

Interactive comment on “Observational evidence for the formation of ocean DMS-derived aerosols during Arctic phytoplankton blooms” by Ki-Tae Park et al.

Anonymous Referee #2

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Review of:

Observational evidence for the formation of ocean DMS-derived aerosols during Arctic phytoplankton blooms Ki-Tae Park, Sehyun Jang, Kitack Lee, Young Jun Yoon, Min-Seob Kim, Kihong Park, Hee-Joo Cho, Jung-Ho Kang, Roberto Udisti, Bang-Yong Lee, Kyung-Hoon Shin

General This is a good study that illustrates a correlation between marine productivity, gaseous emissions of biogenic sulphur, and new particle production in the Arctic region and contrasts a period dominated by marine emissions with that of long-range pollution transport leading to Arctic haze. The authors claim that this study proves a conclusive link, including direct evidence, of DMS emissions leading to new particle

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production, and presents nss-sulphate as the predominant aerosol species of which, isotope analysis concludes the majority sulphates is marine biogenic. The authors overstate their results and their conclusions where they claim DMS-derived sulphate leads to the formation (presumably nucleation and/or growth of nucleated clusters into nucleation mode aerosols at 3-10 nm) of new particles when there are no measurements to distinguish between inorganic, organic or halogen species, the latter which has been shown to overwhelm sulphuric acid in terms of contribution to the particle formation process, even though sulphate may ultimately dominate total mass. In summary, it is a useful study but the results should not be overstated. If the authors wish to maintain their assertion that the new particles are formed by DMS emissions, they have to demonstrate that sufficient sulphuric acid concentrations for nucleation and cluster growth to a few nm can be achieved from the levels of DMS encountered and that the occurrence of the new particle peaks coincide with the peak production rate of sulphuric acid. Recommendation: accept with minor revisions to texts to be consistent with the limitations of the results or if to maintain the claims of what these results illustrate, provide model assessments of the concentration of sulphuric acid available for particle production via DMS oxidation. Specific Comments Title : 'remove ocean' from title. Abstract: The results also showed that a sharp increase in the atmospheric DMS mixing ratio during Arctic phytoplankton bloom events was directly associated with the formation of sub-micrometer SO₄ aerosols, and their subsequent growth to climate-relevant particles.

I would state it the other way around – the formation of submicron sulphate aerosol was associated with increased atmospheric DMS mixing ratios. Introduction

Paragraph starting line 9. The text states that there may be a direct link between marine biota and climate change. I suggest this link is hardly direct. Later, line 14 onwards, states “in particular a lack of observational evidence for a direct association between DMS production and the formation and growth of aerosol particles.”. the two statements are inconsistent.

Line 19-20: I am not sure that the validity of the DMS-climate feedback is in doubt, is it not more the case that has been illustrated that in some regions, this feedback has been shown to be not as significant as perhaps other possible feedbacks or not the only chemical species in the feedback loop. For example, iodine has been suggested to be more important in the actual nucleation processes (O'Dowd et al., Nature, 2002; Sipila et al., Nature, 2016); and organic vapours may dominate in the growth of clusters into stable aerosol particles as often there is estimated to be insufficient sulphuric acid to account for initial growth processes [Dall'Osto, M., et al. (2012), J. Geophys. Res., 117, D12311, doi:10.1029/2012JD017522.]. Moreover, the majority of sulphate formation is estimated to be via the aqueous-phase of heterogenous pathway rather than the homogenous pathway [Hoppel et al., JGR, 99, 14,443-14,459, 1994,].

In addition, the role of primary aerosol feedback, in contrast to secondary aerosol, and involving organics with high activation efficiency [e.g. O'Dowd et al, Nature, 2004; Ovadnevaite et al, GRL, 2011; O'Dowd et al., Scientific Reports, 2015].

Experimental set up Page 3 Line 15: please be specific on the online aerosol size distribution measurements, neither a DMA or a CPC on their own measure size distributions. Were they combined in a SMPS, or DMPS, what configuration? Were the particle dry size, or partly hydrated? Very few SMPS/DMPS size distributions reported are 100% dry size – more is needed here.

Results and Discussion Page 4 line 27: 3 fold 18 is 54 not 47, I would rephrase to “more than double” Page 5 line 1. “The concentration of aerosol particles in the 3–10 nm diameter range (a nucleation mode), which is an indicator of recent nucleation, occasionally exceeded 3000 cm⁻³. These small particles formed more frequently in May than in April (blue line in Fig. 1a). As a result, the 3-day mean DMS mixing ratios and the MSA concentrations were both significantly correlated with the 3-day mean concentration of nucleation mode particles ($r = 0.66$, $n = 14$, $P < 0.05$, Fig. 1c; and $r = 0.71$, $n = 14$, $P < 0.05$, Fig. 1d, respectively); the observed nucleation events also concurrently occurred with high 5 atmospheric DMS mixing ratios (Fig. 1a). This does

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not make sense – this means that, as a result of the small particles being indicators of recent nucleation, and being formed more frequently in May rather than April, DMS and MSA was significantly correlated to nucleation mode particles. This is not scientifically correct.

Line 6: 45% of the variability in new particles can be explained by DMS/MSA then line 11 states “We cannot completely rule out the possibility that sources other than DMS (e.g., iodine) contributed to the formation of nucleation mode particles (Fig. 1a, c and d). However, these strong correlations indicate that the small aerosol particles that were formed newly were probably derived from recently released biogenic DMS.”

To quote from Sipila et al: “In Greenland, we began to observe elevated concentrations of HIO₃ after sunrise in late February, often associated with new particle formation events. During such events, the HIO₃ concentrations tended to be much higher than that of sulfuric acid (Supplementary Fig. 12), and it seems that the cluster formation could be explained almost entirely by the HIO₃ clustering mechanism.” I think it has to be accepted and stated that there is no direct evidence in this study that can state DMS-derived species were responsible for the production of new particles given that HIO₃ was not measured as is also likely to be emitted (or more precisely, produced) in parallel to DMS (or DMS products).

The line 31 same page “The high concentration of small particles (< 100 nm) during phytoplankton bloom period (May) constitutes compelling evidence for new particle formation derived from local DMS emission” Probably derived and compelling evidence are not the same thing.

I do not think you can rule out iodine in cluster formation and the nucleation processes and even perhaps organics contributing to particle formation. We have no handle on whether or not sulphuric acid was present in sufficient concentrations to nucleate clusters or particularly grow clusters to measurable sizes. If you are going to make such strong statements you need to present solid arguments, for example even a box model

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of the maximum concentrations of sulphuric acid likely to be achieved for the DMS concentrations, oxidation rates/solar radiation and condensation sinks. A number of groups have illustrated what concentrations are required for various nucleation and aerosol formation pathways, why not apply this approach here to present some more comprehensive arguments.

Page 6, line 4, I think these days, condensation sink is used in this context more than surface area. What role had supermicron particles in surface area or condensation sink?

Line 9-11 it is stated : These observations support our hypothesis that the formation of new particles resulting from the photo-oxidation of biogenic DMS . Where have the authors presented a hypothesis or tested a hypothesis? The authors have only made tenuous links to new particle formation and DMS. The observations do not support any such hypothesis in any event. If they want to present such hypothesis', and test it, the manuscript needs to be restructured. For example, the seemingly definitive case-closed statement on line 9-11 comes before the whole section on Aerosol formation from biogenic DMS (section 3.3). BTW, is there non-biogenic DMS?

Section 3.3 Aerosol formation from biogenic DMS, while it illustrates a link between DMS and SO₄ aerosol, this does not present anything on the link between new particle formation and DMS or SO₄.

How much of the aerosol mass is accounted for by sulphate and MSA and how much sea salt and or organics. Is there closure between the SMPS/DMPS/APS derived mass distributions, or integrated mass distributions up to 2.5 microns and sulphate/seasalt.

Von Glasow and Crutzen found that in cloud free conditions less than 5-15% of DMS being converted to sulphate while under cloud conditions, 100% conversion occurs. How much of the DMS is available for nucleation/condensation of sulphuric acid to the aerosol phase and over what timescale?

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Conclusions The conclusion is poorly presented, essentially comprising two sentences of overstated results.

This study provided the observational evidence confirming direct relationships between an increase in atmospheric DMS and the formation and growth of aerosol particles, and also an increase in the total mass concentration of nss-SO₄ during Arctic phytoplankton blooms. Concurrent measurements of a suite of parameters (DMS, satellite-derived phytoplankton biomass, concentration and chemical composition of particles) supported the assertion that oceanic emission of DMS significantly affects the properties of sub-micrometer particles in the Arctic atmosphere.

I would think that the authors can only conclude:

During periods high biological activity as illustrated by surrogates for plankton biomass, both enhancements of some aerosol-forming gaseous precursors (e.g. sulphate precursors such DMS and MSA) are seen simultaneous to a growing nucleation mode particles (new particle mode 3-10 nm) and by the time that these particles grow to sizes at which their chemical composition can be identified.

The chemical composition of marine aerosol cannot be resolved using the above instrumentation at sizes below 100 nm. In fact, I would suggest that given the mass mode in the size distribution is certainly larger than 500 nm and closer to 1,000 nm which means that the mass a particle has increased at least another three orders of magnitude when it has been chemically quantified.

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