

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

L. Phinney et al.

Received and published: 9 September 2009

Response to Reviewer #1

We would like to thank Reviewer #1 for thoughtful and constructive comments on our manuscript. Please find below the responses to the reviewer's comments.

1: There were artificially elevated levels of DMS and its particulate phase reaction products (sulfate and MSA) due to a Pymnesiophyceae bloom.

AUTHOR RESPONSE:

Prior to the iron fertilization, the sample area was coincidentally high in productivity, DMSP, and DMS in the surface water, due to a natural bloom. From Levasseur et al., 2006, “The study region was initially rich in DMS with concentrations of up to 15 nmol L⁻¹. Thereafter, DMS concentrations in the unfertilized waters peaked at ca. 25 nmol

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



L^{-1} during days 10-12 and declined to near or below initial levels at the end of the experiment.”

The existence of high levels of DMS in the water and air prior to the iron fertilization, and the decline to near or below initial levels by the end of the experiment were confounding points in understanding the results of the fertilization experiment. However, a detailed and multi-disciplinary look at the population dynamics, levels of DMSP in the water, levels of DMS in the water and in the atmosphere, the DMS flux, and the meteorological conditions (i.e. wind speed, solar irradiance), both IN and OUT of the fertilized “patch”, lead to the following conclusions about the SERIES experiment (see “Canadian SOLAS: Subarctic Ecosystem Response to Iron Enrichment (SERIES). Deep-Sea Research Part II, Vol. 53, 20-22, 2006, for references):

- 1) The ocean-atmosphere DMS flux roughly followed the integrated DMS concentration in the water column.
- 2) The DMS concentrations in the water column were similar IN and OUT of the patch.
- 3) Calculations by Wadleigh et al. (submitted, 2002) calculated DMS flux values ranging from <1 to $109 \mu\text{mol m}^{-2} \text{d}^{-1}$ IN the patch, and 11 to $105 \mu\text{mol m}^{-2} \text{d}^{-1}$ OUT of the patch, with mean values that were not significantly different IN and OUT of the patch.

These 3 points lead to the conclusion that the DMS flux time series was similar IN and OUT of the patch.

- 4) DMS concentrations in the atmosphere were three times higher than the global average prior to the iron addition, were similar IN and OUT of the patch, and did not show any significant change until July 19 when the onset of a 4-day high-wind (45 km h^{-1}) event increased the ocean mixing depth and ventilated the DMS. This ventilation occurred when DMS levels in the water column were similar and at their peak values both IN and OUT of the patch, suggesting no influence from the iron fertilization on

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



measured atmospheric DMS concentrations at any point in the experiment.

Our results show elevated MSA and sulphate due to the influence of a large DMS source area that extended well beyond our sample region.

To section 2, the following final paragraph was added to clarify these points:

“Measurements made at Ocean Station Papa by the SERIES researchers in the days prior to the iron fertilization revealed high levels of DMS in the surface water (up to 15 nmol L⁻¹) (Levasseur et al., 2006). After the fertilization, DMS concentrations in the unfertilized waters surrounding the patch peaked at 27 nmol L⁻¹ on day 10, a natural increase coinciding with a period of lower wind speeds and high irradiance resulting in a shallow wind mixed layer (Levasseur et al., 2006). While the levels of DMS inside the iron-enriched patch peaked at 36.9 nmol L⁻¹ on day 10, the sea-to-air flux of DMS was higher in the patch vs out of the patch only on days 4-7, and reached a peak both inside and outside the patch on days 10 and 11, corresponding to a period of high winds and surface layer ventilation (Wadleigh et al., 2002). The temporal pattern of DMS concentrations inside and outside the patch were not statistically different (Levasseur et al., 2006). The temporal pattern of atmospheric DMS roughly followed the flux, increasing significantly only on days 10 through 15, coincident with the highest DMS fluxes both in and out of the patch. No significant differences in atmospheric DMS concentrations were observed in or downwind of the patch vs out or upwind of the patch (Wadleigh et al., 2002; Norman and Wadleigh, 2007). In a calculation similar to that of Norman and Wadleigh (2007) who estimate the fertilized patch area to be approximately 0.02% of the fetch area sampled at Uclulet, BC, during SERIES, we estimate the linear patch dimension (which ranged from 8 km at the beginning of the experiment, to approximately 35 km by the end), to represent between 0.1% and 0.4% of the linear fetch sampled by the atmospheric measurements on El Puma, assuming an average wind speed of 25 km h⁻¹, a total sample time of 672 hours, and with the assumption that we sampled in or downwind of the patch 50% of the time. All these results suggest that any differences in the concentrations of atmospheric DMS and its

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



oxidation products due to the iron fertilization would be masked by the comparatively large fetch sampled by the measurements. The areal extent of the naturally enriched DMS concentrations encountered in the sample area is estimated in Section 3.2.2.”

2: Although spikes from direct hits of stack gas from the ships were cleaned from the data, general mixing of exhaust into the boundary layer most certainly led to a departure of the aerosol composition and concentration from remote NE Pacific conditions. Given these sampling conditions, the conclusions are misleading and not applicable to the NE Pacific (or other remote oceanic regions) as suggested by the authors.

By ‘remote’ the authors mean to describe the open ocean, not ocean undisturbed by human impact.

Capaldo et al., 1999, show plots of SO₂ emissions and frequency of ship traffic in 2000, and Eyring et al., 2005 show projected frequency of ship traffic in 2050. Though there are areas far away from direct continental influence, like our sample area, there are no areas in the North Pacific that can be considered to have no anthropogenic influences, either in 2000 or projected to 2050.

The average wind speed in the sample region was 25 km h⁻¹ and there were relatively few instances of calm winds. Thus, any direct influence from the three SERIES sample platforms was easily spotted and removed from the data, and otherwise was transported quickly away from the sample region, leaving only the more diffuse influence that would be expected from cruising ships in any region of the North Pacific Ocean. Thus, we maintain that our data represent that region of the North Pacific Ocean that was sampled.

The focus of this paper is on the observation of atmospheric processes, not whether the region is remote, influenced, etc. Therefore, the authors have chosen to remove the word ‘remote’ from the description of the sample area throughout the paper, while maintaining that the results are representative of the region of the North Pacific Ocean that was sampled and that they demonstrate the process whereby diffuse ship emis-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

sions influence CCN concentrations in the presence of oxidized sulphur (i.e. potentially in any part of the ocean). Changes were made on p310 line 2 (removed the word “remote”), p310 line 26 (replaced “remote” with “open”), p312 line 15 (removed the word “remote”).

Capaldo, Corbett, Kasibhatla, Fischbeck, and Pandis, 1999. Effects of ship emissions on sulphur cycling and radiative forcing over the ocean, Nature vol. 400.

Eyring, Koehler, Lauer, and Lemper, 2005. Emissions from international shipping: 2. Impact of future technologies on scenarios until 2050, Journal Geophys. Res. Vol. 110, D17306, doi: 10.1029/2004JD005620.

3: Much of the data reported in this paper were previously published in Phinney et al. (2006).

The Phinney et al., 2006 paper was a general characterization of the size and composition of the aerosol over the North Pacific Ocean, presenting basic time series of data, quality assurance comparisons between instruments, and average bulk mass concentrations and size distributions. Here, we present the CCN data and investigate aerosol processes, including new particle formation and the influence of organics and sulphate on CCN concentrations. The two papers arise from the same measurement campaign and thus have measurements in common as do all companion papers, but they have distinct scientific foci.

4: Given these issues (under-representation of the sampling conditions, majority of the data having already been published in Deep Sea Research, the incomplete analysis/description of the CCN measurements) and the comments below, the paper is not publishable in ACP in its current form.

We have addressed these concerns here and in the manuscript; the CCN measurements are now presented as number concentrations, discussion of the deltaV-number calibration of the CCN counter has been added (see responses below), and the sam-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

pling conditions are explained more clearly. The scientific questions addressed in this paper are different from those discussed in Phinney et al., 2006.

5: Abstract: There should not be a reference to figures in the abstract.

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

6: p. 314: What overall collection efficiency was assumed for the AMS? Was a factor applied to accounted for collection efficiencies < 100% for the submicron size range?

Did the collection efficiency vary as a function of aerosol composition?

The paragraph has been changed to “The transmission of particles into the Q-AMS is nearly 100% in the range of 0.06 to 0.6 μm vacuum aerodynamic diameter (D_{va}), decreasing outside that range (Jayne et al., 2000; Zhang et al., 2002; Liu et al., 2007). The particle collection efficiencies and the relative ionization efficiencies are each incorporated into the analysis of the Q-AMS data. In this analysis the collection efficiency for all aerosol was set to 1 due to the high percentage of sulphuric acid in the aerosol, and the relative ionization efficiencies are as in Phinney et al, 2006. More detailed descriptions of the operation and calibration of the Q-AMS can be found elsewhere (e.g. Jayne et al., 2000; Allan et al., 2003).”

7: p. 315, lines 1 to 3: Why was the fragmentation table not fixed post-experiment so that accurate MSA concentrations are reported? As is, they appear to be underestimated by up to 25%.

This mistake has been corrected. The fragmentation pattern for MSA, sulphate, ammonium, and organics has been improved (see revised Table A2), resulting in a more accurate representation of these species. The new mass spectrum for the pure MSA trial reveals a much cleaner frag pattern for MSA (Fig A5). The new fragmentation table has been used to re-analyse the SOLAS data and results in a 13% increase in the MSA concentrations, and a 4% decrease in sulphate concentrations. The plots and

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



tables throughout the paper have been modified to reflect this improved fragmentation table. No significant changes in the results or conclusions of this paper have resulted from this modification, other than better quantification of mass concentrations and an improved MSA fragmentation table for Q-AMS analysis.

8: p. 315, lines 7 to 10: Why have deltaV values from the CCN measurements not been converted to CCN concentration? A calibration that allows for the conversion has apparently been performed for ammonium sulfate and NaCl aerosol by Leitch et al. (1999). Either these calibrations could be used or new calibrations could be run with an organic proxy and MSA. As reported, the reader has no sense of the magnitude of the dependence of the calibration factor on composition and size. Is the factor affected by the SO₄/Organic ratio? If so, to what extent? If significant, this dependence will affect the magnitude of delta V values shown in Figure 2.

We have replaced :

“The CCN observations are reported here as deltaV, the difference between the voltage signal from the scattered light and the baseline voltage. The calibration factor for converting deltaV to number concentration varies with the size and composition of the particle as well as the supersaturation. This issue is discussed further in Shantz et al., 2008.” (p 315, line 9)

with the following explanation:

“The CCN number concentration is approximately linearly dependent on deltaV (the difference between the signal from the scattered light and the baseline voltage) for sulphate particles and can thus be calculated by multiplying deltaV by a constant. Laboratory calibration of the CCN counter for sulphate particles ranging in size from 75 nm to 240 nm found the following relationships between CCN number concentration and deltaV, independent of particle size:

$$\text{CCN}_{0.19\%} = \text{deltaV} * 185 \text{ (6)}$$

$$\text{CCN}_{0.35\%} = \text{deltaV} * 130 \text{ (7)}$$

for CCN activated at 0.19% and 0.35% supersaturations, respectively. These equations are used to calculate CCN number concentration from deltaV in this paper.”

Re the effect of the SO₄/Organic ratio: The calibrations were performed with pure sulphate particles. In laboratory experiments, the addition of organics to particles has been shown to slow water uptake due to the lower solubility of organics compared with sulphate (Shantz et al., 2003). Thus, for the same number of CCN activated, the growth of CCN in the chamber would decrease with the presence of organics, thus decreasing the scatter and reducing the deltaV. The given conversion of deltaV to CCN number would then yield a lower CCN number in the ‘high organics’ case, making our reports of CCN number conservative when organics comprise a significant fraction of the aerosol.

9: p. 316: It is stated that the measured MSA concentrations were higher than those previously reported for the North Pacific, the South Atlantic and Cape Grim. In addition, measured sulfate concentrations were higher than values reported for coastal Canada and the Southern Ocean. The elevated MSA concentrations are attributed to "elevated DMS concentrations in the region." Why is not emphasized here that these data were collected during an iron fertilization experiment? What anomalous were the DMS levels? How do they compare to previously measured values for the NE Pacific?

As discussed in the response to comment #1, the iron fertilization experiment was not emphasized because no connection between the fertilization and the DMS concentrations in the air was found (Levasseur et al., 2006; Wadleigh et al., 2002 (submitted); and Norman and Wadleigh, 2007).

Regarding levels of DMS_{aq} during SERIES compared with previously measured values, the following is taken from Levasseur et al., 2006 (OSP refers to our sample location Ocean Station Papa; HNLC refers to “high nitrate, low chlorophyll” conditions):

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



“... DMS concentrations above 15 nmol L^{-1} have been previously measured at OSP during the summer (Wong et al., 2006), indicating that the environmental conditions in this HNLC region are conducive to high DMS concentration but the processes responsible for these elevated DMS concentrations are still unknown.”

There are few reports of measurements of atmospheric DMS in the North East Pacific. Our measurements have a mean value of 1.7 ppbv, an order of magnitude higher than the global average and four times greater than that measured by Aranami and Tsunogai (2004) in the North Western Pacific in the winter. Aranami et al. (2002) report atmospheric DMS concentrations in the summertime North Pacific to range between 0.25 ppbv and 0.47 ppbv, with the highest concentrations measured in the eastern region (near our sample site), though the concentrations of DMS in the surface waters in these locations did not differ significantly.

Our results show elevated MSA and sulphate due to the influence of a large DMS source area extending well beyond our sample region.

A final paragraph was added to section 2, clarifying the sampling conditions (please see response to comment #1).

10: p. 317, lines 10 to 17: It is stated that "the highest CCN concentrations were observed on July 18 which coincides with the highest observed organic aerosol concentrations". CCN concentrations are not shown in Figure 2, only delta V values. How do we know the magnitude of delta V is not biased by the large fraction of organics in the aerosol?

The CCN are now presented as number concentrations throughout the paper, based on the calibrations $\text{CCN}_{0.19\%} = \text{deltaV} * 185$ $\text{CCN}_{0.35\%} = \text{deltaV} * 130$

(for details please see response to comment#8).

As in comment #8, any bias from the large fraction of organics would produce lower CCN concentrations. In laboratory experiments, the addition of organics to sulphate

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

particles has been shown to slow water uptake (Shantz , 2003), and for the same number of CCN activated, the growth of CCN is either the same or reduced when organics are involved. Thus, there is either no change in the scattering in the CCN chamber, or it is decreased in which case the deltaV decreases. Unless the calibration takes these relatively subtle effects into account, which it does not, the conversion of deltaV to CCN number, based on pure sulphate particles, would give a lower CCN number in the 'high organics' case, making our results of CCN number conservative, i.e. the true CCN number concentrations will be slightly higher.

11: Also, the high CCN deltaV values correspond to high aerosol mass concentrations in general (including SO₄ and MSA). Why is only the correspondence to organics pointed out?

The CCN correlated well with sulphate+MSA throughout the entire sample period, and poorly with organics (see Figures 12 a and b), but on July 18th the CCN were less correlated with sulphate+MSA than they were for the entire sample period, while much better correlated with organics (see Figures 12 c and d). Thus, we focussed our study on understanding why the organics were so highly correlated with CCN for this time period.

12: p. 318, lines 2 to 6: Not a satisfactory discussion of the calibration of the CCN instrument. It is very difficult to assess what fraction of the particles were activated to form CCN, i.e., the information usually conveyed in such a plot.

Yes, the discussion of the CCN instrument and calibration has now been expanded. Please see reponse to comment #8.

13: p. 318, lines 15 to 20: It is stated that the lower values of r₂ shown in Figure 4 compared with the correlations with number in Figure 3 are due to the difference between measuring particle number vs. mass. Have you tried looking at the mass of MSA and SO₄ for a narrower size range, i.e., using the size distribution data from the AMS to better isolate the size range most relevant for activation at the given supersaturations?.

If we understand the comment correctly, it refers to where in the particle distribution the critical diameter lies on a mass distribution plot? This particular aspect was not looked into, since we saw a good correlation between CCN and aerosol with sizes above the critical diameter (Figure 3). We would also have to isolate the CCN number using the physical size distribution, and then the assumption level increases substantially.

14: p. 318, lines 21 to 26: The text refers to changes in number concentration for particles "as small as 8 nm" and "with diameters of 30 - 60 nm" and refers to Figure 2 for supporting evidence. It is not possible to see changes in number concentration for D_p less than 8 nm and D_p between 30 and 60 nm given the data plotted in the Figure, however. It would be more useful to refer to Figure 5 here.

Thank you. The reference to Figure 2 was removed and the text was changed to:

"On the afternoon of 14 July, number concentrations greater than 1000 cm^{-3} were observed for particles as small as 8 nm, and a subsequent increase in the number concentrations of particles with diameters of 30 nm – 60 nm was observed through the morning of 15 July. Figure 5a shows the change in particle size distribution ($dN/d\log D$) with time for 14 July. The data exhibits a shape characteristic of particle nucleation and growth with peak number concentrations at diameters $< 10 \text{ nm}$ preceding increases in larger particles over time (e.g. Kulmala et al., 2001; Buzorius et al., 2004). " ...

15: p. 318, line 26: What is the submicron surface area concentration for this time period relative to the experiment as a whole? Quantify these values in the text.

Thank you for this suggestion. The text now reads:

"The concentrations of small particles begin to increase at about 14:00, and reach peak values at about 17:00. At $8.0 \mu\text{m}^2 \text{ cm}^{-3}$, the sub-micron surface area in the three hours prior to the increase in particle concentrations is 70% lower than the average of $26 \mu\text{m}^2 \text{ cm}^{-3}$ for the entire sample period (Fig. 5e), a factor favouring new particle formation in regions with lower levels of precursors (e.g. Clarke et al., 1998)."

16: Figure 5: The MSA data might be better represented with a line and symbols than just symbols.

Have changed the representation to line+symbols.

17: p. 319, lines 5 to 10: This discussion is suggesting that the increase in particles with diameters less than 10 to 40 nm is due to boundary layer nucleation. Given the coincident decrease in RH, how can entrainment of newly formed particles from aloft into the boundary layer be ruled out as a source of these particles? Entrainment would also account for the decrease in SO₄ concentrations. Was there a rain event that scavenged surface area? Meteorological conditions appear to have changed over this period going from overcast to clear skies. Is there evidence of the passage of a frontal system that would have resulted in subsidence? Any change in atmospheric pressure at the surface?

This important point was discussed carefully among co-authors. A more thorough explanation of our reasoning has been added:

“Though it is hypothesized that boundary layer particle nucleation is the source of the small particles observed on 14 July, other explanations must be considered. A frontal passage yielding a new particle-rich air mass or subsidence and entrainment of newly formed particles into the boundary layer from the free troposphere aloft may be a plausible explanation for the burst of small particles. Surface analysis maps show little change in atmospheric conditions in the sample region, with a quasi-static low pressure system sitting to the northeast of the sample area from 13 July 23:00 hr to 15 July and beyond (Atlantic Climate Centre, 2002). Drizzle and some rain was observed on 13 July, the precipitation clearing by 00:00 14 July. On 14 July the weather was overcast with some breaks in the cloud, with periods of sun reported at 12:00 and 17:00, and a brief period of fog/drizzle reported at 12:30 followed by breaks in the cloud cover. Between 14 July 03:00 and 15 July 03:00, surface winds were consistently from the northwest and atmospheric pressure varied between 1010 and 1011 hPa. Though

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



there was a change in cloud cover indicated by the insolation curve in Figure 5, there is no evidence from surface meteorological analysis of any frontal passage. It is likely that the drizzle that occurred on 13 July, and briefly on 14 July, scavenged the surface area, and when followed by a brief period of sun provided the right conditions for nucleation.”

18: p. 319, lines 4 to 16: The discussion of binary vs. tertiary nucleation is beyond the scope of the available data given that neither H₂SO₄ or NH₃ concentrations were measured.

Yes, determining the mechanism of nucleation is beyond the scope of the paper; the paragraph is meant to comment on the feasibility of nucleation under conditions similar to those in our study.

19: p. 320, line 22: Should probably make it clear that you are talking about 14 July 12:00 to 18:00 and not 15 July which is also shown in Figure 5.

Thank you for pointing this out. The sentence has been changed to: “Fig. 5e indicates that on 14 July between 12:00 and 18:00 the number concentration of smaller CCN (CCN_{0.34%}) increases, corresponding to the increases in particle concentrations.”

20: p. 320, lines 20 to 21: Why is the distance from the source region being estimated?

Presumably, based on seawater measurements performed by others on the ship, the location of the ship relative to the fertilized patch was known.

The ‘source region’ refers not to the fertilized patch, but to the broad area of enriched phytoplankton activity that surrounded our sample area. This has been clarified by the paragraph added at the end of Section 2, as well as these changes to p320 lines 20 to 21:

“During the 14 July nucleation event, the wind speed was 25-30 km h⁻¹ and increases in small particle concentrations are seen approximately 6 hours after DMS concentrations begin to decrease with the increase in solar irradiation at 09:00. The average winds were from the west, and for a 6-hour lag time for nucleation, the source region

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

would have extended at least 200 km to the west, well beyond the linear extent of the fertilized patch of ocean on day 6 (8-20 km, Law et al., 2006)”

21: p. 320, lines 26 to 28: In the discussion of the 18 to 19 July period, it is stated that the concentrations of smaller CCN decrease as the mass concentrations of sulfate and MSA increase. It is not clear from Figure 2 that MSA is increasing during this period. Also, organics appear to be decreasing.

Thank you, this is a typo ... the discussion refers to Figure 5, and the dates should refer to July 14 and 15, not July 18 and 19 (changed, see next comment).

22: p. 320, lines 28 to 29: Figure 5 only includes 14 and 15 July. How can we look at the sulfate mass distribution for the 18 and 19 July period?

This was a typo, the sentence has been changed to

“Between 14 July 18:00 and 15 July 01:00, the concentrations of the ...”

23: p. 321, lines 5 to 6: Given the simultaneous change in temperature, RH, and surface area concentration, it is not evident that "particle nucleation from biogenic sulfate precursors" was observed. Evidence needs to be provided to rule out subsidence of newly formed particles from aloft.

The discussion that has been added in response to comment#17 addresses this comment. However, we point out that the reviewer is asking for the confluence of two processes on a short timescale.

To be continued in Part 2!

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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)