

Interactive comment on “Organic carbon and non-refractory aerosol over the remote Southeast Pacific: oceanic and combustion sources” by L. M. Shank et al.

Anonymous Referee #2

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This paper presents the analysis of AMS data collected over the Pacific Ocean during multiple campaigns and compares the data with other previously published studies. Attempts are made to characterise the elusive marine organic matter, something that little data exists on in the southern hemisphere. Given the interest in global aerosol composition, these results are highly relevant, especially in comparison with other studies. However, I do think the authors go a little too far in their conclusions, specifically with their implication that the other studies were tainted. In my opinion, this is not adequately supported and the authors must address a number of points in this line of discussion before making these inferences. In spite of this, there is still reasonable science in this paper and I recommend that this paper is published subject to the following comments:

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General comments:

Perhaps the most glaring issue with the paper is that the authors make extensive use of the org/so₄ ratio in their analysis, but do not provide any kind of basis for this approach in the methodology. Given the mechanistic differences in the sources of both species, it must be introduced properly and the approach justified. There seems to be an implied assumption that the relative production of particulate organics and sulphate could be expected to be constant between geographical regions, but this assumption is unsafe, given the number of current unknowns associated with both production routes. There could be variations associated with all kinds of factors including biota, meteorology and atmospheric chemistry. The authors need to discuss the basis for this assumption and caveat where appropriate.

A related issue is the notion that organic matter and sulphate have a common source (stated at P16905, L24). The nss sulphate is known to be secondary in nature, whereas the primary vs secondary nature of the organic matter is currently a matter of debate. Even if the organics are assumed to be secondary, there is nothing to say that its precursors would originate from the same stage of a plankton bloom as DMS, be emitted in consistent relative quantities, or that SOA would be formed on the same timescale as sulphate in the atmosphere. These issues should be discussed in the context of the sulphate/organic ratios discussed above.

The authors should be wary of making too many implied points, especially when making comparisons with other projects. An example is on page 16906 at the end of section 4.1, where they seem to be insinuating that a high org/so₄ could be taken as indicative of the influence of biomass burning at Mace Head. In this instance, I do not consider this to be justifiable, partly for the reasons stated above but also because such a strong biomass burning influence would be very evident in the BC and CO data. In general, the authors should be more definitive about what conclusions they are making and what evidence they are basing these on.

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The comparison of the organics with the SP2 black carbon under low loading conditions is very interesting, as this will not suffer from positive artefacts that beset filter-based measurements such as weakly absorbing or scattering particles. However, an unavoidable point is that the SP2 has issues of its own, particularly the detection limit with respect to BC core size (or overall scattering size, depending on the triggering method) that may decrease the overall sensitivity of the measurement, depending on the size of the particles. In this context, appropriate attention to technical differences in the instruments should be included when comparing the BC filtering methods, as this could partly explain the difference in choices of threshold values. In general, much more technical detail should be provided on the SP2 and its operation. Specifically, the detector configuration (whether PMTs or APDs were used), the calibration method used and the triggering method used (i.e. triggering on scattering or incandescence and the detection limit this entails). These details vary between units and users and could fundamentally affect the nature of the data.

The authors need to cover more of the detail of the different methodologies when comparing organic data of the different studies. This isn't as much of an issue when looking at other AMS datasets, but there may be very fundamental differences when comparing with studies using offline analyses, particularly with relevance to issues such as collection efficiency and lens transmission. The same applies when comparing different BC methods. Ideally, this information should be included in table 1.

Specific comments:

I would recommend reconsidering the title of this work as the biomass burning aspect seems to be supported by very circumstantial evidence (see below). The running title could also do with revising, given that the AMS measures organic matter (as opposed to organic carbon).

The authors do not discuss what inlets are used on the different platforms. It is vital that they specify what inlet system (as distinct from the aerodynamic lens) was used

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for the C-130 in particular, as this can have an effect on the aerosol measured. Also, the authors must also state what humidity the particles were sampled at in each instance, as this is known to affect the collection efficiency, particularly of sea salt based particles.

P16901, L26: The authors should account for the fact that organic matter has a lower effective density than sulphate when measured using the AMS (Cross et al., *Aerosol Sci. Technol.*, 41, 343-359, 2007).

In the interests of fairness, care should be taken when presenting some of the other works. In some cases (albeit not that of O'Dowd and coworkers), the data presented as 'clean' is specifically within the context of the lack of local influences, with long-range transport not being discounted. In this context, presenting these works as previous characterisations of 'background marine' is slightly disingenuous.

Given the general paucity of data in the southern hemisphere and the similarity of the techniques, Zorn et al. (*Atmos. Chem. Phys.*, 8, 4711-4728, 2008) is notable in its omission from the comparisons. The authors should consider including this study.

While $m/z=60$ can be a useful tracer, it is not unambiguous. In addition to biomass burning products such as levoglucosan, $C_2H_4O_2$ can be a minor fragment of many other organic species. If the authors wish to infer the relative importance of biomass burning, they should really compile statistics on its fractional contribution to the total organics rather than the absolute signal, because I currently find figure 8 to be very unconvincing in this regard.

The interpretation of the Van Krevelen plot on P16908 is a little confusing. How is a high organic to sulphate ratio consistent with a non-local source? Also, how is a high H/C indicative of a local source? The authors should state their reasoning and assumptions more clearly.

The ordering of the discussion section is a little curious in that section 4.3, which deals

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with technical issues, occurs partway through. To me, it would make more sense to have it earlier.

P16909, L14: I would contend that the 'worst case' is if the organics were externally mixed with the sulphate and had a CE of substantially less than 0.5. This could be the case if the phase of marine organics is a dry solid, in contrast to those seen in continental environments. If true, the upshot of this would be that the AMS would not be measuring all of the organics present and the org/so4 ratios reported here are too low.

P16909, L24: The approach of comparing the AMS with the OPC to test the presence of coarse organics is flawed. Firstly, it relies on the assumption that the organic fraction of sea salt is constant, which is not necessarily true. Secondly, if sea salt organics were present but a sufficiently large fraction was missed by the AMS (which is likely), a correlation would not necessarily be expected because it may be that a different organic particulate (with a different temporal trend) in the accumulation mode would dominate the AMS data. This would mask what little correlation was caused by the coarse-mode organics. Therefore, the lack of correlation represents nothing more than a null result in this regard.

Technical corrections:

Throughout the manuscript, the authors refer to organic matter as 'Org'. It would be much better to use 'OM', as this is a more universally used term.

P16898, L1: Technically, the role of natural aerosols in the earth's climate should not be described as a 'forcing' if the IPCC definition is used. Suggest changing to 'processes'.

P16898, L27 (and elsewhere): 'Scavenging' is often used to describe specifically the process by which interstitial black carbon is incorporated into cloud droplets. Wet deposition as a whole involves other mechanisms in addition to scavenging (activation and washout), so I would suggest using a more general term to describe the loss mechanism.

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P16900, L12: Drewnick et al. (2005) is an inappropriate reference for the HR-TOF-AMS, as this described the earlier C-TOF-AMS. Suggest DeCarlo et al. (2006) or Canagaratna et al. (Mass Spectrom. Rev., 26, 185-222, 2007) instead.

P16900, L25: The specific changes made to the fragmentation table should be stated.

P16908, L9: Do the authors mean 'lower'?

P16922: Allan et al. (2004) used a VOC tracer (MTBE) to screen for local influences, not back trajectories.

P16926: I feel that having the dates at angles makes the figure difficult to read.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 16895, 2011.

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