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

Anonymous Referee #1

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The paper presents measurements of CCN (although not quantitatively) and aerosol properties (composition and size distribution) during a research cruise in the NE Pacific. Based on these data, the authors conclude that "while the condensation of sulfate and MSA is essential for the activation of the aerosols as CCN, regionally diffused primary emissions of organic particles over the ocean can have a dominant influence on the number concentration of particles active at supersaturations typical of marine stratocumuli." They further conclude that "our findings point to sulfur compounds and ship-sourced organics together having the greatest impact on CCN over the NE Pacific." What is not emphasized in this paper, however, is that the sampling conditions were highly unusual and not those typically found in the NE Pacific during July. In reading a previously published paper (Phinney et al., 2006), the unique conditions of an iron-

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enrichment experiment, of which this study was a part, are better explained. There were artificially elevated levels of DMS and its particulate phase reaction products (sulfate and MSA) due to a Prymnesiophyceae bloom. As stated in Phinney et al. (2006), DMS concentrations were an order of magnitude higher than the global average and 4 times higher than recent measurements over the North Pacific. SO2 concentrations were an order of magnitude higher than those of the global marine boundary layer. In addition, there were three ships in the study area as well as at least one Zodiac. 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. (This departure is evident in Figure 11 of Phinney et al. (2006) which shows mass fractions of nitrate - presumably from ships - elevated above remote marine values). 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.

Much of the data reported in this paper were previously published in Phinney et al. (2006). The CCN measurements appear to not have been reported before but are nonetheless problematic. CCN concentrations are not reported but rather a deltaV value that is the difference between the voltage signal from the scattered light and the baseline voltage. It is stated that the " calibration factor for converting deltaV to number concentration varies with the size and composition of the particle as well as supersaturation" and a reference is cited. The CCN data are the one new piece reported in this paper yet we are not given actual concentrations, information on the calibration factor, or to what degree deltaV depends on composition and size (important when looking at CCN as a function of composition and size).

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.

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

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?

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%.

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 Leaitch 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.

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?

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? 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?

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.

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?.

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 Dp less than 8 nm and Dp between 30 and 60 nm given the data plotted in the Figure, however. It would be more useful to refer to Figure 5 here.

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.

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

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

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system that would have resulted in subsidence? Any change in atmospheric pressure at the surface?

p. 319, lines 4 to 16: The discussion of binary vs. tertiary nucleation is beyond the scope of the available data given that neither H_2SO_4 or NH_3 concentrations were measured.

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.

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.

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.

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?

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.

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.

Figure 6 and text: Need to explain the normalization process. Also "activation diameter at each supersaturation" assuming what composition?

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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.

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?

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

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.

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

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.

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 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.

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?

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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.

p. 310, Line 11: incomplete sentence

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

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.

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

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