Relating atmospheric and oceanic DMS levels to particle nucleation events in the Canadian Arctic

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[1] Measurements of ocean surface and atmospheric dimethyl sulfide (DMS) and particle size distributions were made in the Canadian Arctic Archipelago during the fall of 2007 and the late summer of 2008 aboard the Canadian Coast Guard Ship *Amundsen*. Nucleation-mode particles were observed during the 2008 cruise, which took place in the eastern Arctic from August to September when the atmosphere and ocean were more photo-active as compared to the October 2007 transit in the Beaufort Sea during which no nucleation/growth events were observed. The observed nucleation periods in 2008 coincided with high atmospheric and ocean surface DMS concentrations, suggesting that the particles originated from marine biogenic sources. An aerosol microphysics box model was used to simulate nucleation given the measured conditions in the marine boundary layer. Although other sources may have contributed, we find that the newly formed particles can be accounted for by a marine biogenic DMS source for combinations of the following parameters: $[OH] \geq 3 \times 10^5$ molecules cm^{-3}, DMS mixing ratio is ≥ 100 pptv, the activation coefficient is $\leq 10^{-7}$ and the background particle concentration is ≤ 100 cm^{-3}.

1. Introduction

[2] Sulfuric acid (H_2SO_4) is crucial to new particle formation. In continental regions H_2SO_4 is typically formed from the oxidation of anthropogenic SO_2, while in the marine boundary layer (MBL), H_2SO_4 is thought to primarily originate from the oxidation of dimethyl sulfide (DMS) produced through the planktonic food web [*Bates et al.*, 1987; *Kreidenweis et al.*, 1991; *Shaw*, 1989; *Yin et al.*, 1990a; *Yin et al.*, 1990b]. Particle nucleation takes place when low-volatility vapor molecules (generally involving H_2SO_4)

cluster together to ultimately form a particle. In general, if the pre-existing particle surface area is high, then it is more likely for the gas molecules to undergo mass accommodation to the surface of the existing particles, from which they do not readily desorb, than to nucleate from the gas phase and form new particles.

[3] In the climate feedback loop suggested by *Charlson et al.* [1987], an increase in solar radiation and temperature would be moderated by more reflective clouds produced by an increase in cloud droplet numbers originating from DMS initiated particle nucleation. However, nucleation is rarely observed in the marine boundary layer (MBL) in non-polar regions [*Kulmala and Kerminen*, 2008]. *Covert et al.* [1996] sailed 90 days in the Pacific Ocean over two years from 55°N to 70°S and only observed nucleation once near the state of Washington [*Covert et al.*, 1992] in an event that was attributed to subsidence of new particles formed in the free troposphere [*Hegg et al.*, 1992]. Model results suggest that background aerosol concentrations are generally too high and SO_2 concentrations too low for new particle formation to be favorable in the MBL [*Cainey and Harvey*, 2002; *Pirjola et al.*, 2000]. Instead, DMS is thought to be transported into the free troposphere where it oxidizes [*Davis et al.*, 1998]. Perhaps because the background concentrations and temperatures are lower in the free troposphere, nucleation is more likely to occur [*Cainey and Harvey*, 2002].

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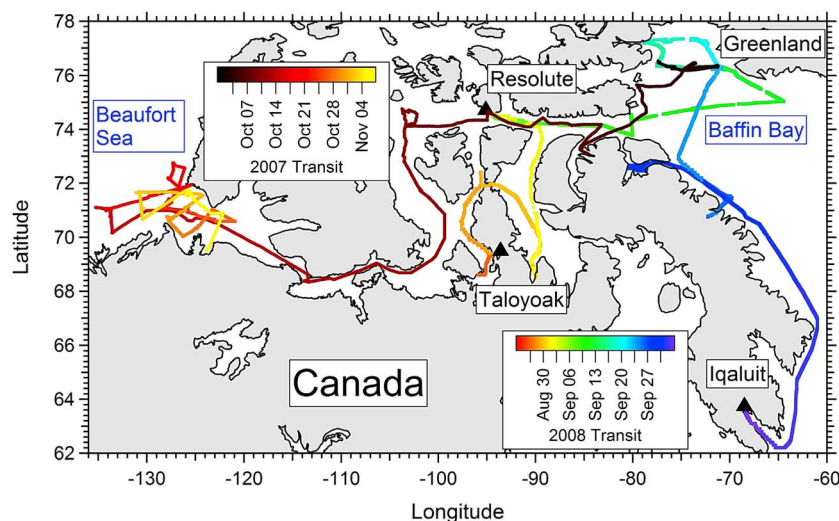
Figure 1. Route of CCGS *Amundsen* during the two transits, colored by date. Grey shading represents land and blue labels denote bodies of water.

These nucleated particles then subside [*Clarke*, 1993] and contribute to the stable aerosol distribution that is observed in the MBL [*Katoshevski et al.*, 1999; *Raes*, 1995].

[4] In contrast, the polar MBL has lower background aerosol concentration and temperatures, likely making it more favorable for nucleation to be observed [*Asmi et al.*, 2010; *Strom et al.*, 2009] and modeled [*Cainey and Harvey*, 2002; *Pirjola et al.*, 2000]. Examples include summertime in Aboa, Antarctica, where nucleation was observed when the air had been influenced by the coast but not when it was primarily from the continent [*Koponen et al.*, 2003]. Back trajectories from this study did not indicate any vertical motion, suggesting that the air had not subsided. Similarly, in Pallas, Finland (68°N), nucleation was only observed when clean marine air from the Arctic or North Atlantic oceans was sampled [*Lihavainen et al.*, 2003]. Finally, *Wiedensohler et al.* [1996] linked ultrafine particles observed in the central Arctic Ocean pack ice to either DMS from the open ocean or from the free troposphere using principal component analysis and partial least squares regression.

[5] The overall effect of aerosols on climate is still highly uncertain, especially in the Arctic where particles can warm the surface, as opposed to lower latitudes where they have a net cooling effect [*Shupe and Intrieri*, 2004]. Since the temperature in the Arctic is increasing twice as quickly as the rest of the earth [*Arctic Climate Impact Assessment (ACIA)*, 2004], it is urgent that our understanding of aerosol sources and processes improves. In particular, the rapid loss of the summer multiyear and first-year sea-ice [*Maslanik et al.*, 2007] and the corresponding areal increase in ice-free waters suggest that nucleation sources that originate from oceanic precursors may also increase with climate warming.

[6] This study reports the first observations of nucleation-mode particles (NMP, particles < 30 nm diameter) simultaneous with increased atmospheric DMS levels in the Canadian Arctic Archipelago. Higher DMS concentrations in the ocean surface waters (hereafter referred to as "ocean surface DMS") at the same time suggest that these NMP originated from marine biogenic sources. In order to test the hypothesis that these NMP formed from DMS oxidation in

the MBL, we use a model of aerosol nucleation and microphysics to show that the particle formation and growth can be accounted purely by DMS oxidation. However, we cannot exclude the possibility of other processes or species contributing to the particle formation.

2. Measurements

[7] The research cruises took place on the Canadian Coast Guard Ship *Amundsen* from 29 September to 7 November 2007 and 29 August to 2 October 2008 as a part of the Canadian IPY Arctic Surface-Ocean-Lower-Atmosphere-Study (SOLAS) and Circumpolar-Flaw-Lead Experiment (CFL) programs. The cruise ranged from Baffin Bay to the Beaufort Sea during 2007 while in 2008, measurements started in Gjoa Haven, Nunavut (NU) in the Eastern Canadian Archipelago and ended near Iqaluit, NU. A map of the routes can be seen in Figure 1. All times presented are in coordinated universal time (UTC).

[8] Atmospheric instruments were housed in a shed on the top deck of the ship with an inlet that was approximately 18 m above sea level. A scanning mobility particle sizer (SMPS, TSI 3080, 3081, 3010) measured the aerosol size distributions between 10 and 500 nm with a sampling time of 5 min and sample and sheath flows of 1 L min^{-1} and 5 L min^{-1}, respectively. An ultrafine condensation particle counter (UCPC, TSI 3025A) measured the total particle concentration > 3 nm. We interpret the difference between the UCPC concentration and the total value measured by the SMPS as an indication of the presence of particles between 3 and 10 nm. Both of these aerosol instruments sampled from a stainless steel tube (9.5 mm outer diameter) with < 1.8 s residence time.

[9] Atmospheric DMS was measured using a proton-transfer-reaction mass spectrometer (Ionicon Analytik) which sampled off a 10 m long, 6.3 mm outer diameter, Teflon line in the shed at the top of the ship. A sample residence time of approximately 2.5 s was calculated from a 3.0 L min^{-1} flow rate. This instrument ionizes incoming gas-phase molecules by transferring a proton from H_3O^+,
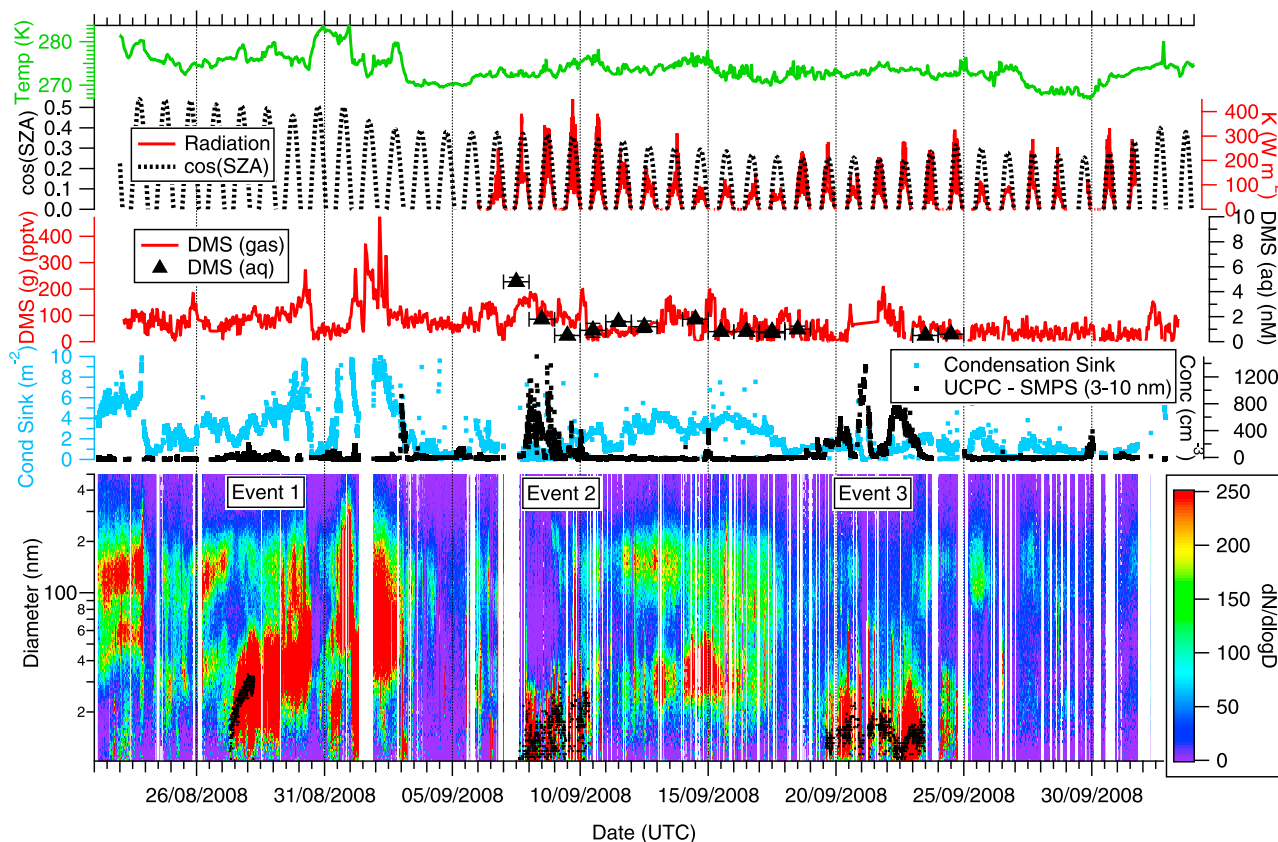
Figure 2. Temperature (first panel), cosine of the solar zenith angle and radiation (second panel), DMS air and ocean surface levels (third panel), reduced condensation sink and concentrations of particles between 3 and 10 nm (fourth panel) and size distributions (fifth panel) during the 2008 cruise. Black dots in the fifth panel are the modes during the three particle formation events.

which is formed through a discharge ion source. The protonated DMS is then detected using a quadrupole mass spectrometer at a mass-to-charge ratio of 63. Backgrounds were measured for 5 min every hour by diverting the sample air through a platinum catalyst heated to 350°C to remove ambient volatile organic compounds. A detailed description of the operation of this instrument can be found in the literature [*de Gouw and Warneke*, 2007] as well as the specific operation during the 2008 transit (S. J. Sjostedt et al., Evidence for the uptake of acetone and methanol by the Arctic Ocean during late summer DMS-emission events, manuscript in preparation, 2011).

[10] Ocean surface DMS, sampled at 2–3 m in depth with Niskin-type bottles, was measured by transferring seawater into 25 mL glass serum bottles with no headspace and hermetically sealed with butyl rubber septa. DMS was concentrated using purge and trap and quantified using a gas chromatograph (Varian CP-3800) with a capillary column (CP-Sil 5CB fused silica, 30 m x 0.32 mm, 4 μm film thickness) and a pulsed flame photometric detector. Calibration was performed using a permeation tube standard (Kin-Tek Laboratories) at 40°C and diluted with helium. Further details of the ocean surface DMS sampling during 2007 and 2008 is provided by *Luce et al.* [2011] and J. Motard-Côté et al. (Dynamics and phylogenetic affiliation of dimethylsulfoniopropionate (DMSP)-degrading bacteria

in Arctic waters, submitted to *Journal of Geophysical Research*, 2011), respectively.

[11] Solar radiation was measured starting on 10 October in 2007 and 6 September in 2008 on the top deck of the ship using a pyranometer (Eppley, model PSP). The sensor was scanned at 2 s intervals and data stored as 1 min averages by a micrologger (Campbell Scientific, model CR23X).

3. Observations

3.1. General Observations

[12] Atmospheric DMS levels reached several maxima during the 2008 transit (see third panel in Figure 2) and because its atmospheric lifetime against OH oxidation ranges from 2.2 to 22 days (for [OH] = 10^5–10^6 molecules cm^{-3}) [*Hynes et al.*, 1986], it is possible that the atmospheric DMS could have originated from lower latitudes. However, corresponding ocean surface DMS levels ranged from 0.52 to 4.75 nM (see third panel in Figure 2), showing that the ocean was biologically active during the 2008 transit (Motard-Côté et al., submitted manuscript, 2011) and suggesting that the atmospheric DMS could have originated from the surrounding ocean instead of lower latitudes. Furthermore, the ratio of DMS concentration in the air to DMS concentration in the water ranged from 0.001 to 0.008, which is lower than the Henry's law constant for
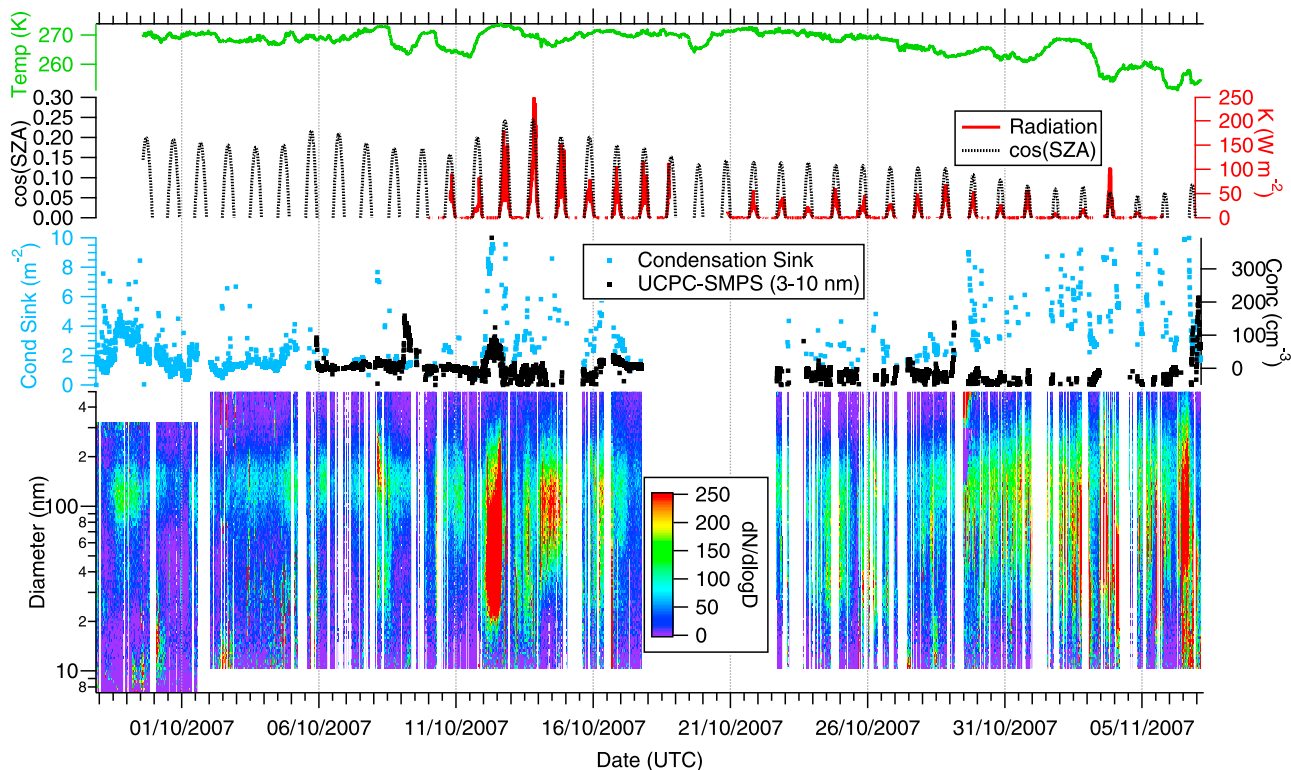
Figure 3. Temperature (first panel), cosine of the solar zenith angle and radiation (second panel), reduced condensation sink and concentrations of particles between 3 and 10 nm (third panel) and size distributions (fourth panel) during 2007. Note that the vertical axis for the fourth panel is different from Figure 2.

DMS at 273 K in seawater (0.028 [*Wong and Wang*, 1997]), and is consistent with the ocean being the source of atmospheric DMS observed during this cruise. This is supported by work done by O. Rempillo et al. (DMS fluxes and the growth of the biogenic sulphur aerosol component: A study aboard an icebreaker in the Arctic in the fall of 2007 and 2008, submitted to *Journal of Geophysical Research*, 2011) who calculated a DMS flux of $0.2 - 1.3$ μmol m^{-2} d^{-1} from the ocean surface during the 2008 cruise.

3.2. Observations of Small Particle Events

[13] Figures 2 and 3 show the aerosol size distribution, atmospheric DMS mixing ratio and solar radiation for the 2008 and 2007 transits, respectively. Periods when ship emissions are suspected are excluded (UCPC concentrations > 20,000 particles cm^{-3} or we assume that the minimum 1 s particle concentration is uncontaminated by ship pollution and that the maximum 1 s UCPC measurement for unpolluted ambient air cannot be greater than two times the minimum within a 5 min sampling window). These figures also include the calculated condensation sink (m^{-2}), as given by *Kerminen et al.* [2004]:

$$CS' = \frac{1}{2} \sum_j \frac{d_j N_j (1 + Kn_j)}{1 + 0.377 Kn_j + 1.33 Kn_j (1 + Kn_j)},$$

where d_j is the diameter of the particle at the jth size bin, N_j is the particle number concentration at that size bin and Kn_j

is its Knudsen number and is equal to $2\lambda/d_j$, where λ is the mean free path of air (fixed at 0.0608 μm for STP).

[14] During 2008, NMP were observed during three periods that coincided with increases in DMS mixing ratios to > 150 ppt and condensation sink < 5 m^{-2}. The size of these small particles (<30 nm) suggests that they had recently nucleated.

[15] The first distinct period shows particle growth starting on 27 August 2008 12:00 and ending on 28 August 2008 06:00 when the ship anchored at Taloyoak, NU (69.5°N,93.6°W). Particle growth was observed in this time period (see fifth panel of Figure 2) but the smallest particles (<10 nm) were relatively low in concentration, probably having formed earlier in a region not sampled by the ship's path. It is also possible that the initial 10 nm particles originated from exopolymer secretions of marine organisms emitted directly into the atmosphere by bubbles bursting in the ocean [e.g., *Leck and Bigg*, 2005, 2010] and the observed growth was caused by DMS oxidation products.

[16] The second and third periods occurred from 7 September 2008 21:00 to 10 September 2008 3:00 and from 19 September 2008 12:00 to 25 September 2008 6:00, respectively. During both of these periods, particles < 30 nm were observed with no evidence of further growth. In contrast to the first event, the number of particles between 3 and 10 nm also increased significantly to > 800 cm^{-3}, suggesting that nucleation had recently occurred, although it was not followed by growth beyond 30 nm. Furthermore, HYSPLIT back trajectories show that the air originated from the
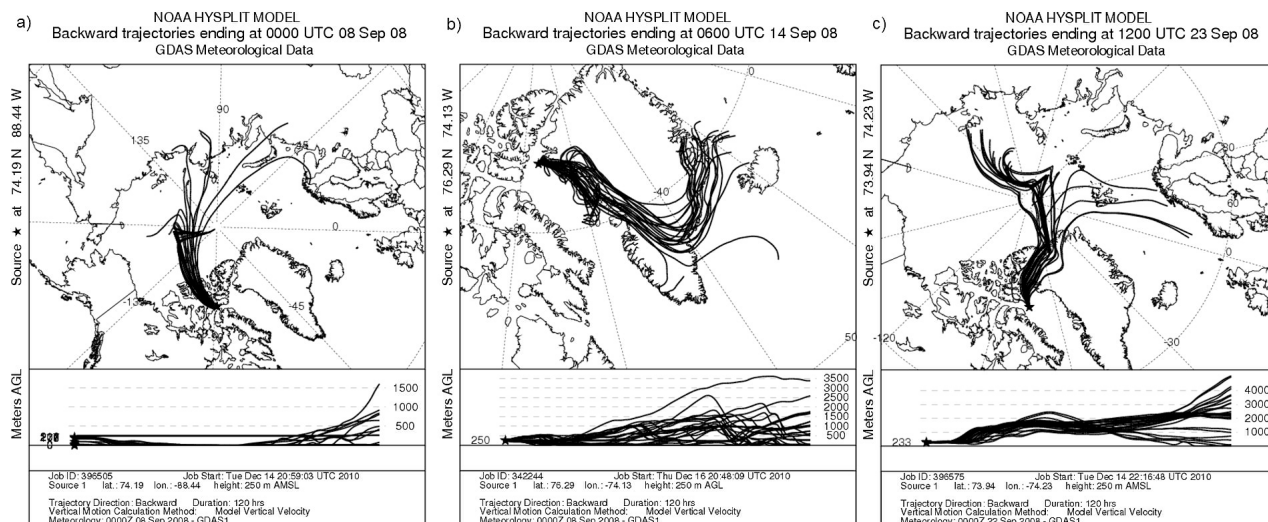
Figure 4. Back trajectories of nucleation and growth periods from Figure 2: (a) event 2, (c) event 3 and (b) the intervening period. Trajectories were calculated using NOAA's Ready HYSPLIT (Draxler and Rolph, online publication, 2010; Rolph, online publication, 2010) using the trajectory ensemble option which runs 27 trajectories starting from the specified location and an array of locations offset from it.

northwest and northeast during these two periods R. R. Draxler and G. D. Rolph, HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model, 2010, http://ready.arl.noaa.gov/HYSPLIT.php; G. D. Rolph, Real-time Environmental Applications and Display sYstem (READY), 2010, http://ready.arl.noaa.gov) (hereinafter Draxler and Rolph, online publication, 2010; Rolph, online publication, 2010) when the air had passed over regions of pack ice (Figures 4a and 4c). This air was likely cleaner with lower condensation sink (<1 m^{-2} before the two events), allowing particle formation to occur in the region surrounding the ship. However, lower DMS levels and reduced irradiance may have contributed to the absence of growth during these two events compared to the first.

[17] These two periods were separated by nine days of significantly higher levels of background aerosol (30–500 cm^{-3}) with modes at 30 and 150 nm, resulting in an increased condensation sink (1.7–4.6 m^{-2}). In addition, the solar zenith angle throughout the cruise (Figure 2, second panel), calculated based on the ship's location and day of year, compared with the measured total radiation, suggests that the period between these last two nucleation events was cloudy, which we infer lowers OH production rates. HYSPLIT back trajectories show that the air was from the southeast (Figure 4b), having subsided from Greenland to a large degree. This combination of potentially lower OH production and increased background aerosol likely contributed to the suppression of particle formation.

[18] During the 2007 study, particles < 20 nm were rarely observed (Figure 3). The two short periods of increased particle concentration between 3 and 10 nm in size (9 and 12 October) maximized at roughly 100 cm^{-3}, low relative to the 2008 cases when concentrations increased up to 1000 cm^{-3}. The most likely reason for the lower prevalence of nucleation events during the 2007 cruise is that it took place one month later when solar radiation was lower resulting in lower OH production rates and lower ocean surface DMS concentrations (0.05 to 0.80 nmol L^{-1} in 2007 [Luce et al.,

2011] compared to 0.52 to 4.75 nmol L^{-1} in 2008 (Motard-Côté et al., submitted manuscript, 2011). The 2008 transit received more insolation (median 67 W m^{-2} compared to 27 W m^{-2} in 2007) which should have increased the OH production rates as well as phytoplankton activity. The average radiation for the 2nd and 3rd nucleation events combined was 52 W m^{-2}, which is greater than 85% of the radiation measurements made during the 2007 transit. However, the sampling areas during these two studies also differed greatly. Since the oceanographic conditions of the Beaufort Sea (2007 transit) and the Baffin Bay (2008 transit) are different, the biological activity would also be expected to differ, which could have contributed to the presence of NMP.

[19] We also note that at a later time in the 2008 cruise, from 26 September to 1 October, the condensation sink was also low and yet no nucleation events were observed. However, at this time the DMS mixing ratios were especially low. These observations imply that a combination of high sunlight, low condensation sink and sufficient DMS is required for nucleation and growth events to be observed, as consistent with prior understanding.

4. Modeling of Nucleation and Growth

[20] In order to gauge whether the NMP can be explained by the oxidation of DMS, a microphysics box model is used to address the following questions: (1) Are the aerosol size distributions during the nucleation and growth events consistent with known processes involving only DMS? (2) Is another chemical species required in the nucleation and growth process, as constrained by the observations and our knowledge of the kinetics and mechanisms of these processes?

4.1. Model Description

[21] To determine if the sulfate generated from DMS oxidation could potentially account for the measured nucleation and growth, we used a box-model version of the

Table 1. Range That Model Parameters Were Varied, Independent of Each Other[a]

Parameter	Tested Parameter Values
A (s^{-1})	10^{-10}, 10^{-9}, 10^{-8}, 10^{-7}, 10^{-6}
Initial DMS mixing ratio (pptv)	100, 200, 400
[OH] (molecules cm^{-3})	1×10^5, 3×10^5, 1×10^6
Background aerosol concentration (cm^{-3}) [Condensation Sink (m^{-2})]	10 [0.70], 20 [1.41], 100 [7.0], 500 [35.2]

[a]The condensation sink was calculated from the background aerosol concentration.

TwO-Moment Aerosol Sectional (TOMAS) microphysics algorithm [*Adams and Seinfeld*, 2002; *Pierce and Adams*, 2009a, 2009b; *Riipinen et al.*, 2011]. This version of TOMAS is configured to simulate the number of particles and mass of hygroscopic aerosol (e.g., sulfate, sea salt, oxidized organics) within 44 lognormally spaced size bins that span dry diameters of 0.5 nm and 10 μm. TOMAS calculates the nucleation, condensation and coagulation that shape the aerosol size distribution. The model includes gas-phase sulfur chemistry (DMS, SO_2 and H_2SO_4) based on work by *Chin et al.* [1996], which has been shown to perform well in Arctic environments compared to other schemes [*Karl et al.*, 2007]. Uncertainties associated with chemistry will be discussed in the results section.

[22] Since little is known about nucleation mechanisms in the Arctic, we use the simple activation nucleation parameterization to predict nucleation rates. This nucleation scheme has the form $J_{nuc} = A[H_2SO_4]$ where J_{nuc} is the nucleation rate and A is an empirical parameter [*Sihto et al.*, 2006]. The theoretical basis for this linear dependence on sulfuric acid is that stable but sub-critical clusters exist that need just a single additional sulfuric acid molecule to reach a critical size where it can continue to undergo stable condensational growth. Although we do not have evidence that this nucleation is the dominant mechanism in the Arctic, it allows us to easily scale nucleation rates up and down. As we do not have enough observed nucleation events to determine if observed nucleation rates are dependent linearly on sulfuric acid, we cannot conclude based on the results of this paper if activation-type nucleation was actually occurring in these events. The primary question we are addressing with this model is whether or not sulfuric acid generated from DMS could simultaneously account for both the nucleation and growth of the particles, and the exact details of the nucleation mechanism are less important. We will find cases where the correct number of particles both nucleated and grew to observed sizes by adjusting the A-factor in activation nucleation theory. Using these best fit cases we can compare the efficiency of sulfuric acid to nucleate particles in the Arctic to continental sites where activation nucleation has been directly quantified (e.g., If the Arctic cases have a lower A-factor than continents then nucleation is less sensitive to the presence of sulfuric acid at least in these tested cases).

[23] To account for uncertainties in the nucleation rate, we perform simulations with A factors ranging from 10^{-10} to 10^{-6} s^{-1} (see Table 1). Nucleated particles are added to the size bin corresponding to 1 nm dry diameter. The model is initialized with a pre-existing aerosol size distribution (mode = 150 nm, σ = 2, number concentration variable to represent measured condensation sink values) and DMS mixing ratios varying across the range of measured values (Table 1). In this way, we can test the sensitivity of nucleation and growth to these parameters. The initial aerosol is assumed to have the properties (density and hygroscopic growth) of ammonium bisulfate. Changing the assumed aerosol density and hygroscopic properties across potential values likely has a smaller effect on nucleation/growth than varying the pre-existing aerosol size distribution across the range of values we are testing. We assume that the box passes over a significant marine source of DMS followed by a region with zero or low DMS emissions, thus there is no source of DMS into the box after initialization. SO_2 and H_2SO_4 vapor concentrations were assumed to be initially zero and the vapor pressure of H_2SO_4 was assumed to be zero. No other condensable species other than H_2SO_4 (e.g., organics) are included in the model and the model does not account for cloud cycling. The [OH] was assumed to be constant, but we perform simulations with several typical diurnal-average values for polar latitudes [*Jefferson et al.*, 1998] (Table 1). Simulations were run for 48 h, which is representative of the longest we expect initial ambient conditions to remain relevant, especially as the ship was moving throughout the study. All possible permutations of model inputs (Table 1) are simulated, for a total of 180 simulations. In contrast to other modeling studies, we begin with DMS oxidation because SO_2 at sufficient time resolution and H_2SO_4 were not measured during the two cruises.

[24] The model uses many uncertain input parameters. However, the overall purpose of the model runs is to test if DMS could have driven the aerosol nucleation and growth under the conditions measured during the experiment. If under even the most favorable measured conditions for DMS-driven nucleation and growth (high DMS mixing ratios, low pre-existing aerosol concentrations, most intense solar radiation) the model cannot produce both the number of nucleated particles and their growth, it is likely that another species must be contributing to the nucleation and/
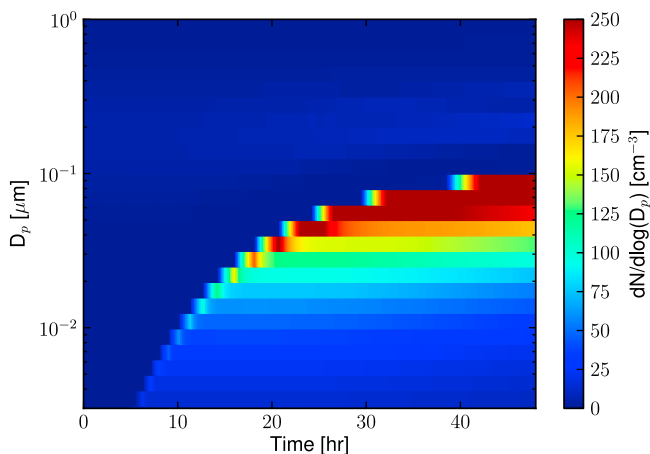

Figure 5. Simulated aerosol size distributions (dN/dlogDp) showing nucleation and growth from the box model using an A factor of 10^{-10} s^{-1}, initial DMS mixing ratio of 400 pptv, condensation sink of 0.70 m^{-2} and [OH] of 10^6 molecules cm^{-3}.
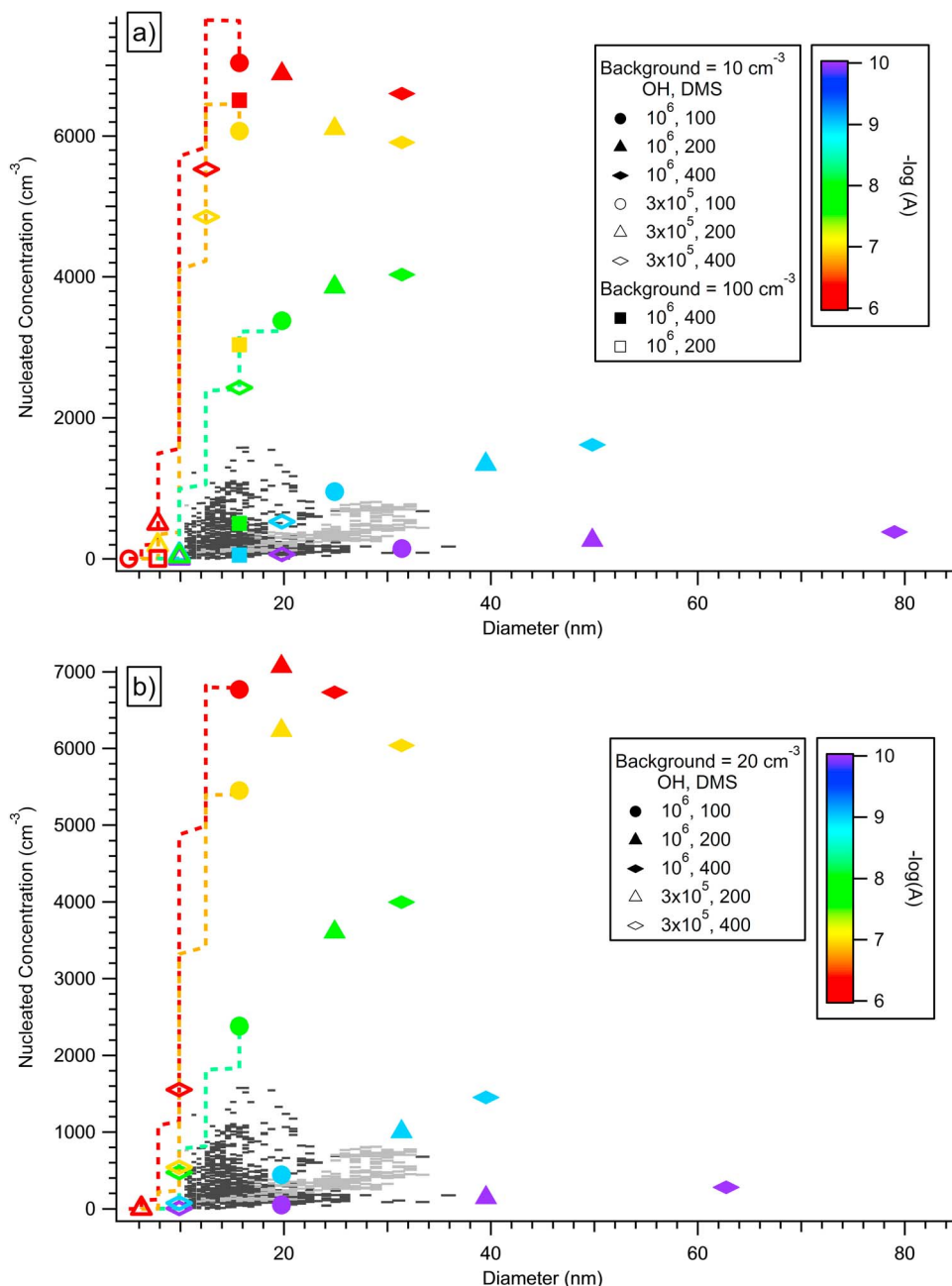
Figure 6. Nucleated number concentration and modal diameter for different model runs. Closed and open symbols are for $[OH] = 10^6$ and 3×10^5 molecules cm^{-3}, respectively. The shape of the symbol represents the atmospheric DMS mixing ratio (pptv) and the color represents different A factors (s^{-1}). Shaded gray bars represent the observed number concentration and modal diameter during the three periods, with the lighter bars representing the first event and the darker bars representing the 2nd and 3rd events. Dashed lines represent the trajectory for selected model runs. (a) For a background particle concentration of 10 and 100 cm^{-3} and (b) for background concentrations of 20 cm^{-3}.

or growth of the aerosols, or the particles are not formed locally. On the other hand, if there are sets of input parameters that do reproduce the nucleation and growth, it is possible that DMS is the dominant species involved with the nucleation and growth. This does not, however, rule out the possibility of other species contributing due to uncertainties in the actual values of the inputs.

4.2. Model Results and Discussion

[25] A simulated nucleation event using TOMAS is shown in Figure 5, assuming that the initial condensation sink is 0.70 m^{-2}, A factor is 10^{-10} s^{-1}, DMS mixing ratio is 400 pptv and [OH] is 10^6 molecules cm^{-3}. As shown in this example, it is possible, under favorable conditions, for nucleation followed by growth to 80 nm to occur. In this

Table 2. Parameter Combinations of Model Runs That Coincide With Observed Nucleation and Growth Events Identified in Figure 2[a]

A (s^{-1})	Bkgd (cm^{-3})	[OH] (molecules cm^{-3})	DMS (pptv)	Event
10^{-10}	10	3×10^5	≥ 200	1,2,3
10^{-10}	10	10^6	≥ 100	1,2,3
10^{-9}	10	3×10^5	≥ 200	1,2,3
10^{-9}	10	10^6	≥ 100	1,2,3
10^{-9}	100	10^6	400	1,2,3
10^{-8}	10	3×10^5	≥ 200	2,3
10^{-8}	10	10^6	≥ 100	2,3
10^{-7}	100	10^6	400	1,2,3
10^{-7}	10	3×10^5	400	2,3
10^{-7}	10	10^6	≥ 100	2,3

[a]Bkgd refers to the background aerosol concentration and DMS refers to the initial DMS mixing ratio.

analysis, simulations that resulted in the number concentration of particles larger than 10 nm to be greater at the end of the 48 h run compared to the beginning are classified as nucleation and growth events. The end point of all model runs that resulted in nucleation and growth are shown as colored symbols in Figure 6. The vertical axis in this figure represents the number of nucleated particles at the end of the simulation (i.e., the increase in the number of particles > 10 nm) and the horizontal axis represents the diameter of the mode. The dashed lines illustrate the evolution of the number concentration and mode of the nucleated particles and these intermediate values should be considered when comparing to observations since the particles may have had < 48 h to nucleate. Only the trajectories of selected model runs are included to keep the graph clear, however, model runs with the same initial DMS mixing ratio follow similar trajectories for concentrations < 2000 cm^{-3}, although initial higher DMS mixing ratios cause the nucleated particles to grow larger. The gray bars shown in the background are measured number concentrations and modes from the three event periods in 2008 and correspond to the modal diameters shown by the black dots in the fifth panel of Figure 2.

[26] Given the assumptions made in our model and described above, Figure 6 shows that there are conditions under which sulfate from DMS oxidation can account for the nucleation and growth observed during the 2008 study. Since the SMPS has a lower cutoff point of 10 nm, measured particle modes of 10–15 nm may correspond to modeled cases with modes < 10 nm whose distribution extends to sizes larger than 10 nm (e.g., modeled particles with a mode of 8 nm will have a tail that extends to > 10 nm where it would be observed by the SMPS). This is supported by the particle concentration between 3 and 10 nm (Figure 2, black dots in fourth panel). In general, the conditions required are an A factor $\leq 10^{-7}$ s^{-1}, [OH] $\geq 3 \times 10^5$ molecules cm^{-3} and background particle concentrations of ≤ 100 cm^{-3} (summarized in Table 2). These model runs have maximum H_2SO_4 concentrations of 10^6 to 10^7 molecules cm^{-3}. In our simulations, an A factor of 10^{-6} s^{-1} tends to promote too much nucleation and not enough growth, resulting in too many particles that are smaller than those observed. In addition, for lower [OH] (i.e., 10^5 molecules cm^{-3}) nucleation is not predicted.

[27] The observations in Figure 6 are colored by date, with the dark gray bars representing the second and third periods in

which NMP were observed, when the particles rarely grew beyond 30 nm. For example, for a background particle concentration of 10 particles cm^{-3}, the model can reproduce the observed aerosol properties if [OH] = 10^6 molecules cm^{-3}, the A factor $\leq 10^{-7}$ s^{-1} and DMS(g) mixing ratio ≤ 400 pptv (Figure 6a). As can be seen from Figures 6a and 6b, other combinations of parameters could result in the small particles observed, and these are summarized in Table 2. In contrast, in order to reproduce the growth event observed during the first period (27 to 28 August 2008), shown in Figure 6 as light gray bars, lower A factors (10^{-10}–10^{-8} s^{-1}) are needed.

[28] The A factors found to fit the observations (10^{-10} to 10^{-7} s^{-1}) are 0–4 orders of magnitude lower than those observed at continental sites (10^{-8} to 10^{-4} s^{-1}) [*Riipinen et al.*, 2007; *Sihto et al.*, 2006] and laboratory experiments (3×10^{-6} s^{-1}) [*Sipila et al.*, 2010]. These results are consistent with *Korhonen et al.* [2008], who used an A factor of 2×10^{-6} s^{-1} for the Arctic in a global chemical transport model but also overpredicted the number concentration in the summer nucleation-mode. Similarly, *Yu et al.* [2010] used a global model with an A factor of 10^{-6} s^{-1} and overpredicted particles with diameters > 4 nm in tropical and polar oceans. Our results show that either activation nucleation (with stable sub-critical clusters requiring a single sulfuric acid molecule exist in abundance) is not occurring or the number of stable sub-critical clusters is much less abundant in the Arctic. Recent laboratory findings have indicated that the nucleation rate depends linearly on the product of both sulfuric acid and low-volatility organic concentrations [*Metzger et al.*, 2010], i.e., J = k[NucOrg] [H_2SO_4], where [NucOrg] is the concentration of low-volatility organic compounds and would make A = k[NucOrg]. It is possible that fewer low-volatility organic compounds are present in the Arctic compared to the continental sites where higher A values have described nucleation rates when fit to activation theory. If the nucleation mechanisms measured by *Metzger et al.* [2010] are relevant in the Arctic, smaller low-volatility organic concentrations would lead to a lower apparent A factor when fit to activation theory. It is also possible that other contributing species, such as ammonia or alkyl amines, are also at lower levels in marine environments. However, as Arctic nucleation mechanisms are still poorly understood, other factors that inhibit aerosol nucleation but favor growth may be present.

[29] Another explanation, especially in the case of the first episode when particle growth was observed and for which low A values were needed to explain the observations, is that the particles did not nucleate from DMS-derived H_2SO_4 but were instead 10-nanometer-sized primary particles originating from the sea surface microlayer [*Leck and Bigg*, 2005, 2010]. The observed growth could then be attributed to the condensation of DMS oxidation products onto these primary particles, which we did not attempt to model.

[30] A final explanation is that [H_2SO_4] is overpredicted in our model, whether due to OH concentrations or SO_2 yields that are too high, which would increase the A-factor so that it is closer to literature values. This can be observed in the open red, orange and green circles and triangles in Figure 6a which corresponds to lower DMS mixing ratios (equivalent to decreasing the SO_2 yield), [OH] = 3×10^5 cm^{-3} and A-factors of 10^{-8}–10^{-6} s^{-1}. Under these conditions, particle formation - not growth - is predicted to occur. Therefore, an additional

condensable material such as low-volatility organics [*Riipinen et al.*, 2011] would be necessary for growth.

[31] In these model runs, the accommodation coefficient was assumed to be 0.65 and its effect on the results was not tested. If the accommodation coefficient was lower (e.g., 0.02 [*Van Dingenen and Raes*, 1991]), sulfuric acid vapor concentrations would increase and the A-factor would need to be lowered in order for the model to match both the number and size of particles. Conversely, if the accommodation coefficient was higher (e.g., ~1 [*Jefferson et al.*, 1997]), the opposite would be true. However, neither would change our conclusion that DMS could account for nucleation and growth of the particles in the Arctic.

[32] The sensitivity of model results to uncertainties in DMS chemistry was also untested. In the oxidation of DMS by OH addition, the branching ratio between SO_2 and methane sulfonic acid (MSA) is uncertain and, following *Chin et al.* [1996], we used a value of 75:25. Laboratory studies report percent yields of SO_2:MSA of 65:4 [*Yin et al.*, 1990a], 27:6 [*Sørensen et al.*, 1996] and 38:11 [*Arsene et al.*, 2001], for example. These SO_2 yields are as low as a third of our model value. However, lower SO_2 yields would only lower SO_2 production and subsequent H_2SO_4 production, resulting in lower nucleation rates as well as growth rates. Furthermore, this would have the same effect as decreasing the initial DMS mixing ratio (i.e., halving the SO_2 yield has the same effect as halving the initial DMS mixing ratio), to which our results are least sensitive compared to the other tested parameters (e.g., OH concentration, A-factor). Similar arguments can be made for the presence of the NO_3 and BrO oxidants, which would effectively enhance the OH abstraction and addition pathways, respectively. In both of these cases, SO_2 yields would increase and result in greater sulphur mass in the system, the effect of which is captured by the range of initial DMS mixing ratio and OH concentrations tested with the aerosol box model. In general, however, we suspect that the NO_3 mixing ratios would be low in this pristine environment, and BrO mixing ratios tend to be elevated in the springtime. Nevertheless, without measurements we cannot be fully confident that OH is the prime oxidant of DMS.

5. Conclusions and Atmospheric Implications

[33] This study reports the observation of nucleation in the Arctic MBL coinciding with high atmospheric DMS during August to September 2008. Elevated surface ocean DMS concentrations suggest that the local ocean was biologically active enough to be the source of atmospheric DMS (Motard-Côté et al., submitted manuscript, 2011). An aerosol microphysics box model including a sulfur scheme using observed DMS mixing ratios as an initial condition was run to simulate the observed nucleation and growth events. Based on our model results, we show that MBL DMS alone could explain the observed aerosol nucleation and growth for an initial DMS mixing ratio of $\geq$ 100 pptv, $[OH] \geq 3 \times 10^5$ molecules cm^{-3}, an A factor $\leq 10^{-7}$ and a background particle concentration $\leq$ 100 cm^{-3}. Although we cannot rule out the role of condensable organic compounds, ultrafine primary oceanic particles arising from bubble bursting, or subsidence from the free troposphere, we have no need to invoke them to explain the observations. These findings are complementary to those of Rempillo et al. (submitted manuscript, 2011) who observed biogenic contributions to the sulfur in particles $\leq$ 10 μm during the cruise. Taken together, the results from both of these studies suggest that biogenic sulfur in the Arctic can affect both small particles, by forming new particles, as well as larger particles, by contributing particle mass. Both of these effects can affect the overall radiation budget of the Arctic.

[34] In contrast, measurements taken later in the season (fall 2007) at similar latitudes did not reveal any nucleation or nucleation-mode particles. This is likely due to lower solar radiation, which resulted in lower OH production rates, lower ocean surface DMS concentrations, and possibly differences in marine biology between the western and eastern Canadian Arctic. As more of the Arctic marine regions become increasingly ice free in summer, oceanic input of gaseous aerosol precursors into the atmosphere will become more important. Further measurements of the type presented in this paper are needed to document how the particle numbers in the Arctic are responding to such climate change.

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