

I thank the authors for the replies and the work they've put into it!

Thank you again for taking the time to (re)examine our manuscript. Your input and opinions are appreciated. We have decided to remove the discussion on the refractory OM. As you pointed out, with the available information, there are too many uncertainties to make a solid conclusion. We have addressed each of your additional comments below.

Nevertheless, the case presented for the refractory OM is still not convincing. The explanation provided does not exactly rule out the possibility of the overload by the sea salt. Indeed, concentrations up to $100 \mu\text{g m}^{-3}$ or higher can be measured by the instrument, but these refer to flash vaporising species. So, in normal conditions, where mass concentration is dominated by the non-refractory flash vaporising species, the instrument can measure such high concentrations, but it has never been shown that it is similarly capable of measuring such high concentrations of slow vaporising species. Quite on contrary. The fact that background (filter) OM did not show significant changes over the course of the campaign (Figure R1) does not exactly point to the lack of the overload (sea salt m/z 's would be more applicable, like the background signal of NaCl at m/z 58 and Na at 23, to see the overload issue),

Although there are uncertainties in interpreting the time series of the missing mass, and the hypothesis behind the attribution of this missing mass to organic matter, we believe that the ACSM measurements do not suffer from overloading of the instrument and provide additional information to back-up this discussion (also now included in the paper). First, the total concentrations measured by the SMPS simultaneously to the ACSM were on average $1400 \# \text{cc}^{-1}$ (75% were below $1600 \# \text{cc}^{-1}$) which is very close to ambient concentrations that can be found in the Mediterranean atmosphere. Second, in the figure below we show the time series of the background signal at m/z 58, in Figure a) the variation of the m/z 58 is shown as a function of time. We observe that this signal varies with the total mass loading but does not increase progressively over time. In b) and c) two zero particle periods are shown from the start and the end of the campaign. The filter periods show that the zero particle periods did not become progressively higher from the start to the end of the campaign.

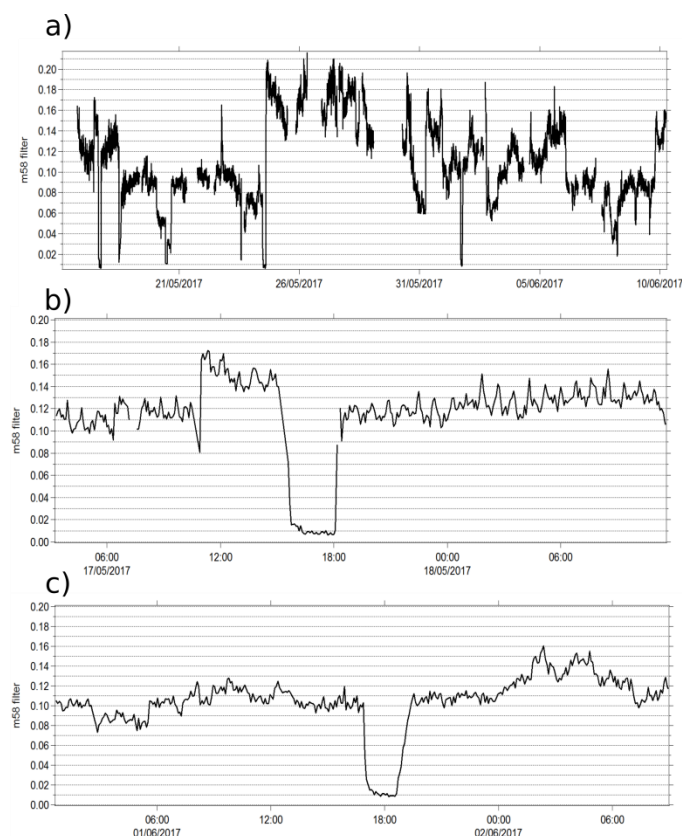


Figure 1 Time series of the filter m/z 58 over the a) whole time period, b) over a filter period at the start of the campaign and c) at the end of the campaign.

We have added the following text to the discussion in Section 3.1 (lines 380-387 in the current version):

« We ruled out the possibility that the high fraction of inorganics in the SSA led to an accumulation of refractory or semi-refractory material on the vaporizer and a corresponding decrease in the ability to measure non refractory material by examining the background (filter) signals. Figure S11 shows the background signal at m/z 58 (NaCl^+) as a function of time; this signal varies as a function of total mass loading but does not progressively increase over time. Similarly, particle free sampling periods at the start and the end of the field campaign show that m/z 58 background levels dropped to comparably low values. Therefore, we conclude that overloading of the ACSM by refractory, or semi-refractory slowly vaporizing, material did not occur and the missing mass is due to increased refractory content. »

but, actually, it shows that there was no significant amount of refractory OM. E.g. if refractory OM contribution is so much higher in the second part of the campaign would it not manifest in the higher background OM concentrations? But now, the OM behaves exactly as SO_4 for the part when refractory OM is not anticipated and the part where it is?

We assume that by refractory OM you mean slowly vaporizing OM. We agree that the refractory mass cannot be unambiguously attributed to organic matter and have removed the discussion on the refractory OM.

Moreover, looking at figures 3, S3 and S13, I struggle to see the coherent picture. Why S3 has fewer points for filter than S13? E.g. S13 has filter OM data since 16th May, while in S3 filter points start after 19th?

These three figures are updated, to include only data points from the 17th onwards. Prior to this period our Airbeam values were unstable

Big emphasis is attributed to the discrepancies between ACSM and Filter/DMPS at the end of the campaign, however, there are similar if not larger discrepancies between filter and ACSM OM at the beginning of the campaign (16th-21st May) and these are not reflected in the volume comparisons. The filter and ACSM volumes seem to agree for the period where Filter-ACSM OM disagrees by a lot (16th-21st May). While looking at Figures 3 and S3, it seems that ACSM volume is larger than DMPS volume for the period where ACSM OM is much lower than the filter OM (19th-20th May)?

We are aware of this discrepancy, where the AMS volume comparisons are similar at the start but that the organic aerosols do not agree with the filters. However, the OM concentrations are only a small part of the total mass so we do not think that this would necessarily impact the total volume concentrations.

Also, the 'oversampling' (~19th May and ~25th-29th May) by ACSM is not discussed anywhere, which is now on the order of the 'under-sampling' later in the campaign (after the 1st June). The latter is attributed to the 'refractory' OM, so how do authors explain the former (oversampling)? Is that just uncertainty (both) due to density assumptions?

An incorrect calibration value was introduced when revising these two figures in the last version of the paper. This has been corrected, and the difference between ACSM and SMPS volumes during the periods of 19th May and 25-29th May are within the uncertainties of the measurements, (including, as the reviewer suggested, the uncertainty on density).

All these would make me very cautious in attributing the discrepancies between ACSM and DMPS to the refractory OM. It is a bit like cherry picking – authors attribute under sampling to refractory but ignore oversampling. Also, ignore the fact that high OM discrepancies between filter and ACSM still lead to good agreements in volumes at the first part of the campaign...To me, the explanation of

different sensitivity to sea salt for distinct water composition and different sea salt ions, would be much more feasible explanation than the refractory OM.

The volume/volume discrepancies trends do not coincide with OM composition (neither from filters as in WSOC/WIOC trends nor PMF as in trends for different factor contributions), which really makes the refractory OM explanation quite unlikely. Also, the ssSO₄ behavior mimics that of 'refractory' OM, which points again to the sea salt rather than OM. More so that OM is more oxidised for the later part of the campaign.

The reviewer has made a number of valid points. Although we have kept the discussion comparing the DMPS with the ACSM and state that there is missing mass, we have removed all discussion of this missing mass being attributed to refractory organic fraction. We have replaced the observed relationship between the refractory organic matter and POC with the observed relationship between the offline filter OM and the POC.

The following text is added (lines 592-596 in the current version:

« We initially examined the relationship with offline filter organic measurements of water insoluble and water soluble organic matter fractions (FWIOM and FWSOM, respectively) with POC (Eq. 2 and 3). These showed positive correlations of both WIOM and WSOM with POC measurements.

$$\text{FWSOM} = 0.002 [\text{POC}] - 0.0393 \quad r = 0.55, n = 19, p < 0.01 \quad \text{Eq.2}$$

$$\text{FWIOM} = 0.002 [\text{POC}] + 0.031 \quad r = 0.54, n = 12, p < 0.05 \quad \text{Eq. 3} \text{ »}$$

On a minor note:

Figure S3 b) is difficult to read as points are not properly represented in the legend. Which ones are the ACSM and which ones are the Filter?

The figure is updated.

Also, density of 2.165 is applicable to sea salt, but not other inorganic species. E.g. NH₄ (line 350 of the revised manuscript). Presence of NH₄ would mean the presence of nss-SO₄ in addition to ssSO₄? Were these significant or on the level of noise? Do not include them in the calculations if the latter.

The NH₄ and NO₃ are close to the zero during this campaign, so we don't think that this would matter. However, we recalculated the volume concentration without contributions from these species. The text and figures are updated.

Reply No 9: 30% noise is very high; this is not typical for PMF. Does that 'noise' have meaningful time trend or mass spectrum, could it be some unresolved OM factor?

No, we believe that this high noise was a result of low mass concentrations and low temporal evolution of the mass spectra. It may be some unresolved OM but the contribution remained constant throughout the sampling.

Reply 13: 'In addition, during sampling the ToF-ACSM was run with a 2 min filter/8 minute sample. When sampling with long times between filters, any drift in sensitivity can result in a difference signal that is an artefact.' – I would not expect any significant drift in sensitivity for 8 minute period? Where can it come from? Change in SEM, filament? They would not occur on the 8 minute time scale. Provide reference or do not refer to it in the manuscript.

Unfortunately there is no reference for this observation. This was concluded from direct observation and discussion with other co-authors and Aerodyne. The sensitivity of the detector in the ToF-ACSM is quite temperature dependent and we do see fluctuations of several percent over a few minutes in response to room temperature changes. Unfortunately, this can cause an artefact at m/z 's that have high backgrounds due to air or water.

Some typos and missing spaces should be corrected, especially for the newly added text.

We have read over the manuscript and have corrected these errors.