 1853 line 12

Given no active drying was installed, it may be worth commenting on the relative temperatures in and outside the laboratory.

The outside temperature was most of the time a few degrees cooler than the inside temperature. The AMS water data was corrected for the corresponding change in relative humidity (using the outside RH and temperature to calculate the absolute humidity and the inside temperature to calculate the RH inside of the sampling lines after the

aerosol has equilibrated to the inside temperature). The details of this correction have been added to Appendix A.

9. Page 1853 line 19

Was the nephelometer sampling dry aerosol or were these deliquesced for some or all of the time?

Three nephelometers were operated during this campaign (Pikridas et al., 2010). The data we used to compare with the AMS are from the nephelometer that measured the dried aerosol. We compared these measurements to the dry PM_1 concentrations from the AMS (see section 2.3.3).

10. Page 1854 line 9

This is written generally, was the AMS used in this project operated with a high throughput lens?

Yes, it was. We have updated the corresponding sentence to:
"In addition, the high throughput lens used during this study may reduce the transmission efficiency of larger aerosol particles."

11. Page 1855 line 26

The oxygenated ion at m/z 57 should be $C_3H_5O^+$

Corrected.

12. Page 1857

Sections 2.3.3 to 2.3.5 are too short to form full sections, it would be better if they were merged.

We have merged the sections.

13. Page 1858 lines 18-19

e.g. should be i.e. and it is stated that y is the mean value for the whole campaign. This should be given an overbar.

We have added the overbar. We left the "e.g." because we are using f_{44} as an example.

14. Page 1858: line 20

"C is the amplitude, k is the harmonic number," should be "Ck is the amplitude of the kth harmonic,. . ."

This has been corrected in the revised manuscript.

15. Page 1860 lines 9-19

The CE of the AMS: The CE is derived from the comparison between the volume derived from the SMPS weighted by the component densities and the AMS mass distribution. Figure 2 shows that the peak in the mass distribution of the AMS is shifted to large sizes, presumably because the aerosol is well aged. However, this means that much of the AMS mass may well be above the size of the majority of channels of the SMPS. What was the largest size of the SMPS scan? And what were the uncertainties in the comparison based on counting statistics from the SMPS? If not all the volume was captured by the SMPS then the derived CE will be biased high and may be closer to 0.5. Whilst the aerosol is slightly acidified, it does not appear to be greatly so from the data shown in figure 1. What was the calculated humidity in the line based on in and outside T and outside humidity? Figure 3 shows good agreement between measurements of sulfate and OM from the AMS, steam-jet and filters. This is good evidence that the CE was correctly estimated but no comment is made in this section.

We first want to emphasize that the matching algorithm developed by Kostenidou et al. (2007) and used here to estimate the CE in the AMS does not use the total SMPS volume but rather the SMPS volume distribution. The fitting of the distributions up to approximately 500 nm mobility diameter minimizes the importance of the tail of the distributions where both of the instruments have problems. This is now mentioned in the text. The details of the CE estimation are presented in our companion paper (Lee et al., 2010).

The aerosol was slightly acidified for most of the campaign. The inorganic acidity for the sub-micrometer particles, presented as the molar ratio $NH_4^+/(2 \times SO_4^{2-} + NO_3^-)$ was 0.82 on average with a standard deviation of 0.09 (values below 1 suggest acidic aerosol). This information has been added to the text. The relative humidity inside of the line, calculated from outside RH and temperature and inside temperature was 34% on average, ranging from 15 to 64%. The ambient particles always contained some water. This could explain the higher collection efficiency. In summary, the collection efficiency was likely higher because the particles were in a liquid state, which can (in part) be explained by:

1. slightly acidic aerosol
2. the observation that even the organic aerosol was highly oxidized (and hence probably hygroscopic)

As noted by the reviewer, the higher collection efficiency is consistent with the comparison to other instruments. A comment regarding this has been added to the text.

16. Page 1860 line 25

repetition of site

Corrected.

17. Page 1861 line 23

It is peculiar to cite a personal communication with a co-author.

True. This citation has been removed.

18. Page 1861 lines 21-23

One wonders whether the differences in the size distributions between sulfate and OM is due to change in the sulfate:OM over time. The sulfate mass is much higher than the OM in periods of long range polluted transport compared to other periods but the OM does not change too much. It is not inconceivable that the size distribution of sulfate and possibly also OM increased during long range pollution transport. If a campaign average is taken then the average size will be shifted in proportion to the mass.

We investigated this hypothesis by looking in detail at four time periods: two more polluted periods when the sulfate/organic ratio was high (periods 2 and 3), and two cleaner periods (1 and 4) when sulfate/organic was much lower. The results are summarized in the table below.

Period #	Dates	Source	Sulfate mode	Organic mode	mean Sulfate/Organic
1	May 9-10	Marine	413 nm	370 nm	1.0
2	May 14-15	Continental	471 nm	451 nm	1.7
3	June 1-2	Continental	495 nm	454 nm	2.7
4	June 3-4	Marine	474 nm	416 nm	0.8

The reviewer's hypothesis is consistent with the comparison of periods 1 and 2: during the relatively clean period 1, sulfate/organic is lower and the aerosol mass mode for sulfate and for the organics is lower than during the more polluted period 2. During period 2, the organics are at a smaller mode than the sulfate, but the difference in the modes (sulfate - organics) is smaller than during the cleaner period. The hypothesis may also be consistent with the comparison of periods 3 and 4, even though the differ-

ence in the sulfate mass mode between these two periods is quite small (and possibly not significant).

This could in part explain the shift of the sulfate mode to the right in the campaign average. This does not rule out the shift in the sulfate distribution due to slower evaporation, and it does not change any further analysis or conclusions in this manuscript. Thus, we have simply added a comment regarding this alternative or additional explanation to the revised manuscript:

"The sulfate distribution is slightly shifted to the right of the others. This could be due to slower vaporization times of sulfate and to changes in the sulfate/OA ratio over the course of the campaign: During periods of higher NR-PM$_1$ concentrations, sulfate/OA was usually higher and the size of the particles was often larger. This moves the sulfate distribution to the right of the organic distribution when averaging over the whole campaign. This has only a small effect; aerosol composition was rather homogeneous with size."

19. Page 1862 line 11

How well has the zero calibration of the nephelometer been applied? It may be possible that this is a real offset in that instrument.

There is always the possibility of error; however the nephelometer was calibrated before the campaign, so we believe that this offset was not due to the instrument.

20. Page 1863

The discussion of the rather weak dependence on subsequent photochemical processing time of OA that has aged by more than one day already is a useful one. I would have liked to have seen this developed so that the result is compared with previous experiments (e.g. Volkamer et al; Morgan et al) and results from chamber studies.

This discussion has been extended. In particular, we have added the following sen-

tences:
"This is unlike the results of laboratory experiments, where an OH exposure of 4×10^{10} molecules cm^{-3} s (a factor of 10 lower than in the FAME-08 example above) has resulted in an f_{44} increase from 5% to 12% in aged Diesel OA (Sage et al., 2008) and an f_{44} increase from 4% to 8% in aged woodsmoke OA (Grieshop et al., 2009a; Grieshop et al., 2009b). The slow increase in f_{44} observed during FAME-08 is also different from the generally rapid photochemical processing of OA on a regional scale observed by Morgan et al. (2009) and in this study: after only 1 day of aging, the OA is very processed and highly oxidized. Slow further processing of oxidized OA could be due to fragmentation of organic compounds, which becomes more important at higher O:C (Kroll et al., 2009). When compounds fragment upon oxidation, they may volatilize, thereby slowing the oxidization of the ensemble organic material in the particulate phase."

21. Page 1865 lines 20-28

The discussion at this point may give the reader the impression that the chemical processes acting on this aerosol are different from those observed to be acting elsewhere. The key difference is one of age of the aerosol. As I am sure the authors are well aware the biggest reason for the inverse correlation between f_{44} and volatility in other lab and near pollution field studies is that there is substantial change in chemistry of the ensemble OA due to oxidation and f_{44} reflects the balance between the more and less processed organic material. Whereas in their study the ageing process is much further advanced and there is little fresh material to affect the f_{44} throughout the experiment. I think that this discussion could be better developed.

This paragraph has been revised to better develop this discussion. The first part of the paragraph is now:
"This is in contrast to observations in many laboratory experiments (Grieshop et al., 2009a) or in field studies closer to the sources (Huffman et al., 2009). In these stud-

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ies, the thermodenuded organic aerosol is observed to have a larger f_{44} compared to the ambient aerosol. These observations are consistent with an inverse relationship between extent of oxidation and volatility: holding the carbon number of the molecule constant, more oxidized (functionalized) compounds have a lower volatility and are therefore more likely to remain in the aerosol phase upon heating. The OA sampled in these studies is a mixture of fresher and more oxidized OA, and the more oxidized OA is typically less volatile. Hence, the thermodenuded OA, from which the fresher, more volatile components have been stripped, exhibits higher f_{44}. During FAME-08, however, almost all OA was highly oxidized, and the aged aerosol was not mixed with fresher OA (except possibly on May 19-21 as mentioned above). In this highly oxidized organic aerosol, f_{44} does not have an inverse relationship with volatility."

22. Page 1866 lines 20-22

In the nomenclature of the introduction any OPOA is indistinguishable from added SOA. This probably should be stated.

We have added the following sentence to the introduction:
"While AMS factor analysis cannot usually distinguish between OPOA and SOA, the source types of OPOA (emitted as particles) and SOA (emitted as gases) are often different, and hence the distinction is useful for the development of policy actions."
We also added a comment to the sentence referenced by the reviewer. The modified sentence reads:
"The sources influencing the site surely contain primary as well as secondary organic aerosol, but when the aerosol reaches the site, it has been diluted and oxidized enough that all organic aerosol has been converted to OOA, a mixture of OPOA and SOA."

Response to Referee 2:

1. Page 1850, lines 19 and 20.

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According to Jimenez et al. (2009), SV-OOA should be semi-volatile OOA (not higher-volatility OOA), and LV-OOA should be low-volatility OOA (not lower-volatility OOA).

This has been changed in the revised manuscript as suggested by the reviewer.

2. Page 1855, line 26.

C3H7O+ should be C3H5O+.

Fixed.

3. Page 1859, section 2.3.8.

I assume PMF is applied to the non-denuded data? This should be made clear.

PMF was applied to the ambient data and the full dataset (ambient and thermodenuded data together). We have made this clearer in the revised manuscript.

4. Page 1862, line 1.

It is not clear at this point how the authors get an OM:OC of 2.2. Later in the paper (page 1863, line 2) the authors wrote "the average f_{44} of 18.2% corresponds to an O:C ratio of 0.8 and an OM:OC ratio of 2.2 using the correlations introduced in Sect. 2.3.1. This sentence should be mentioned earlier in Page 1862.

We have updated the sentence to:
"... we use an OM:OC ratio of 2.2, estimated using the correlations developed by Aiken et al. (2008) presented in section 2.3.1 and the campaign-average f_{44} of 18.2% (Section 3.2.1)."

5. Page 1864, line 10 onwards

The authors suggested that the fractional changes in f43 and f44 appear to be close to zero throughout the campaign (possible exception 19-21 May). However, by looking

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at Fig. 6, once could almost argue that there are some variations in the changes in f44 and f43 between the non-denuded and denuded aerosol. For instance, from the data points in Fig. 6, it almost looks like on average the change in f43 would be negative. Also, towards the end of the campaign it appears that on average there would be a roughly -5% change in f43. The data points in Fig.6 do not have error bars, so it is difficult to judge whether these changes are statistically significant. Error bars should be added in the revised manuscript. If the change in f43 towards the end of the campaign is significant, what may be causing this?

The data are rather noisy. However, since we also wanted to show the trend (if any) over the course of the campaign, we decided to present 12-hour averages rather than only the campaign-average. The updated figure in the revised manuscript also includes the 25th and 75th percentiles of each 12-hour average. As can be seen, the interquartile ranges of the percent change cross the 0-line for all but one point during the campaign. This one point was when the air mass was influenced by major cities in Africa. That air mass also exhibited the highest concentration of elemental carbon and a lower OC:EC ratio, suggesting that the aerosol sampled during this time period was the fresher. In fact, the f_{43} and f_{44} behave "as we would expect" in fresher aerosol: f_{44} is higher in the thermodenuded aerosol than in the ambient aerosol, consistent with the inverse relationship between volatility and f_{44} that is often observed. We have included this information in the revised manuscript.

6. Page 1865, line 23.

Based on the thermodenuder results, the authors suggested that the aerosol sampled is composed of compounds of similar O:C but different volatilities. While fragmentation provides an alternative mechanism for changing O:C and volatility that is different from the "typical" inverse relationship between the two, it does not necessarily support the observation that O:C is the same but volatility changes.

We agree that this paragraph was a bit confusing as written. We have re-written the

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last part of the paragraph as follows:

"In this highly oxidized organic aerosol, f_{44} does not have an inverse relationship with volatility. The lack of correlation between volatility and O:C$_{44}$ is consistent with compounds produced via fragmentation or oligomerization. In the fragmentation pathway, O:C increases by net loss of carbon rather than net addition of oxygen (Kroll et al., 2009). Thus, an increase in O:C is not necessarily associated with a decrease in volatility since the decrease in volatility due to the addition of oxygen can be offset by an increase in volatility due to fragmentation. While fragmentation can result in compounds with different O:C but similar volatility, oligomerization can result in compounds of different volatility with similar O:C. The fragmentation pathway is more likely in highly oxidized organic aerosol; thus it may be the dominant pathway in the late stage of the oxidation process observed during FAME-08. The available data do not allow us to more than speculate about the importance of this process."

7. Page 1865 and page 1866

The arguments in these two pages should be better laid out, as it almost sounds like two contradictory conclusions are being presented. On page 1865, the authors argued that the aerosol appears to be composed of compounds of similar O:C but of differing volatilities. On page 1865, however, two OOA factors were obtained and these two factors have different O:C but similar volatility. Both arguments are solid on their own, but the authors need to explain things more clearly to link these two together.
On page 1866, line 26. The authors stated that "however, OOAa is not less volatile than OOAb according to the thermodenuder data". How did the authors come to this conclusion? This should be explained in more detail.
a) According to the authors, the MS of the denuded and non-denuded aerosol are similar. If the denuded aerosol corresponds to the more oxidized OOA (i.e OOAa), one would expect the MS of the denuded aerosol to have a higher f44. Since this is not the case, it suggested that the PMF factors and the denuded and non-denuded aerosol do not directly correspond to each other. This should be stated explicitly in the manuscript.

b) The OOAa and OOAb have a big difference in f44 but the denuded and non-denuded aerosol appears to have very similar MS. One possible explanation is that OOAa and OOAb have similar volatility AND the relative fractions of OOAa and OOAb in the denuded and non-denuded aerosol are the same. However, it is not obvious from the data that the relative fractions of OOAa and OOAb in the denuded and non-denuded aerosol are the same. The authors should do some calculations to evaluate this. Is the PMF analysis performed on the denuded or non-denuded data? If it is done on the non-denuded data, one can easily calculate the fractions of OOAa and OOAb in the non-denuded aerosol based on the PMF factor time series. One can also express the denuded data as a linear combination of these two factors and determine the time series and relative fractions of these two factors in the denuded data.

The distinction between ambient and thermodenuded OA is independent of the distinction between the two OOA factors. We have made this clearer in the revised manuscript. In fact, the relative fraction of the two OOA components relative to the total OA mass is the same in the ambient and the thermodenuded OA. We have added a figure to the revised manuscript (Figure 9 in the revised manuscript, Figure 1 below) to emphasize this fact.

8. Fig. 4

Can add a legend with slope and intercept of the fit.

We prefer to include this information in the caption of the figure, as we did in the revised manuscript.

9. Fig. 5

I assume these are the non-denuded data? This should be made clear.

Yes, they are. We have made this clear in the revised manuscript.

10. Fig.8

I suggest the authors to show the time series of the two factors over the whole campaign (Fig.9 only shows the times series for selected time periods). For instance, it would be useful to see how the time series of OOAa and OOAb look like for the time periods when there seem to be larger differences in f43 between the denuded and non-denuded aerosol (Fig. 6, towards the end of the campaign).

We have changed Figure 10 in the revised manuscript (formerly Figure 9) and are now showing the full time series of the two OOA factors. This figure is included below (Fig. 2 of response file).

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 1847, 2010.
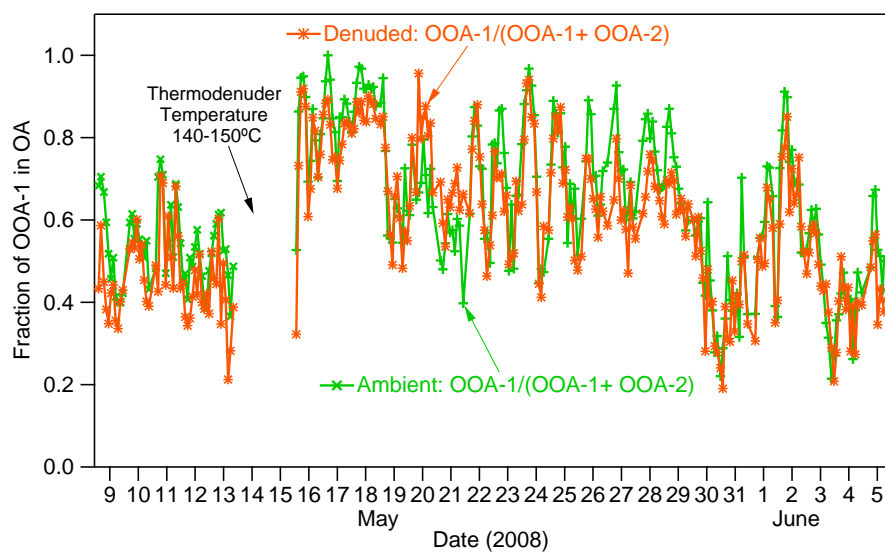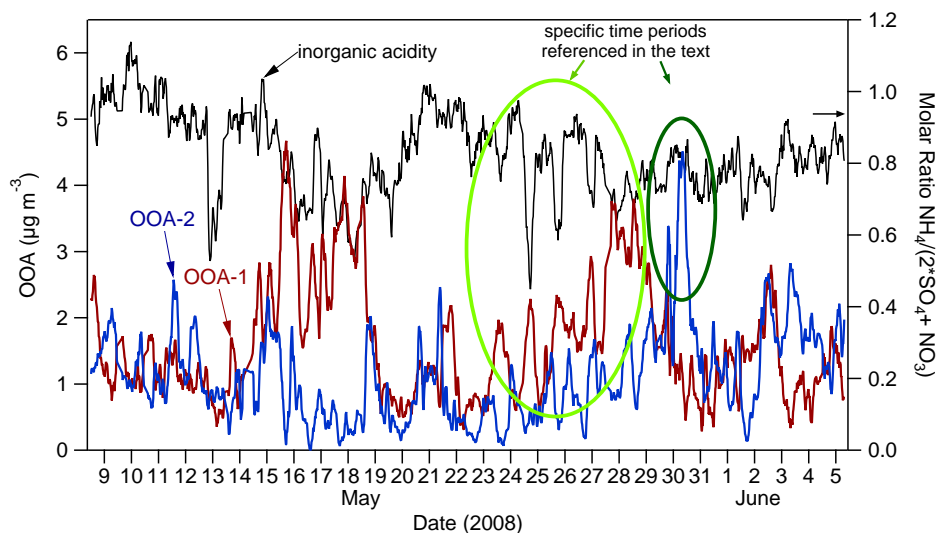
Fig. 1.

Fig. 2.

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