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Atmospheric
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Discussions

Interactive comment on "Sources and atmospheric processing of organic aerosol in the Mediterranean: insights from aerosol mass spectrometer factor analysis" *by* L. Hildebrandt et al.

L. Hildebrandt et al.

lea.hildebrandt@gmail.com

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AUTHOR COMMENTS

We would like to thank the two anonymous reviewers and Dr. Xinlei Ge for their helpful comments and suggestions. All comments are addressed below. Comments are included in italics and author responses are in plain text.

Response to Referee 1:

- *The authors should also comment that dust is an important submicron component also, not only in the main dust events but at other times.*

A comment regarding the contribution from dust has been added to the revised manuscript.

- *Coarse mode aerosol were shown to be principally dust, sea salt and nitrate, though there was also a contribution from nss Sulfate that the authors should recognize.*

A comment regarding the contribution from non-sea-salt sulfate has been added to the revised manuscript.

- *However, the authors should note (Ng et al., 2010 and Morgan et al., 2010) that the factor in one campaign need not be chemically identical to the same factor in another campaign as the factor analysis simply picks out a factor in the mass spectral time series that best describes the variability in that time series. Hence the OOA in FAME2009 need not be as processed as the OOA in FAME 2008.This is an important caveat and one that should be included in any revised paper.*

We have clarified this issue in the revised manuscript. The end of section 3.3 now reads:
"The OOA components extracted from different field campaigns are not expected to be identical since PMF analysis simply separates OA into those components that best explain the OA variability. However, f_{43} and f_{44} can still be used to characterize the extent of oxidation of the OOA (Ng et al., 2010). ... Thus, we find that OOA observed during the winter (FAME-09) is similar to the OOA observed during the summer (FAME-08) in terms of volatility and extent of oxidation."

- *One concern I do have is that amines can be surface ionized, a fact noted by the authors, but the same analysis as they conducted in FAME-2008 is not presented. It would be good if the authors could demonstrate surface ionization is not important.*

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We addressed this issue in the auxiliary material of our previous publication (Hildebrandt et al, 2010b). In summary, we cannot detect evidence for surface ionization considering that:
1. the "amine" signal (*m/z* 58) does not correlate with AMS-potassium (*m/z* 39), which suffers from surface ionization and
2. the correlation between the amine signal and AMS-potassium did not change after we retuned the instrument in the middle of the campaign in an attempt to decrease surface ionization.

- *The biomass burning factor does not have the typical mass spectral fingerprint of many previous BB studies using AMS. The authors demonstrate that the factor is consistent with some burning events and state that olive branch burning is the most likely cause. It would have been good to have shown a representative source sample mass spectrum of olive branch burning to prove the hypothesis.*

Unfortunately, a source sample mass spectrum for olive branch burning is currently not available. We are planning to run a group of these challenging burning experiments within the next few months. The source sample mass spectrum will then be used together with new measurements at Finokalia to test our hypothesis.

- *Pg 19641 Abstract: It might be good to include something of the duration and seasonality of the measurements in the abstract.*

We have included this in the revised manuscript.

- *Pg 19645 line 18: To what extent are the CE values consistent with the more widely used CE of Matthews et al which is based directly on the AMS component mass. This is quite important as it affects other studies.*

We found that the available CE parameterizations based on AMS composition and relative humidity do not agree with our CE estimates. Other recent studies (Middlebrook et al., 2012) have suggested that CE is enhanced when the ammonium nitrate mass fraction (ANMF) in PM_1 exceeds 0.4 and/or when the ratio of measured and "predicted" ammonium (the ammonium needed to neutralize PM sulfate, nitrate and chlorine) exceeds 4.5. During both FAME-08 and FAME-09, ANMF was always (and usually quite significantly) below 0.4 (FAME-08 average: 0.1, FAME-09 average: 0.02). The $NH_4/NH_{4,predicted}$ ratio was also always too low to affect CE (FAME-08 average = 0.82 FAME-09 average = 0.83), even though the variability during FAME-09 was higher (maximum ratio = 3.1). RH was high enough at times to affect CE, but not greatly. After applying the RH correction according to Middlebrook et al. (2012) the average CE for FAME-08 was 0.49 and the average CE for FAME-09 0.51, compared to our average estimates of 0.85 and 0.6 for FAME-08 and FAME-09, respectively. For FAME-08, CE estimated using these two methods is thus quite different. For FAME-09, the average values are more similar, but the time series of CE do not follow the same trend. For example, during one time period the parameterization based on AMS composition gives CE=0.75 and our method estimates CE=0.6; during another time period the parameterization gives CE=0.5 and our method estimates CE=0.85.

Thus, the CE parameterizations based on aerosol composition do not appear to be applicable to the FAME aerosol and the corresponding AMS instruments. The comparison to other measurements (filter samples for FAME-08 and FAME-09 and also steam sampler data for FAME-08) suggest that our CE estimates are appropriate for these data.

- *Pg 19645 line 24: What was the CE during FAME-08?*

The average CE of ambient PM_1 was 0.85. This number and a reference to the work where we described the calculations and estimates in more detail have been added to the revised manuscript.

- *Pg 19646 line 4: could the Matthews et al correction be used when SMPS data were* *not available?*

As mentioned above, the Matthew et al. (2008) and Middlebrook et al. (2012) parameterizations would result in different CE values, different corrected PM_1 concentrations from the AMS and different correlations between AMS and ancillary data. For FAME-08, using the Middlebrook correlations would result in over-prediction of PM_1 by almost a factor of 2. For FAME-09 the differences between the CE are smaller. When using the CE estimated from Middlebrook et al. (2012), the slope of the sulfate AMS vs. filter correlation is closer to 1 (0.8) and the slope of the organics AMS vs. sulfate correlation is larger than 1 (1.3), whereas it was 1.0 before. However, an overestimation of AMS organics is more difficult to explain than an underestimation of AMS sulfate due to the different size distributions of organics and sulfate (see main text). Therefore, it appears that our CE estimates are more appropriate for this data set.

- Pg 19647 line 12 and Pg 19671 figure caption: There is a significant contribution to PM_1 from dust that even away from the events that should be commented on. It is insufficient to say that sulfate, organics and ammonium dominate. There is also significant nss SO_4 in the coarse mode.

A comment regarding the contribution from non-sea-salt sulfate has been added to the figure caption and the main text of the revised manuscript.

- Pg 19647 line 19: I see little point in quoting the slope of the OM filter/AMS regression given the OM/OA of the filters is based on the AMS.

The estimate based on the AMS is OM/OC, not OM/OA. The OM/OC ratio is not derived from total AMS organics measurements but rather from f_{44}, the fraction of total organic signal which is due to ions at *m/z* 44, using the correlations developed by Aiken et al. (2008). Thus, the OM/OC estimate does not use measurements of the AMS organic concentrations, and the correlation is indeed meaningful. This has been clarified in the revised manuscript. The updated sentences now read:

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“Organic mass from the filter samples was estimated by multiplying filter measurements of organic carbon by the ratio of organic mass to organic carbon (OM:OC). The OM:OC was estimated from AMS measurements of f_{44} (the fraction of total OA mass due to fragments at *m/z* 44) using the correlations developed by Aiken et al. (2008).”

- Pg 19649 lines 19-21: “concentrations of air ions”. This implies that ions charged naturally in the atmosphere were measured. Is this so? There is no reference to this in the list of instruments. If you mean UF particles you should say so.

Yes, here we refer to measurements taken by an air ion spectrometer, which are described in much more detail in Pikridas et al. (2012). In order to avoid confusion, air ion concentrations and a reference to Pikridas et al. (2012) have been added to the list of measurements in the revised manuscript.

- Pg 19650 line 21: The authors suggest that OB-OA is converted rapidly to OA by implying that the sources are near to the sample site. However, the paragraph beginning on line 11 of Page 19653 clearly states that this is not necessarily the case. The arguments need to be made to be consistent – I see no evidence for rapid conversion of OBOA to OOA from the data.

Our measurements suggest that local as well as regional fires influenced the observed OA during FAME-09. As we stated on page 19653 line 18-19: “While the local fires are reflected by spikes in the OB-OA, the regional fires are represented by longer periods of elevated OB-OA concentrations.” The OB-OA spikes occur at times when we visibly observed fires from the field site. Our argument for the rapid conversion of OB-OA to OOA is that most of the spikes in the OB-OA are also associated with spikes in OOA (Pg 19650). The spikes in OOA are also consistent with other olive branch burning emissions aiding in the formation of OOA. We have revised this part of the manuscript to take this possibility into account. It now reads:
“We note that the spikes likely associated with the burning of olive branches are also

visible in the concentrations of OOA. This is consistent with gaseous emissions from the burning of olive branches aiding in the formation of OOA and with the rapid conversion of fresh OB-OA to OOA."

Outside of the period with spikes (pg. 19653) OB-OA can be elevated in air masses from essentially all source regions, suggesting the presence of regional fires. This is consistent with the fact that olive wood is burned throughout Greece and the Balkans during this time of the year. We have slightly rewritten the first sentence of that paragraph to avoid confusion. It now reads:
"Most of the fires influencing the observed OA are not local."

- Pg 19654 line 22: "highly correlated" The R2 values do not imply a high degree of correlation, I suggest removing "highly".

We removed "highly" in the revised manuscript.

- Pg 19657: top paragraph: Was m/z 28 excluded from the PMF? No mention is made but the m/z 28 in the figure is derived from m/z 44 in the fragmentation table as far as I understand it.

The organic signal at *m/z* 16, 17, 18 and 28 are all derived from *m/z* 44 in the fragmentation table. We have used the standard way to address this by multiplying the error estimates of all five fragments by sqrt(5) (Ulbrich et al., 2009). This decreases the weight of these fragments in the calculation of the PMF solution. We have added this information to section A.1 of the appendix in the revised manuscript.

- Pg 19673: It would be good to show a shaded region representing the range of particle size distributions observed - possibly using the standard deviation of the number at each size.

Shaded regions representing one standard devision of each size have been added to

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the figures in the revised manuscript.

- Pg 19675: The m/z 28 is equal to m/z 44 because it is set to be equal in the fragmentation table. This needs to be made clear.

We have added a comment regarding this in the revised manuscript.

Response to Referee 2:

The value of this paper would be substantially enhanced if the authors put their results into a broader context, i.e. how their results compare with those obtained at other studies on organic aerosol. A few questions that the readers might be interested in knowing: 1) how do the OA (and EC) levels measured here compare with those in continental Europe, or those in more polluted sites, or those in even more remote environments? 2) how about the contribution of OA to total submicron particulate matter here and elsewhere? 3) there are many ways by which OA can be classified, even based on AMS data alone. How do these results compare with classifications made by other methods? 4) where do these data lie in the f_{43}/f_{44} "triangle" as compared with what has been observed at other field sites and in laboratory experiments? The authors could write a short sub-section to address these questions or, at the very least, spent a paragraph on this issue.

We have added a sub-section addressing some of these questions to the revised manuscript: “3.4 Comparison to measurements at other sites”. Regarding other ways in which OA can be classified: we tried the approaches of Ng et al. (2011) to classify the OA into HOA and OOA based on the AMS composition alone. However, as we note in the manuscript, the results are not sensible (HOA concentrations < 0) suggesting that these estimation methods are not appropriate for our data, probably at least partly due to the very low concentrations.

We have also added a figure to the revised manuscript, showing our data in the Ng et al. triangle. The FAME-09 OOA falls within the triangle. The bulk composition does not fall within the triangle due to the presence of the other OA components (Amine-OA and OB-OA).

The paper Pirikdas et al. (2011) referred to in section 3.2 seems to be missing from the references list. The authors should check out the reference list is complete and updated.

We have confirmed that this paper is in the list of references and have updated the list.

Response to Dr. Ge:

(1) The amine-OA factor shows a characteristic m/z 58, most likely C3H8N+, which is associated with trimethylamine, TMA (C3H9N). m/z 86 can be C5H12N+ (can come from TEA and DEA salts). This can be verified from a number of ambient studies (many of them are from ATOFMS, see lists in our recent review: Ge et al., Atmospheric Environment, 2011, 45, 3, 524-546). TMA is the most common and abundant amine in the atmosphere, with marine emissions as an important source. Although in this study, the authors found that amine-OA is not linked to sea salt, it is possible that it is a secondary OA factor. Based on thermodynamic equilibrium, it is possible that gas phase TMA (probably abundant in the sampling site near the ocean) could transformed into particulate aminium salt, and this transformation is favored by conditions of cold temperatures and high RH (see Ge et al., atmospheric Environment, 2011, 45, 3, 561-577). This is somehow in consistent with the authors' finding that amine-OA peak during night and abundance of clouds.

We have added a comment regarding the possible transformation of TMA into aminium salt, and the appropriate references, in the revised manuscript.

(2) A recent study for TMA particles from ATOFMS by Rehbein et al (Environmental Science and Technology 45 (10), 2011, 4346-4352) also verified this assumption.

The findings in this study are consistent with our suggestion that the presence of the Amine-OA may be associated with cloud processing. We have added a reference to this study in the revised manuscript.

(3) From AMS, Sun et al. (Atmos. Chem. Phys., 11, 1581–1602, 2011) also identifieda nitrogen-rich factor with a unique peak at m/z 58 from C3H8N+ during the NYCcampaign (near the ocean).

We have included a reference to this work in the revised manuscript.

(4) The amine-OA factor is non-volatile. Can the authors provide the correlation of this amine-OA factor with SO4? Sulfate is the major inorganic species in the aerosols (correct?), it is possible that TMA is associated with SO4. Although in (Ge et al., Atmospheric Environment, 2011, 45, 3, 561-577), the formation of TMASO4 is not predicted due to unavailable data, it is likely an non-volatile species similar as (NH4)2SO4.

As noted in Table A2, the Amine-OA factor does not correlate significantly with SO_4 (R^2 = 0.05), nor with the other ancillary data.

(5) Amines have been found to play important role in new particle formation (more efficient than ammonia, there are a number of papers recently, for example about TMA, see Erupe et al., Atmospheric Chemistry and Physics 11 (10), 2011. 4767-4775). Is there any correlation of the amine-OA factor with nucleation mode particles?

As noted in Fig. 9 and the text, Amine-OA concentrations did not correlate with SMPS number concentrations (which are dominated by smaller particles). Furthermore, no nucleation events were observed during the first 5 days of the study when Amine-OA concentrations were high (Fig 5). This lack of correlation could be due to the fact that

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nucleation mode particles only comprise a small fraction of the mass which cannot be detected by the AMS. In our other forthcoming publication (Pikridas et al., 2012) we find and discuss that nucleation events at Finokalia may be associated with amines.

(6) The OB-OA factor is not like the BBOA factor identified from other studies. Is it possible to correlate the OB-OA mass spectra with BBOA and HOA factors (sincethis OB-OA also has significant contributions from m/z 55 and 57) from other studies, also with ones for the particles directly emitted from Olive tree branches burning (if available)? It maybe interesting to see the difference.

The correlations of OB-OA with standard HOA and BBOA spectra are low. For example, the correlation coefficient between OB-OA and the average HOA and BBOA mass spectra suggested by Ng et al. (2011) are 0.17 and 0.09, respectively. As noted in our response to referee 1 above, a source mass spectrum of olive wood burning OA is, unfortunately, not yet available. When it becomes available we will test the correlation with the OB-OA derived from ambient measurements.

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