

***Interactive comment on* “Ship impacts on the marine atmosphere: insights into the contribution of shipping emissions to the properties of marine aerosol and clouds” by M. M. Coggon et al.**

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We thank the reviewers for helpful comments. Please see responses below.

Response to Anonymous Referee #1

Specific Comment 1

Given that the exact chemical source of the m/z 42 and 99 ions is not identified, I would

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be a little more conservative with the conclusions, especially seeing as these have not generally been reported in previous studies and shipping emissions are already known to be highly variable. I am not suggesting that the apportionment work in this paper be taken out, but rather than propose it as a universal tracer, I would say that this warrants further investigation to assess their suitability as tracers.

Author Response to Specific Comment 1

We agree that the variation of m/z 42 and 99 cannot be linked to a specific source using the data reported in this study. We have noted in the discussion and conclusions that the exact chemical source of m/z 42 and 99 remains unknown and requires further investigation. We also believe that elucidating this chemical source might help to better understand the chemical transformation of shipping emissions in the marine atmosphere.

Specific Comment 2

The authors should give more extensive and quantitative examples from the literature (beyond McInnes et al.) of what could be considered 'clean marine'. While this is covered in table 1, the results are presented in a purely qualitative manner, so are not much use in this context. It should also be noted that a number of studies have reported organic matter in clean marine environments in addition to sea salt and DMS-derived aerosol.

Author Response to Specific Comment 2

We have extended our discussion of what could be considered “clean” in Section 3. We have provided examples of studies that have observed varying degrees of aerosol mass originating from remote marine environments. Our measurements are most similar to McInnes et al. (1996) and Phinney et al. (2006). We acknowledge, however,

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that studies such as those by Ovadnevaite et al. (2011) have observed primary organics that may be linked to biological origins other than MSA. We note that the “clean” condition is highly variable and can be affected by a number of processes including biological activity and meteorology.

Technical Comment 1

Page 14408, Line 19: The term ‘LV-OOA’ was coined in Jimenez et al. (2009). Ulbrich et al. referred to this component as OOA-1, as no direct volatility data were available for that study.

Author Response to Technical Comment 1

This has been corrected to reflect that LV-OOA was first used by Jimenez et al. (2009).

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Response to Anonymous Referee #2

Major Comment 1

P14401, line 24 to P14402, line 4 - This is an interesting and important observation, but does Figure 4 only mean what you imply? The mass concentrations of organics are comparable to those of sulphate (in and out of cloud) as shown in Figure 2. Therefore, if I interpret this correctly, the org:so₄ ratio of 1.5-2.0 associated with LWC implies much more organic produced in cloud than sulphate - if that is the only process leading to the result in Figure 4. That would be an extraordinary conclusion. This needs a more comprehensive discussion. Are there other processes that may contribute to your result in Figure 4? E.g., can deposition from clouds perhaps skew the ratio of organics to sulphate?

Author Response to Major Comment 1

Ultimately, the purpose of presenting Fig. 4 is to show that cloud processing might have played a role in affecting aerosol composition (and likewise, shipping emissions). However, we agree that other processes may have affected the organic:sulfate ratio. Above the cloud tops, the free tropospheric aerosol exhibited high organic loading. Had this aerosol been entrained into the clouds, this would have certainly affected the organic:sulfate ratio of aerosol at higher altitudes. Furthermore, it's possible that aerosol with higher amounts of sulfate activated in cloud, leaving interstitial aerosol with higher organic:sulfate ratios. Though later in the paper we discuss new organic markers (*m/z* 42 and 99) that form as a result of cloud processing, we do not intend for Fig. 4 to suggest that this is the only process that would lead to an increase in organic:sulfate ratio with altitude. We are primarily interested in illustrating that cloud processing likely played a role in affecting aerosol chemistry during the E-PEACE campaign.

We have re-written this section to reflect this discussion. We have elaborated on other

processes that could affect the organic:sulfate ratio besides the chemical formation of low volatility organics.

Minor Comment 1

P14395, lines 14-15 – do 42 and 99 really dominate the organic mass or just stand out? It is difficult to tell the exact m/z from Figure 10.

Author Response to Minor Comment 1

We've adjusted Figure 10 to clearly illustrate m/z 42 and 99 in the mass spectra of perturbed cloud residuals. On the basis of this revised figure, we see that m/z 42 is the prominent mass in the spectra. Mass at m/z 42 comprises 14% of the total organic mass whereas m/z 99 comprises 3%. We've added these numbers into the abstract and do not imply that these masses dominate the spectra.

Minor Comment 2

P14398, lines 17-19 – Perhaps say something like “However, there are relative differences between periods of low and high mass cns”.

Author Response to Minor Comment 2

We have made this adjustment to clarify the sentence.

Minor Comment 3

P14398, line 30 – This is the first and only mention of the “sub-isokinetic inlet”. Some further discussion is needed.

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Author Response to Minor Comment 3

We have included a reference that has characterized the Twin Otter aerosol inlet and note that under the airspeeds performed in this study, no appreciable loss of particles is observed below $3.5 \mu\text{m}$.

Minor Comment 4

P14399, lines 9-11 – wind speed can also affect DMS ventilation.

Author Response to Minor Comment 4

This is a good point, especially since we only discuss particle sources and not particle losses. We have included this effect in our discussion. We also note that particle losses due to deposition and evaporation may also affect aerosol concentrations.

Minor Comment 5

P14399, lines 26-27 – many components of the marine aerosol can be categorized using the AMS, but not sea salt.

Author Response to Minor Comment 5

We have changed this sentence to note that only non-refractory components can be consistently measured using the AMS.

Minor Comment 6

P14401, lines 8-9 – Yes, it may be indicative of cloud processing, but does it have to be? Can that sort of distribution not also form from other reasons: e.g. take the ship distribution, dilute it and mix it with an aged marine aerosol or an aged anthropogenic

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aerosol?

Author Response to Minor Comment 6

It is certainly true that the 200 nm mode could be affected by other sources. During the E-PEACE campaign, we did not observe primary emissions with modes much greater than 100 nm (see fresh ship distributions, Figure 3 bottom), and therefore we had not considered dilution processes as a possible formation mechanism. However, this is certainly not representative of all shipping emissions (e.g., Phinney et al. 2006 observed organic modes with vacuum diameters of 150 - 200 nm in samples affected by direct ship fumigation). We have corrected this sentence to reflect the fact that accumulation from cloud processing is not the only process that could lead to this mode. We have included some discussion as recommended by the reviewer. In the remainder of the paper, we no longer refer to this mode as being strictly “cloud-processed.”

Minor Comment 7

PP14401, line 24-25 – Do the products of aq-phase oxidation have to remain in the particles? E.g. could not oxalic acid volatilize.

Author Response to Minor Comment 7

This comment ties in with Reviewer 2’s major comment. This is a good point, since organic production is a function of cloud water pH. At higher pH, oxalic acid is produced efficiently from precursors as a result of higher uptake and more ideal reaction conditions (Sorooshian et al. 2007). However, if oxalic acid were to react further to regenerate higher volatility species, these products could be lost from the particle upon drying. We’ve restructured much of this section so that it is clear that only low volatility products remain in the particle upon drying. However, we note other processes that can lead to the accumulation or loss of organics.

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Minor Comment 8

P14402, lines 8-12 – You say that the Ca, Mg and K are representative of the total metal content, but then say you assume they originate from soluble species. I think this paragraph could be made a little clearer.

Author Response to Minor Comment 8

We agree, this can be made clearer. We intended to present cloud water chemistry in a similar fashion as Straub et al. (2007) and Benedict et al. (2012) (which were studies performed off the California coast) so that our results could be easily compared. In those studies, ion species were measured using ion chromatography. In our study, we used ICP-MS, which measured total metal content rather than soluble species. In order to calculate concentrations in terms of normality, we assumed that the species we measured came from highly soluble sea salts. Furthermore, we assumed that these species were in their most stable valence state (for example, magnesium would be present as Mg^{2+}). We have clarified this point and used magnesium as an example to illustrate our assumptions.

Minor Comment 9

P14403, line 11 (section header) – “background” or clean? I like your earlier discussion of the issues with defining a background aerosol, but the use of ‘background’ here seems like a violation.

Author Response to Minor Comment 9

This was an oversight and has been corrected. The term “background” has been removed.

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Minor Comment 10

P14403, lines 20-21 and Figure 6 – Is the difference between 0.23 and 0.27% significant, and is there any further interpretation of the comparison of critical supersaturations mean when you have 90% of the total activated in one case and only 60% in another?

Author Response to Minor Comment 10

In the discussion about CCN data, we calculate the supersaturation so as to be as thorough as possible, however we don't believe that a difference of 0.04% is significant. What is more striking, as Referee 2 pointed out, is that a higher fraction of particles activate during a perturbed flight than during a clean flight. This is most interesting given that perturbed flights have much higher loadings of sulfate and only a slight difference in particle size. While we can't be certain that sulfate is the primary factor responsible for the difference in increased particle activation, Fig. 6 seems to indicate that higher CCN activation is observed under perturbed conditions, which is consistent with previous studies (e.g., Langley et al. 2010).

Minor Comment 11

P14404, lines 15-16 – do you mean “we show that increased sulfate...”?

Author Response to Minor Comment 11

Yes, this is a more concise statement. We've adjusted this sentence according to this comment.

Minor Comment 12

P14404, lines 17-18 (and line 22) – Certainly increased sulfate will lower the activation

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threshold, but what about the carbonaceous component? For example, Langley et al (2010) showed that the increased CCN number concentrations were better correlated with ship emissions of organics.

Author Response to Minor Comment 12

Yes, Langley et al. (2010) showed that CCN number concentrations were well correlated with organics, but only during periods of ship fumigation. Langley et al. (2010) ultimately conclude that sulfate and MSA (not organics) controlled CCN activation. This appears to be consistent with our results. Included in our response below is a plot showing the correlation of CCN number concentrations at 0.7% supersaturation with sulfate and organic, respectively. We note that this plot is not size-resolved. Over the entire campaign, we find that CCN concentrations are better correlated with sulfate (bottom left, $R^2 = 0.3$) than with organics (top left, $R^2 = 0.005$).

Similar to Langley et al. (2010), we also observed good correlation between organics and CCN concentrations during periods of ship fumigation. In this study, periods of high sulfate (i.e., perturbed conditions) imply ship fumigation. If we consider perturbed conditions (sulfate $> 2 \mu\text{g m}^{-3}$), we find that CCN number concentrations correlate well with organics (bottom right, $R^2 = 0.46$). However, during perturbed periods, organics also correlate very strongly with sulfate (not shown, $R^2 = 0.8$). Langley et al. (2010) observed similar behavior and concluded that the organic particles likely acted as condensation sites for sulfur species, which then leads to an increase in the number of CCN-active particles. In Fig 6., we see that higher sulfate leads to an increase in the fraction of particles that activate. If we color these markers by organic, we do not see the same behavior. Thus, we feel that our results are consistent with Langley et al. (2010) and suggest that the sulfur content of the aerosol played a larger role in lowering the activation threshold than organics.

Minor Comment 13

P14405, line 13 – concentrationS.

Author Response to Minor Comment 13

This is now corrected.

Minor Comment 14

P14408, lines 18 and 22-24 – Phinney et al. (2006) showed AMS spectra of ship emissions.

Author Response to Minor Comment 14

We've included Phinney et al. (2006) as a reference regarding the mass spectra of marine aerosol and direct ship emissions.

Minor Comment 15

P14410, lines 7-10 – You may be overstating the “cloud-processed mode”. What evidence do have that the 77 nm mode was cloud processed, since the skies were clear?

Author Response to Minor Comment 15

After considering previous comments, we agree that we cannot definitively categorize this mode as being “cloud-processed.” In general, we are interested in illustrating that RF27 had two modes, but that the second larger mode did not peak at the same diameter as the other flights illustrated in Fig. 11. While this may or may not be due to cloud processes (or the lack thereof), it does seem to imply that the particles had not grown as a result of cloud processing. This, along with the lack of liquid water content from vertical soundings, seems to suggest that cloud processing was not a major contributor

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to the mass measured by the AMS. We have corrected this sentence and elaborated on our rationale about why we believe that cloud processing was unlikely contributing to the aerosol during RF27.

Minor Comment 16

P14410, lines 26-28 and P14412, line 24 – It is curious that only these two fragments stand out, the difference of which is 57. Do you see a significant oxygenated fragment in your Hi-Res m/z 57?

Author Response to Minor Comment 16

We agree that the prominence of the masses at m/z 42 and 99 is very interesting. However, the mass at m/z 57 is predominantly due to the reduced ion $C_4H_9^+$. We do not believe, however, that m/z 42 and 99 are the only masses that are linked to the cloud-processed ship emissions. It is possible that aged masses, such as m/z 44 and m/z 43, are also prominent in these sources. However, given that typical aged masses are prominent even in the absence of aged ship emissions (see Fig. 10), it may be that the signal from these masses does not stand out once an aged ship emission has been detected. While we could perform PMF on these measurements to determine if other masses can be linked to m/z 42 and 99, we believe that this is beyond the scope of this paper. Ultimately, we believe that these masses are unique markers for detecting cloud-processed ship emissions. We have added to this discussion to indicate that other masses (such as oxidized masses at m/z 44) might also originate from cloud-processed ship emissions, but that we focus on m/z 42 and 99 due to their unique presence in cloud-processed ship emissions.

Minor Comment 17

P14411, line 12 – this may be another suggestion of aq-phase processing.

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Author Response to Minor Comment 17

Yes, the correlation of m/z 42 and 99 with sulfate could also be an indication of aqueous-phase processing. However, we think that it might also imply that m/z 42 and 99 are linked to shipping emissions, given that the sulfate measured during this study was primarily linked to ships. We've included a statement that implies that either process could be responsible for the correlation.

Minor Comment 18

P14411, lines 24-28 – but only for cloudy conditions?

Author Response to Minor Comment 18

Yes, we state on P14411, line 22 that the metric we propose only applies under cloudy conditions.

Minor Comment 19

P14413, line 19 – wording – it is not the evaporation that produces the m/z 42 and 99.

Author Response to Minor Comment 19

We've corrected this sentence so that it is clear that m/z 42 and 99 result from cloud-processed ship emissions.

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