

***Interactive comment on* “Contributions from DMS and ship emissions to CCN observed over the summertime North Pacific” by L. Phinney et al.**

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Received and published: 9 September 2009

Continued from Part 1.

24: Table 1 and corresponding text: The table and text only show that higher MSA mass corresponds to a higher number concentration. More meaningful would be a comparison of MSA mass with the fraction of activated particles, i.e., CCN/CN.

This is a great suggestion, the ratio illustrates the influence more clearly. Table 1 and corresponding discussion has been changed to include the CCN/CN ratio (it is approximately 70% higher in the “high-MSA” case than in the “low-MSA” case, emphasizing our original discussion point). Some modifications to the corresponding text have been made (p321-322):

“Higher mass concentrations of MSA are a marker for DMS oxidation and biogenic sul-

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phate. To investigate the relationship of biogenic sulphate and CCN in this study, properties of the aerosol during times associated with peak MSA concentrations greater than $0.50 \mu\text{g m}^{-3}$ (the 98th percentile value) are compared with those during times when MSA concentrations are lower than $0.50 \mu\text{g m}^{-3}$. Number concentrations of $\text{CCN}_{0.19\%}$ and $\text{CCN}_{0.34\%}$ increase by 30% during times associated higher MSA concentrations (i.e. 20 July and 27 July) over those with lower MSA concentrations (Table 1). At both supersaturations, the fraction of particles activated as cloud condensation nuclei (CCN/CN) is approximately 70% higher during times when MSA concentration is high versus when MSA concentration is lower, and the slope of the sulphate- $\text{CCN}_{0.19\%}$ relationship increases by 45% (the slope of the sulphate- $\text{CCN}_{0.34\%}$ relationship showed no change). Possible explanations for the increase in CCN and slope may include a smaller CCN effective diameter (i.e. the size distribution of CCN is shifted to smaller, more numerous particles) or greater aerosol activation (i.e. particles have the same size distribution, but more of them activate) when MSA is present. Figures 6a and b show the number and volume distributions, respectively, of particles measured during times of high and low MSA concentration, normalized by dividing the dN values by the peak dN value of their respective distribution. The number distribution indicates a relative increase in numbers of particles $>58 \text{ nm}$ (the theoretical activation diameter for sulphate particles at 0.34% supersaturation) and $>86 \text{ nm}$ (theoretical activation diameter for sulphate particles at 0.19% supersaturation) when MSA concentrations are high, and shows that the distribution of particles large enough to act as CCN is not shifted towards smaller sizes. This suggests that the source of the higher CCN/CN ratio is greater aerosol activation, rather than a shifted size distribution. Figure 6b indicates that, though the CCN numbers increase, changes in the volume (=proportional to mass) distribution are not apparent for particles in the activation range. This comparison of number and volume distributions at lower and higher MSA concentrations suggests that the impact of DMS oxidation on CCN in this instance is to increase the number concentrations of CCN active at supersaturations representative of marine stratiform clouds.”

25: Figure 6 and text: Need to explain the normalization process.

Included the phrase “normalized by dividing the dN values by the peak dN value of their respective distribution” in text and figure caption.

26: Also "activation diameter at each supersaturation" assuming what composition?

Changed phrase to:

“The number distribution indicates a relative increase in numbers of particles >58 nm (the theoretical activation diameter for sulphate particles at 0.34% supersaturation) and >86 nm (theoretical activation diameter for sulphate particles at 0.19% supersaturation) when MSA concentrations are high, and shows that the distribution of particles large enough to act as CCN is not shifted towards smaller sizes.”

27: p. 322, line 23: These plots give no indication of mixing state of sulfate and organics only that there was four times more organics than sulfate in this size range.

The plots indicate that there is up to $3 \mu\text{g m}^{-3}$ of $[\text{MSA}+\text{SO}_4]$ and up to $1.2 \mu\text{g m}^{-3}$ of $[\text{Org}]$ in particles 80-90nm in diameter. If the only difference in the plots was that the mass of organics is lower, then the slopes of the lines would be identical and in plot b the dots would simply reside at the lower left end of the plot. The fact that the *slope* of Fig. 7b is twice as high as that of the upper curve in Fig. 7a (stated in line 19) means that for a given increase in the mass of organics there is a greater increase in 80-90nm particles than for the same increase in sulphate mass. Generally, more particles for a given mass may be attributed to smaller particles, but this is not an explanation here because these plots show points for the same narrow size range of particles. Another way to put it: as the particle number goes up, the org/sulphate ratio of these particles goes down. Thus, the particles are not homogeneously mixed in this size range.

The argument is clarified in the text by changing p322 lines 20-26 to read:

“The greater slope means that for a given increase in organic mass there is a greater increase in particle number than for the same increase in $[\text{MSA}+\text{SO}_4]$ mass. Equally,

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as the particle number goes up, the ratio of organic to sulphate mass goes down, indicating that throughout this size range the particles are not homogeneously mixed. Thus, the number concentration of 80-90nm particles is more sensitive to increases in organic mass than to increases in SO_4 +MSA mass. While more particles for a given mass can often be attributed to smaller particle sizes, this is not an explanation here because these plots show points for the same narrow size range of particles (80-90 nm). It is hypothesized that the increase in organic mass is directly related to increases in particles, whereas most of the sulphur mass condenses onto pre-existing particles, which increases the mass concentrations but leaves the numbers of particles unchanged. This hypothesis is investigated here.”

28: p. 324, lines 1 to 3: Why could it not be emissions from the ships associated with the fertilization experiment? Were they not in the region at that time?

Yes, indeed emissions from the ships involved in the experiment could have diffused in the regional circulation and returned to impact our measurements. To avoid this misinterpretation, the word “crossing” on p324 line 3 has been replaced with the word “in”, more clearly acknowledging the potential of our own emissions to impact the measurements.

It is important to note, however, that *direct* emissions from our ships are *not* included in this organic spectrum, as all direct fumigation has been removed from this dataset. Ship influence, including from ships involved in the study, is restricted to emissions that have diffused in the regional circulation and subsequently impacted the measurements.

29: p. 325, 2nd paragraph: "Evolution of the aerosol" is not an appropriate term unless the experiment is Lagrangian in nature.

Here, “evolution of the aerosol” refers to the changing nature of the aerosol measured on July 18, as discussed extensively in the preceding paragraphs. The terms “evolution” and “progression” are used interchangeably in the preceding discussion to describe the changing properties of the measured aerosol, and, as it is not implied

anywhere in the text that the experiment was meant to be Lagrangian, there should be no confusion here.

30: Figure 11 and p. 325: The described interpretation of changes in the size distributions of organics, sulfate, and MSA is not clear when looking at Figure 11. It is stated that during periods 2 through 6, the aerosol was more of an external organic-sulfate mixture compared to the internal mixture observed during periods 5 and 6. What are the modal diameters for each mode of each component during these periods? To me, period 5 looks as externally mixed (if not more) than period 3.

The modal diameters that were not stated in the text are now stated (i.e. Periods I and II are monomodal at 486 nm; Period III is developing a shoulder mode in sulphate at 370 nm corresponding to a shift in the organics distribution to smaller sizes, and developing a mode in sulphate at 150 nm; the shoulder mode at 380 nm remains in Period IV; and in Period V the shoulder mode at 380nm has combined with the dominant mode to make a single mode at 500 nm; finally, in Period VI the monomodal distribution is centred at 500 nm).

31: p. 325, line 15: In the presence of S produced from biogenic and ship emissions...

This line has been changed to the suggested wording.

32: p. 325, 2nd paragraph: There is no direct evidence (such as SEM analysis or tandem DMA analysis) for the statement that "the smaller organic particles from ship emissions act as condensation sites for the sulfate and MSA". Hence, to go on and say that "these observations support the above hypothesis" is unwarranted.

The evidence presented in Figure 11 supports an external mixture of organic and sulphate (based on distinct distributions) followed by overlapping or coincident size distributions of organic and sulphate. We agree that this is not direct evidence of an internally mixed aerosol. However, as in using tandem DMA and SEM observations to determine mixing states, statistics is fundamental to this determination. General

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knowledge of aerosol processes, the many previous observations, and modeling all tell us that the probability that pure organic particles and pure sulphate particles grew to exactly the same size completely independently is extremely low compared to the probability that the particles were mixed to some degree. Hence it is reasonable to state that these observations support the hypothesis; more reasonable than not.

We also demonstrate that the organic mass spectrum is consistent with that of ship exhaust, which makes the point that the most of the organic was not secondary.

The entire complement of evidence presented in Figures 6 through 12 supports our hypothesis. However, in the text, it is a case of stating our conclusion before presenting all the evidence, particularly the evidence pertaining to CCN. Thus, the wording of p325 lines 15-20 has been changed to (starting with a new paragraph at line 15):

“The increase in particle number concentrations shown in Fig. 7c, which occurs largely during this 18 July time period, is attributed to the presence of the organics. These observations lend support to the hypothesis that, in the presence of biogenic sulphur, the smaller organic particles from diffuse ship emissions act as condensation sites for the sulphate and MSA, eventually returning the aerosol to an internal mix of organics, MSA and sulphate. The hypothesis is investigated further below.”

and the final two sentences of the paragraph have been removed (“These observations support the above hypothesis, and the increase in particle number concentrations shown in Fig. 7c, which occurs largely during this 18 July time period, is attributed to the presence of the organics. The organics provide a distribution of small, numerous particles to act as condensation sites for the sulphate and MSA, subsequently activating as CCN at supersaturations typical of marine stratus clouds.”)

33: p. 325 to 326: What is supporting the statement that "the condensation of sulfate and MSA onto the smaller organic particles affects the level of CCN activity"? Based on the data shown in Fig. 10 the first increase in CCN(0.34%) at 04:00 on 7/18 corresponds to a large increase in number concentration and SO₄. How can the organic

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effect be teased out of these data? Also, the increase in CCN(0.19%) is very difficult to see on the scale plotted for the y-axis.

Please see next comment

34: Figure 12: As above, how can the stronger correlation of organics than MSA+SO₄ with CCN for the 7/18 case be attributed to the specific mechanism of condensation of sulfate and MSA on smaller organic particles?

To address Comments #33 and #34:

In Fig. 10, the CCN_{0.19%} is now plotted on the right-hand axis to expand the plot so the increase can be seen.

The statement “the condensation of sulphate and MSA onto the smaller organic particles affects the level of CCN activity” has been removed from this section. Our conclusions regarding the mechanism of condensation of sulphate and MSA onto organics, subsequently activating as CCN, are based on assimilation of the evidence presented in Fig. 10 (time series), Fig. 11 (size distributions), Fig. 12 (CCN correlations with sulphate and organics for different time periods), and Fig. 13 (sulphate mass increasing 2.5 hours after organics). Therefore, statements that discuss the mechanism have been left for later in the results section, after these plots have all been discussed, and in the Summary and Conclusions section, where the analysis presented in each plot can be assimilated.

p325, lines 15-22 now reads:

(begins new paragraph)

“The increase in particle number concentrations shown in Fig. 7c, which occurs largely during this 18 July time period, is attributed to the presence of the organics. These observations lend support to the hypothesis that, in the presence of biogenic sulphur, the smaller organic particles from diffuse ship emissions act as condensation sites for the sulphate and MSA, eventually returning the aerosol to an internal mix of organics,

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MSA and sulphate. The hypothesis is investigated further below.” and Section 3.2.5 now reads:

“In the Monterey Area Ship Track (MAST) experiment, unprocessed diesel emissions were found to be inefficient as CCN due to their hygroscopicity characteristics (Russell et al., 1999), and condensation was found to be the key mechanism responsible for adding sulphate mass to the primary organic emissions. We speculate that a similar process is at work in the marine environment in which we sampled.

Figure 10 showed an increase first in smaller CCN ($\text{CCN}_{0.34\%}$) as small organics increased, followed by an increase in larger CCN ($\text{CCN}_{0.19\%}$) as sulphate and MSA concentrations increased at larger sizes. In Figs. 12a and b, the correlations of organics and of $[\text{MSA}+\text{SO}_4]$ each with CCN are shown for the entire sample period excluding 18 July. In Figs. 12c and d, the same regressions are shown for the 18 July time period only. The correlation of CCN with organics throughout the entire study is weak (Fig. 12a), whereas the correlation of CCN with $[\text{MSA}+\text{SO}_4]$ is much higher (Fig. 12b), indicating that the sulphur species exert some control over the CCN throughout the sample period. For 18 July, however, a different pattern emerges. In this case, the CCN better correlate with organics (Fig. 12c) than with $[\text{MSA}+\text{SO}_4]$ (Fig. 12d), and those correlations with organics are significantly higher than those for the whole sample period. Thus, over the majority of the study period the CCN are controlled by the MSA and sulphate, but on 18 July when the concentrations of organics increased due to regional ship emissions, these particles exerted more control over the CCN than did the sulphur species. The slope of the regression for $\text{CCN}_{0.34\%}$ increases by about 50% during the 18 July time period compared with the rest of the sample period, for both sulphate and organics, indicating that for a given increase in mass concentration there are 50% more CCN on 18 July than for the rest of the sample period. This difference in slope is not evident for $\text{CCN}_{0.19\%}$ (larger CCN).

It is interesting that the correlation of sulphate with organics during the 18 July time period is relatively weak (Fig. 13a). A close look at Fig. 10 reveals that the sulphate

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and organics exhibit a similar shape on 18-19 July but shifted in time, with sulphate rising after the organics. The correlation between $[MSA+SO_4]$ and organics is highest ($r^2 = 0.57$) when the sulphate and MSA time series are shifted back by 2.5 hours (Fig. 13b). This time delay in MSA and sulphate concentrations requires further investigation, but lends support to the theory that sulphate and MSA condense onto the organics over time, resulting in a delayed increase in their mass concentrations relative to the increase in organic mass.

The influence of organics on CCN for higher mass fractions of organic in the particles has been observed for anthropogenic aerosols (Chang et al., 2007; Wang et al., 2008), suggesting that the organic material can significantly impact the water uptake. However, in the 18 July case water uptake does not appear to be the main role of the organic mass (Shantz et al., 2008), likely because the organic mass fraction was not high enough relative to sulphate. Rather, the higher slopes of CCN versus $[MSA+SO_4]$ for this time period reflect the sulphate and MSA distributing over a larger number of particles (principally primary organic emissions), yielding more CCN for a given value of $[MSA+SO_4]$. Modelling results from Pierce et al. (2007) showing that the addition of insoluble primary organic aerosol increases the concentration of CCN active at 0.2% supersaturation by 40-50% globally due to the ability of organics to act as condensation sites for sulphuric acid, are consistent with these findings.”

35: p. 328: Given that these measurements were made during an iron fertilization experiment with artificially elevated levels of S from biogenic and ship emissions, these conclusions, that generalize the findings to the remote NE Pacific, are inappropriate.

Please see responses to comments #1 and #2.

36: p. 310, Line 11: incomplete sentence

Thank you, this was a typo. The phrase “(see Fig. 2). In Fig. 7c, the 80-90 nm particle concentrations” has been removed.

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37: p. 310, lines 21 to 23: no verb in sentence.

The indicated line reads “The Canadian Surface Ocean – Lower Atmosphere Study (C-SOLAS) conducted the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) in the North Pacific Ocean in July, 2002 (Boyd et al., 2003).” (the verb is ‘conducted’.)

38: Figure 9: The right y-axis may be dimensionless but it still needs a scale indicating the values of the ratio. Identify the green and black points.

The scale and units have been indicated on the right hand axis and a legend has been added.

Minor changes have been made in the Summary and Conclusions section; it now reads:

“Seasonal relationships have been found between DMS, MSA, and cloud condensation nuclei (CCN) in the marine environment (Ayers and Gras, 1991; Ayers et al., 1991; Andreae et al., 1995), and correlations among sulphate, MSA, and SO₂ on a shorter temporal scale are reported in Huebert et al. (1996). In Phinney et al., 2006, DMS and MSA showed anti-correlated behaviour, while anti-correlations in DMS and SO₂ are reported elsewhere (i.e. Davis et al., 1999). The variations in these relationships are in part owing to the timescale of sampling. Similarly, in contrast to the findings of Hegg et al. (1991), no correlation between DMS and CCN was found during this study. This is not surprising considering that the timescale for oxidation of DMS is on the order of hours to one day and that our measurements are at 15-minute to 1-hour resolution. High wind speeds will complicate these relationships over the relatively short timescales and small geographical distribution of our measurements.

With one exception, the baseline CCN concentrations over 18 days were maintained without obvious nucleation events, and several periods of increased CCN were observed without accompanying nucleation events. The one exception was from 14 July.

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On that day, increased nanoparticle concentrations corresponded to a decrease in gaseous SO_2 concentrations that followed a decrease in DMS concentrations. About 6 hours later, an increase in the CCN was observed. The increase in the CCN was consistent with the growth and evolution of particle size, linking the CCN increase back to the oxidation of DMS. The timeframe for nucleation and growth of particles to detectable sizes implies that the DMS source region was 200 km – 400 km upwind (to the west) of the sample region.

The most significant results of this paper relate to the interaction between organics and sulphate in the marine environment. Our findings suggest that naturally-derived aerosols are not solely responsible for the DMS-sulphate-CCN connection proposed by Shaw (1983) and Charlson et al. (1987), nor do biogenic marine organics likely play a large role as CCN in this environment as in O'Dowd et al., 2004. In general, the CCN observed in this study were significantly correlated with MSA and sulphate, and were not correlated with organic mass concentrations. However, in one case (18 July), an increase in particulate organic mass associated with diffuse regional ship emissions increased the number concentrations of particles with diameters less than 90 nm, and the MSA and sulphate mass concentrations increased 2-3 hours later. The organics during this time were correlated with CCN number concentrations, and the evolution of the mass distributions of organics, sulphate and MSA indicate the sulphur species condensed onto the smaller organic particles. Over several hours the aerosol evolved to become more internally-mixed with most particles >90 nm, and the CCN concentrations increased. Thus, while the condensation of sulphate and MSA is essential for the activation of the aerosols as CCN, primary emissions of organic particles over the ocean can have a dominant influence on the number concentrations of particles active at supersaturations typical of marine stratocumuli on a regional scale.

Finally, O'Dowd et al. (2004) suggested that the concentrations of marine biogenic organics in the atmosphere over the Atlantic Ocean are especially high during plankton bloom periods, and discuss implications for the marine biota-aerosol-cloud-climate

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feedback mechanism. Here we find little support for a role of these particles as CCN, as evidenced by the weak correlation of organics with CCN over the entire sample period. Rather, our findings point to sulphur compounds and ship-sourced organics together having the greatest impact on CCN over the northeast Pacific Ocean.”

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 309, 2009.

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9, S3021–S3032, 2009

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