

Importance of submicron surface-active organic aerosols for pristine Arctic clouds

By ULRIKE LOHMANN^{1*} and CAROLINE LECK², ¹*ETH Institute for Atmospheric and Climate Science, Schafmattstr. 30, CH-8093 Zurich, Switzerland;* ²*Department of Meteorology, Stockholm University, S-106 91 Stockholm, Sweden*

(Manuscript received 1 October 2004; in final form 14 January 2005)

ABSTRACT

Recent results from summer measurement campaigns over the partly ice covered central Arctic Ocean show that the high Arctic aerosol has a larger organic fraction than previously thought. We use a Lagrangian parcel model to infer the properties of the unexplained organic aerosol fraction that is necessary for reproducing the observed concentrations of cloud condensation nuclei (CCN). With increasing distance from the open ocean a highly surface-active Aitken mode, associated with particles found in the open lead surface microlayer, becomes increasingly important for cloud droplet formation. The presence of such an Aitken mode population increases the high Arctic indirect aerosol effect (added cooling) relative to just a marine source of CCN from oxidation products of dimethyl sulfide (DMS) released from phytoplankton.

1. Introduction

Atmospheric aerosol particles consist of a variety of chemical compositions, including both organic and inorganic constituents. Traditionally only water-soluble inorganic constituents such as ammonium sulfate or sea salt were thought to act as cloud condensation nuclei (CCN) in the Arctic (Heintzenberg and Leck, 1994; Leck and Persson, 1996b). However, two local sources involving organic compounds have been found recently (Leck et al., 2002): particles derived from bubbles bursting on open water between ice floes (film and jet drops) and particles reaching CCN size by acquisition of oxidation products of dimethyl sulfide (ammonium sulfate and bisulfate, methane sulfonate and sulfuric acid). The film drop particles were mainly organic in nature and the jet drop mode was composed largely of sea salt. Organic coatings of atmospheric particles containing surface-active carboxylic acids have also been found recently (Russell et al., 2002). Surface-active organic aerosols lower the surface tension, which could enhance the number concentration of cloud droplets and cloud albedo and thus lead to a global mean negative forcing of up to -1 W m^{-2} (Facchini et al., 1999). This is of the same magnitude as the estimated indirect aerosol effect of increasing cloud albedo and cloud lifetime (Lohmann and Lesins, 2002).

In searching for a relationship between the properties of the summer high Arctic aerosol and its ability to form CCN, given the presence of a multiphase (inorganic/organic) aerosol system, it was found by assuming equilibrium Köhler theory and measured number size distribution that components other than sulfate or sea salt, probably organics, depressed the nucleating ability of the particles during cloudy conditions (Leck et al., 2002). However, on clear sky days there were a majority of occasions on which measured CCN concentrations were greater than predicted from a pure sulfate/sea salt composition. These opposing results indicated that the observed presence of organic constituents in the aerosol will play an important role in determining the ability of the atmospheric aerosol to act as CCN.

Intrigued by the results of Leck et al. (2002), in this paper we examine in more detail the aerosol chemical composition and surface activity required to explain the observed CCN concentrations at various locations over the pristine summertime central Arctic Ocean. Since the Köhler theory cannot take kinetic effects into account, which can cause erroneous results when the competition of different size aerosol particles for water vapour is studied (Phinney et al., 2003), the cloud nucleation process is instead simulated with a Lagrangian parcel model (Shantz et al., 2003; Lohmann et al., 2004).

2. Data description

Data from the mostly ice-covered central Arctic Ocean between 73.5 and 90°N, from 15 July to 23 September 1996, obtained

*Corresponding author.
e-mail: ulrike.lohmann@env.ethz.ch

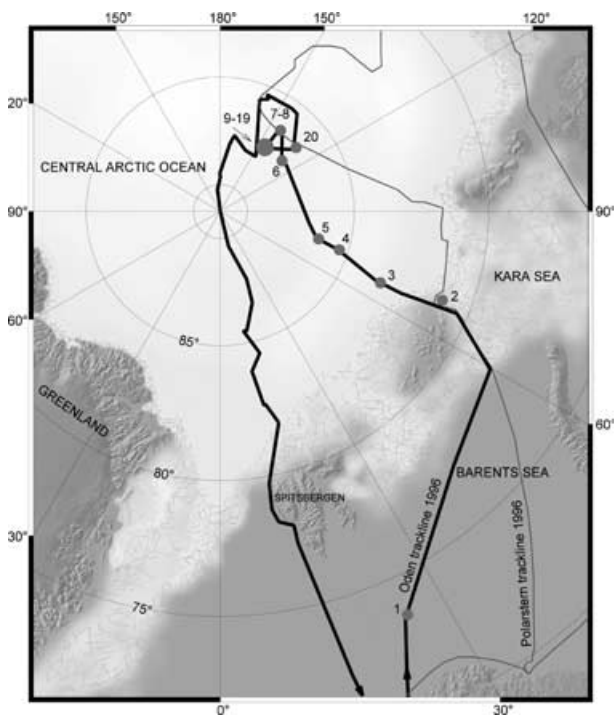


Fig. 1. Map of study area showing the ice breaker *Oden* during the Arctic Ocean Experiment, 1996 (AOE-96) adapted from Leck et al. (2001). Stations with between 12 to 24 h continuous sampling are marked in red. The “ice camp” (station 19) is in the immediate vicinity of stations 9–18. The edge of the ice is illustrated as the grey line.

during the Arctic Ocean Experiment (AOE-96) (Leck et al., 2001) are used in the analysis. The experiment was designed to obtain detailed measurements of the aerosol system with a minimal influence of anthropogenic sources, as the Arctic polar front is furthest north in summer (Leck et al., 2001).

Figure 1 shows the cruise track and the locations of the 20 most intensively sampled stations of 12–24 h duration. These stations were classified as not affected by anthropogenic sources at the height of the sampling inlet. The sampling system inlet for aerosol particles was equipped with an Anderson impactor removing particles larger than $5 \mu\text{m}$ aerodynamic radius. The inlet was located 25 m above the sea surface. Direct contamination from the ship was excluded by control of condensation nuclei with a wind controller. Leck et al. (2001) describe the sampling system in more detail. A similar DMPS (differential mobility particle sizing system) to that used by Covert et al. (1996) and an added PMS PCASP-X optical particle counter gave dry number size distributions in the geometric mean radius size range of 2.5 nm to $5 \mu\text{m}$ every 10 min. For further interpretation in the present study the 27+32-channel number size distributions were aggregated into three log-normal size distributions referred to as the Aitken, accumulation and coarse modes. They were fitted to the measured data with the method of Birmili et al. (2001). To measure the growth of particles of a given size from the dry state

to a set relative humidity (RH) a tandem differential mobility analyser was used (Zhou et al., 2001).

To measure size-resolved aerosol mass, duplicate high-volume ($80 \text{ dm}^3 \text{ min}^{-1}$) low-pressure Berner cascade impactors (BCIs) (Berner et al., 1979) collected particles at a controlled RH of 50% in the size ranges <0.081 , $0.081\text{--}0.333$, $0.333\text{--}1.06$, $1.06\text{--}2.5$ and $2.5\text{--}5 \mu\text{m}$ aerodynamic radius with a 50% collection efficiency. Converted to dry (20% RH) geometric mean radius the BCI size ranges corresponded to <0.056 , $0.056\text{--}0.245$, $0.245\text{--}0.790$, $0.790\text{--}1.87$ and $1.87\text{--}3.74 \mu\text{m}$ (Tang and Munkelwitz, 1994). The BCIs collected enough substrate material for analysis of water-soluble anions (chlorine, Cl^- ; methane sulfonate (MSA), CH_3SOO^- ; oxalate, $\text{C}_2 \text{O}_4^{2-}$; succinate, $\text{C}_4\text{H}_4 \text{O}_4^{2-}$; glutarate, $\text{C}_5 \text{H}_6 \text{O}_4^{2-}$; nitrate, NO_3^- ; sulfate, SO_4^{2-}) and cations (ammonium, NH_4^+ ; sodium, Na^+ ; potassium, K^+ ; magnesium, Mg^{2+} ; calcium, Ca^{2+}) in 4 h in the early stages of the voyage and in up to 12 h later in the voyage. Analysis of the BCI substrate extracts was performed using ion chromatography (Leck et al., 2002). More details about the BCIs can be found in Hillamo et al. (2001) and Leck et al. (2002). Concentrations of CCN were measured every 48 s using a system that compared the number of particles emerging from a supersaturated (0.1–0.4%) thermal diffusion chamber with those from an otherwise identical isothermal chamber, described by Bigg and Leck (2001b). All systems apart from the BCIs were sampled at 20% RH.

Here we select data observed at four of the stations encountered between 20 July and 24 August. The locations of these stations were: (1) over the open water, (2) within the marginal ice zone (MIZ) with 20–70% ice cover, (3) within the pack ice (80–95% ice cover) and (4) station 19, referred to as the “ice camp”, located furthest north. The geographical coordinates are given in Table 1. Furthermore, the selected stations represent different times of advection of air from the dimethyl sulfide (DMS) source area in the open ocean just south of MIZ (Leck and Persson, 1996a,b). Air masses at stations 3, and the “ice camp” had their last contact with the open ocean 38 and 100 h ago respectively (Kerminen and Leck, 2001; Nilsson, 1996). This provided a semi-Lagrangian data set to investigate the life cycle of the high Arctic aerosol with its two sources, DMS and the open lead primary particle source.

The non-sea-salt sulfate component (nss-SO_4^{2-}) was calculated by using the observed Na^+ concentrations and the Na^+ to SO_4^{2-} ratio in sea water (Tang et al., 1997). These authors state the molar ratio of sea salt to be composed of 83.5% NaCl , 10.8% MgCl_2 and 5.7% Na_2SO_4 yielding a molecular weight of the sea salt mixture of 67.18 g mol^{-1} . For molar ratio values of $\text{NH}_4^+/\text{nss-SO}_4^{2-} > 1$, the aerosol was supposed to be composed of ammonium sulfate. The remaining fraction of nss-SO_4^{2-} that was not being neutralized by the available NH_4^+ was assumed to be sulfuric acid. For $\text{NH}_4^+/\text{nss-SO}_4^{2-} < 1$ an internal mixture of ammonium bisulfate and sulfuric acid was assumed. Because of the discrepancy in RH of the different aerosol

Table 1. Measured concentration of sulfur compounds (MSA+nss-SO₄²⁻), ammonium (NH₄⁺), sea salt and the sum of the analysed organics (oxalic acid, succinic acid and glutaric acid) and modal parameters of the aerosol size distribution: total and unexplained aerosol number concentration N_a and N_{unexpl} , respectively, mode radius r_N , and standard deviation σ , CCN concentration and maximum supersaturation S_{max} and their standard deviations. All values represent an average for each station. The marine transport time (Mtr) refers to the time elapsed since the air last had contact with the marine source as calculated from back trajectories (Kerminen and Leck, 2001)

Compound/modal parameter	Aitken mode	Accum. mode	Coarse mode
Station 1 (73.5°N, 25.3°E, Mtr = 0 h)			
MSA+nss-SO ₄ ²⁻ (ng m ⁻³)	51.9	1152.9	548.3
NH ₄ ⁺ (ng m ⁻³)	13.9	246.7	104.2
Sea salt (ng m ⁻³)	–	124.0	5656.9
Organics (ng m ⁻³)	2.0	32.2	36.1
N_a (cm ⁻³)	411.	191.	18.3
N_{unexpl} (cm ⁻³)	166.	125.	4.7
r_N (nm)	30.9	121.	299.
σ	1.37	1.53	1.61
CCN (cm ⁻³), S_{max} (%)	245.8±91.6	0.22±0.03	
Station 2 (81.2°N, 68.5°E, Mtr = 12 h)			
MSA+nss-SO ₄ ²⁻ (ng m ⁻³)	20.5	55.1	1.1
NH ₄ ⁺ (ng m ⁻³)	2.6	12.0	0.
Sea salt (ng m ⁻³)	–	39.7	2425.6
Organics (ng m ⁻³)	1.9	38.9	32.8
N_a (cm ⁻³)	186.	81.6	12.
N_{unexpl} (cm ⁻³)	147.	65.3	—
r_N (nm)	37.3	88.1	253.
σ	1.49	1.50	1.43
CCN (cm ⁻³), S_{max} (%)	104.4±34.6	0.25±0.04	
Station 3 (83.5°N, 66.0°E, Mtr = 38 h)			
MSA+nss-SO ₄ ²⁻ (ng m ⁻³)	12.5	21.0	1.51
NH ₄ ⁺ (ng m ⁻³)	4.7	4.7	13.6
Sea salt (ng m ⁻³)	–	1.6	88.8
Organics (ng m ⁻³)	4.3	15.4	6.9
N_a (cm ⁻³)	291.	13.2	1.1
N_{unexpl} (cm ⁻³)	162.	8.0	0.5
r_N (nm)	26.1	85.7	376.
σ	1.36	1.32	1.30
CCN (cm ⁻³), S_{max} (%)	33.6±13.8	0.25±0.03	
“Ice camp” (87°N, 143°E, Mtr = 100 h)			
MSA+nss-SO ₄ ²⁻ (ng m ⁻³)	4.0	33.0	3.5
NH ₄ ⁺ (ng m ⁻³)	2.0	4.5	1.7
Sea salt (ng m ⁻³)	–	11.3	146.0
Organics (ng m ⁻³)	0.3	1.0	0.6
N_a (cm ⁻³)	173.	5.2	0.7
N_{unexpl} (cm ⁻³)	136.	3.8	0.2
r_N (nm)	25.2	148	309
σ	1.43	1.43	1.37
CCN (cm ⁻³), S_{max} (%)	40.0±13.8	0.25±0.02	

samplers, we have calculated the water uptake associated with ammonium sulfate and sea salt from 20% RH to 50% RH, at which the BCI sample was taken, following Seinfeld and Pandis (1997) and Tang (1997). This reduces the sea salt density from a dry density of 2.24 g cm⁻³ to a density of 1.52 g cm⁻³

at 50% RH and the density for ammonium sulfate from 1.77 to 1.42 g cm⁻³.

Also shown in Table 1 is the number fraction not explained by the chemical analysis (N_{unexpl}), which was calculated according to the following assumptions. The size range collected by

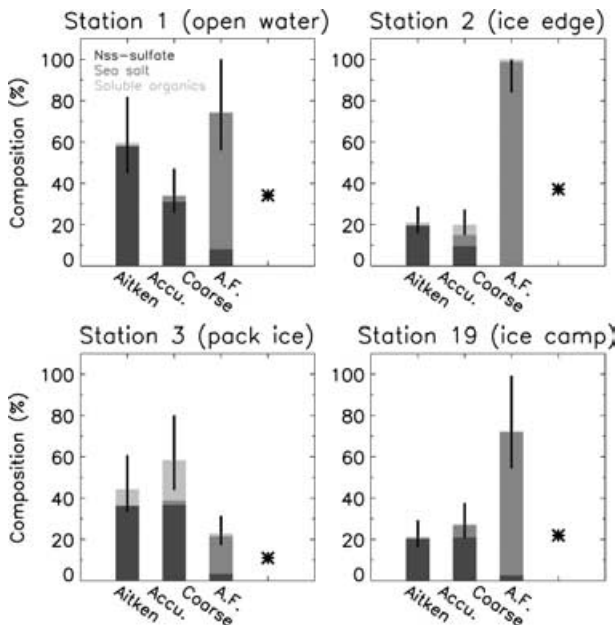


Fig. 2. Chemical composition (%) in each mode and activated fraction (A.F.) at the four Arctic stations. The vertical bars denote the explained fraction assuming a 10% smaller or larger mode radius, respectively.

each impactor stage was designed to correspond to the most common modes of appearance of the number size distribution. The analysed mass at each stage was converted to a number of particles by assuming a particle density and the relevant modal radius. The resulting number was then compared with the actual particle number observed in this size range.

As can be seen in Fig. 2 only the coarse mode at station 2 was fully explained by the analysed water-soluble components, dominated by sea salt. However, the chemistry of both the coarse mode (still dominated by sea salt) at the remaining stations and the Aitken and accumulation modes at all stations could at best be explained to 80%, overall varying between 25 and 80%. Uncertainties in the number-to-mass analysis that could influence our results stem from: (1) fitting log-normal distributions to a number distribution, which is not always entirely accurate; (2) the fact that conversions from mass to number are fraught with difficulty given the highly non-linear relationship involved; (3) the fact that the size cuts from the Berner impactor are not delta functions, even though there is no overlap between the different size functions; (4) the uncertainty in mass that arises from the chemical analyses; (5) uncertainties in the measured growth factors. Therefore we repeated each subsequent simulation twice, once using a 10% smaller radius in each mode for the conversion from mass to number and once using a 10% larger radius in each mode. This increases the explained fraction up to 30% in the coarse mode at stations 1 and 19 (Fig. 2).

The explained number fraction of the Aitken mode at all stations was dominated by nss-SO_4^{2-} , organics being of secondary

importance and sea salt not being detected. The overall dominance of nss-SO_4^{2-} also applied to the accumulation mode followed by sea salt, except at station 3 where soluble organics were the second most abundant compounds. However, a large percentage of the particle number concentration was still not explained. Electron microscope examinations of single airborne particles showed distinct particle types that might provide an explanation. Examples are shown in Fig. 3. The first consists of single or aggregates of a few water-insoluble Aitken sized particles. The latter were held together by a gel-like material that was found to be associated with particles of the ocean surface microlayer (Bigg et al., 2004; Leck and Bigg, 2005). In the accumulation mode, liquid particles that wet the surface were present and included many of the small water-insoluble Aitken particles. Finally, *in situ* generated sea salt particles were nearly always surrounded by an organic film which was probably due to the breakdown of the gel component associated with the jet drops that result in the formation of a sea salt particle. Aged in the atmosphere, the sea salt particles were found to be internally mixed with sulfuric acid. In each case, but for the single Aitken mode particles, a surface-active organic component seems to have been an important internally mixed part of the particles.

3. Model description and design of the sensitivity simulations

To simulate the cloud nucleation process a Lagrangian adiabatic air parcel model (Lohmann et al., 2004) that solves the kinetic formulation for condensation of water on aerosol particles, based on the diffusional growth equation, was used. In all simulations we assumed a trimodal log-normal aerosol size distribution with the observed modal number radius and standard deviation given in Table 1. Also listed in Table 1 are the aerosol chemical properties used as input data. The chemical information needed for each salt in the parcel model is summarized in Table 2. For simplicity we treated the three analysed organic constituents (oxalic acid, succinic acid and glutaric acid) as oxalic acid. Sensitivity studies assuming glutaric acid instead of oxalic acid gave very similar results (not shown). As a surrogate for the unexplained number fraction in the reference case (simulation Ref - see Table 3) we used the organic aerosol adipic acid, a slightly water-soluble dicarboxylic acid, which has been observed in ambient particulate matter including in the Arctic (Narukawa et al., 2002). Guided by the electron microscope analysis (Fig. 3 and Bigg and Leck, 2001b; Leck and Bigg, 2005), we assumed the adipic acid particles to be externally mixed in the Aitken mode and internally mixed in the accumulation and coarse modes in the reference simulation (simulation Ref). To ensure that the adipic acid Aitken mode aerosol retained water at RH below saturation a 0.1% sulfuric acid coating was added (see also Lohmann et al., 2004). The surface tension of the internally mixed accumulation and coarse modes aerosol was obtained by weighting the surface tension of each soluble constituent by its mass fraction.

Fig. 3. The changing nature of particles in different size ranges: A, a single particle with pentagonal/hexagonal habit, crystalline and water insoluble (20 nm); B, same as in A but larger (40 nm); C, aggregates of A and B type particles held together with a gel-like material (70 nm); D, a gel-like material with type A and B inclusions surrounding an ammonium bisulfate particle (90 nm); E, an aggregate surrounded by a marine film drop particle with surfactant properties (150 nm); F, a sulfur particle in which any nucleus has been obscured by the surrounding of a sulfate–methane sulfonate–ammonium complex (300 nm); G, a sea salt particle and a rod bacterium surrounded by an organic film and sulfuric acid (500 nm).

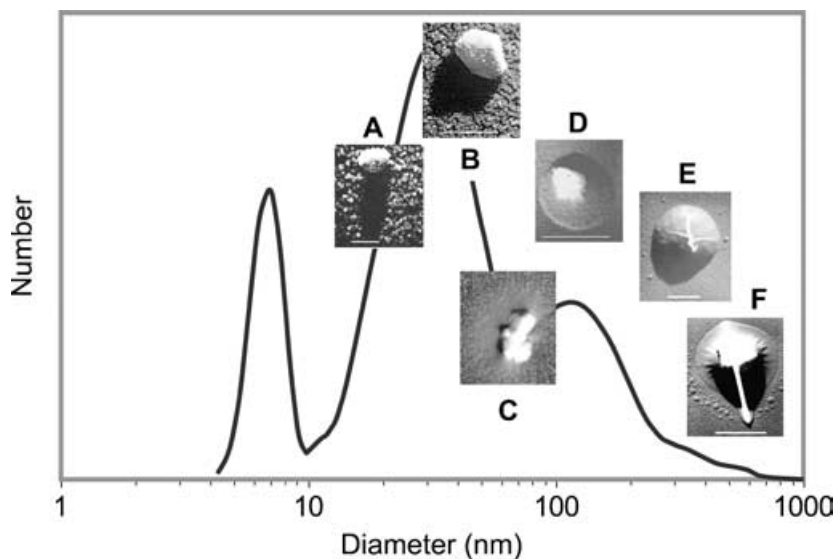


Table 2. Chemical properties of investigated compounds^a

Chemical constituents	Formula	Molecular weight (g mol ⁻¹)	Density (g cm ⁻³)	Solubility (g l ⁻¹)	Surface tension (mN m ⁻¹)	ν
Ammonium sulfate	(NH ₄) ₂ SO ₄	132.1	1.77	Full ^b	76 ^c	3
Ammonium bisulfate	NH ₄ HSO ₄	115.1	1.78	Full	76 ^c	3
Sulfuric acid	H ₂ SO ₄	98.1	1.84	Full	76 ^c	3
Sea salt	NaCl	67.18 ^d	2.24	Full	76 ^c	2.2
Oxalic acid	C ₂ H ₂ O ₄	90.0	1.90	Full	73 ^{e,f}	1.6
Adipic acid	C ₆ H ₁₀ O ₄	146.1	1.36	25	68 ^e	1
Nonanoic acid	C ₉ H ₁₈ O ₂	158.2	0.91	0.26	31 ^e	1

^aData taken from Broekhuizen et al. (2004) and Kumar et al. (2003).

^bFull solubility means that these constituents are assumed to be fully dissolved at the starting RH of 99%.

^cSolute- and temperature-dependent data are taken from Pruppacher and Klett (1997).

^dSea salt is assumed to consist of NaCl, MgCl₂ and Na₂SO₄ as described in the text (Tang et al., 1997).

^eValues refer to the saturated solution.

^fPolynomial fits from Shulman (1995) are used.

Again guided by electron microscope images (Fig. 3) that showed examples of particles covered with some highly surface-active material, we performed simulations in which we assumed that the surface tension of a fraction of the unexplained Aitken mode (15 or 65%) or the entire Aitken mode and of the accumulation and coarse modes are as surface active as nonanoic acid (see Table 3). In the case Ref/AANA the particles are as soluble as adipic acid whereas in the case Ref/NA the solubility of nonanoic acid is used. The choice of nonanoic acid as a surrogate for the surface-active compound was based on the laboratory results by Broekhuizen et al. (2004) but other substances such as benzene, acetone or styrene would be as surface active (Seinfeld and Pandis, 1997). As discussed below, the choice of making the accumulation and coarse mode surface active is not crucial because the majority of these particles were already activated in simulation Ref.

The Ref cases were repeated but assuming an internally mixed Aitken mode because an internally mixed Aitken mode is (a) consistent with an aged aerosol and (b) cannot be discarded from the electron microscope images. This is due to shortcomings with the detection of insoluble inclusions, which arise if their opacity to electrons is similar to the opacity of the surrounding material, if the thickness of overlying material is too great to allow electrons to penetrate as far as the inclusions, or if a shadowing metal was used that rendered the surface opaque to electrons. Lastly, because the notion of an organic fraction in the Arctic aerosol is rather new, we also conduct a simulation (simulation Sol) in which the unexplained fraction is set to zero, i.e. the aerosol consists only of sea salt, sulfate, ammonium and the soluble organics.

In the parcel model cloud droplets were defined as particles with a wet radius larger than 1 μm and having a positive growth

Table 3. Sensitivity simulations

Simulation	Description
Ref	Using all analysed compounds from Table 1 and assuming the unexplained fraction to be adipic acid
Ref/NA	As simulation Ref, but assuming the unexplained fraction to be nonanoic acid
Ref/AANA	As simulation Ref, but assuming that the surface tension of the unexplained Aitken mode and of all the particles in the internally mixed accumulation and coarse modes is governed by that of the highly surface active nonanoic acid
Ref/AANA15	As simulation Ref/AANA, but assuming that 15% of the unexplained Aitken mode is as surface active as nonanoic acid
Ref/AANA65	As simulation Ref/AANA15, but assuming that 65% of the unexplained Aitken mode is as surface active as nonanoic acid
Int	As simulation Ref, but assuming that the Aitken mode is internally mixed as well
Int/NA	As simulation Ref/NA, but assuming that the Aitken mode is internally mixed as well
Int/NAsp	As simulation Int/NA, but including a surface partitioning model (Sorjamaa et al., 2004)
Sol	As simulation Ref, but assuming the unexplained fraction to be zero

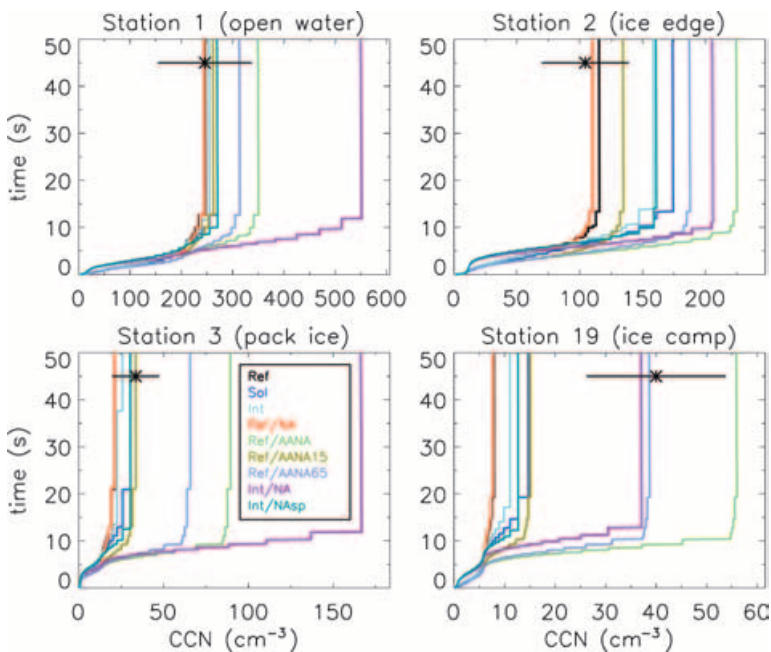


Fig. 4. Simulated CCN number concentration (cm^{-3}) as a function of time at the four Arctic stations for the different scenarios. The observed CCN concentrations are marked with stars and the horizontal lines denote ± 1 standard deviation.

rate. All simulations started at 99.9% RH using the observed temperatures and pressures. The model was set up to mimic a cloud condensation nuclei counter such that it reached the prescribed supersaturation of 0.22–0.25% (Table 1) within 1.5 s (Shantz et al., 2003). The total simulation length was 50 s corresponding to the residence time of the particles in the CCN counter (Bigg and Leck, 2001a).

4. Results

As depicted in Fig. 4, the observed CCN concentrations can be reproduced within the observed standard deviation over the open ocean (station 1) for all scenarios except Int/NA. This demonstrates that the CCN concentration at this station is dominated by the explained species. In the marginal ice zone (station 2)

the disagreement between the simulations is larger. Here we need to assume that at most 15% of the unexplained Aitken mode particles are as surface active as nonanoic acid (simulations Ref and Ref/AANA15). However, if all particles were assumed to be composed of the analysed soluble inorganic and organic compounds only (simulation Sol), if the Aitken mode is also internally mixed (simulations Int, Int/NA, Int/NAsp) or if a larger fraction is surface active (simulations Ref/AANA, Ref/AANA65), the observed CCN levels were over-predicted. These simulations of the CCN levels at station 2 thus indirectly confirmed the previous findings that (a) organic material is present in the aerosol collected within the marginal ice zone and that (b) the Aitken mode particles consist of an external mixture between the analysed water-soluble inorganic and organic compounds and some almost water-insoluble organic

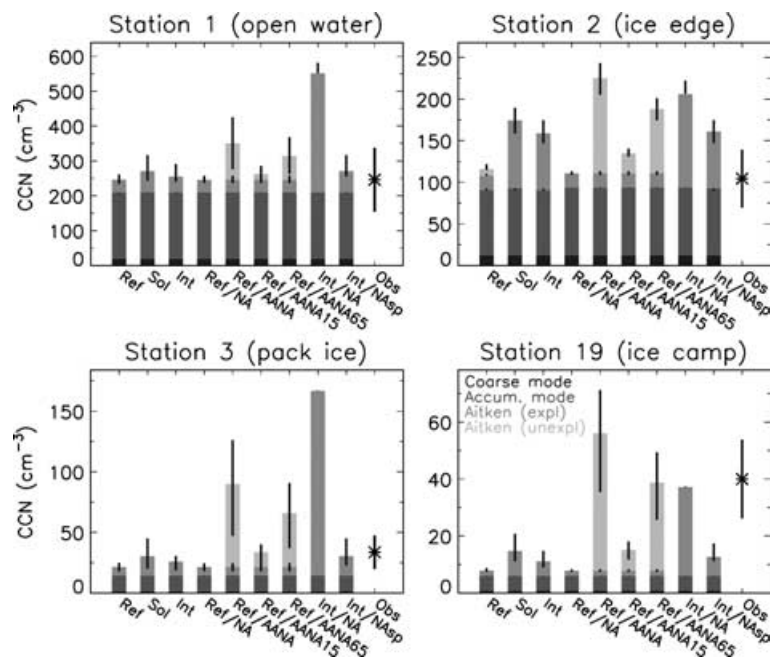


Fig. 5. Contribution of the different aerosol modes to the simulated CCN number concentrations (cm^{-3}) at the four Arctic stations for selected scenarios. The observed CCN are marked with stars and the vertical lines denote ± 1 standard deviation. The vertical bars for the simulations denote the results assuming a 10% smaller or larger mode radius, respectively.

material (Leck and Bigg, 1999; Bigg and Leck, 2001a; Leck et al., 2002).

As the time of advection from the open ocean over the pack ice increased, the relative contribution of Aitken mode particles to the observed CCN population increased, and a source of particles over the pack ice was required to maintain the population. This is clearly demonstrated in Table 1 and Fig. 5. Only at stations 1 and 2 was the sum of the accumulation and coarse mode particles by number sufficient to explain the observed CCN levels within the standard deviation. At station 3 and the ice camp the sum of the accumulation and coarse mode particles by number was less than half of the observed CCN concentration. The chemical composition and the surface activity of the Aitken mode from either the open ocean or over the pack ice is therefore likely to be important in determining CCN concentrations over the pack ice.

As depicted in Figs 4 and 5, the observed CCN concentrations at station 3 were well captured by applying the Sol case. However, this agreement is fortuitous given that the electron microscope images showed the presence of other substances (Fig. 3) on the one hand, and on the other hand because the unexplained fraction at this station varied between 40 and 75% for respective modes (*cf.* Fig. 2). To match the observations, either 15% of the unexplained fraction of the Aitken mode particles need to have trace amounts of a highly surface-active organic, such as nonanoic acid in an external mixture (sim Ref/AANA15), or all modes can be an internal mixture of the explained substances and nonanoic acid when a surface partitioning model (Sorjamaa et al., 2004) is applied (sim Int/NA65). This assumes that part of the soluble surface-active material resides in the interior of the internally mixed aerosol particle.

At the “ice camp” (station 19) where air masses had no contact with the open water for more than 4 d, the contribution of accumulation and coarse mode particles to the observed CCN levels was smallest and comprised only 15% of the CCN. Here the model simulations suggested that 65% of the unexplained fraction of the Aitken mode particles needs to be as highly surface active as nonanoic acid and as soluble as adipic acid in an external mixture in order to match the observed CCN levels (simulation Ref/AANA65). On the other hand, the observed CCN levels can also be reproduced if an internal mixture of the explained substances and nonanoic acid is assumed with all the nonanoic acid being preferentially at the surface. The former approach is more consistent with the observed nature of the individual particles (Leck and Bigg, 2005).

5. Conclusions

The main conclusion from this work is that it is necessary to invoke an activated Aitken mode with increasing time of advection from the open ocean over the pack ice. This activated Aitken mode over the pack ice has to be composed of surface-active particles from the ocean surface microlayer. If it consisted just of DMS oxidation product particles, that are not surface active, the observed CCN population over the pack ice at stations 3 and 19 cannot be explained. We therefore have a larger natural source than can result from DMS oxidation products alone. If there should be an increase in anthropogenically produced particles in the area at some future date the effect of the presence of activated Aitken mode particles on resulting CCN concentrations depends entirely on the relative spread of supersaturations at which the two groups can form cloud droplets. The natural particle

population is likely to be active at lower supersaturations than the anthropogenic one, because of the surface-active material. In any case, the indirect aerosol effect (added cooling) is enhanced relative to a DMS–oxidation product source of CCN alone. Any external source of CCN will further increase the cooling.

6. Acknowledgments

This work was supported by the Natural Science and Engineering Research Council of Canada and the Swedish Science Foundation. Ulrike Lohmann thanks the International Meteorological Institute for an extended visit. We thank Keith Bigg, Keith Broekhuizen, Glen Lesins, Nicole Shantz and two anonymous reviewers for useful comments and suggestions.

References

- Berner, A., Lürzer, C., Pohl, F., Preining, O. and Wagner, P. 1979. The size distribution of the urban aerosol in Vienna. *Sci. Total Environ.* **13**, 245–261.
- Bigg, E. K. and Leck, C. 2001a. Cloud-active particles over the central Arctic Ocean. *J. Geophys. Res.* **106**, 32 155–32 166.
- Bigg, E. K. and Leck, C. 2001b. Properties of the aerosol over the central Arctic Ocean. *J. Geophys. Res.* **106**, 32 101–32 109.
- Bigg, E. K., Leck, C. and Tranvik, L. 2004. Particulates of the surface microlayer of open water in the central Arctic Ocean in summer. *Marine Chem.* **91**, 131–141.
- Birmili, W., Wiedensohler, A., Heintzenberg, J. and Lehmann, K. 2001. Atmospheric particle number size distribution in Central Europe: statistical relations to air masses and meteorology. *J. Geophys. Res.* **106**, 32 005–32 018.
- Broekhuizen, K., Kumar, P. P. and Abbatt, J. P. D. 2004. Partially soluble organics as cloud condensation nuclei: role of trace soluble and surface active species. *Geophys. Res. Lett.* **31**, doi:10.1029/2003GL018203.
- Covert, D. S., Wiedensohler, A., Aalto, P., Heintzenberg, J., McMurry, P. H. and co-author 1996. Aerosol number size distributions from 3 to 500 nm diameter in the arctic marine boundary layer during summer and autumn. *Tellus* **48B**, 197–212.
- Facchini, M. C., Mircea, M., Fuzzi, S. and Charlson, R. J. 1999. Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature* **401**, 257–259.
- Heintzenberg, J. and Leck, C. 1994. Seasonal variation of the atmospheric aerosol near the top of the marine boundary layer over Spitsbergen related to the Arctic sulphur cycle. *Tellus* **46B**, 52–67.
- Hillamo, R., Kerminen, V.-M., Aurela, M., Mäkelä, T., Maenhaut, W. and co-author 2001. Modal structure of chemical mass size distributions in the high arctic aerosol. *J. Geophys. Res.* **106**, 27 555–27 571.
- Kerminen, V.-M. and Leck, C. 2001. Sulfur chemistry over the central Arctic Ocean during the summer: gas-to-particle transformation. *J. Geophys. Res.* **106**, 32 087–32 099.
- Kumar, P. P., Broekhuizen, K. and Abbatt, J. P. D. 2003. Organic acids as cloud condensation nuclei: laboratory studies of highly soluble and insoluble species. *Atmos. Chem. Phys.* **3**, 509–520.
- Leck, C. and Bigg, E. K. 1999. Aerosol production over remote marine areas—a new route. *Geophys. Res. Lett.* **26**, 3577–3580.
- Leck, C. and Bigg, K. 2005. Biogenic particles over the central Arctic Ocean. *Tellus* in press.
- Leck, C., Nilsson, E. D., Bigg, E. K. and Bäcklin, L. 2001. Atmospheric program on the Arctic Ocean Expedition 1996 (AOE-96): an overview of scientific goals, experimental approach, and instruments. *J. Geophys. Res.* **106**, 32 051–32 067.
- Leck, C., Norman, M., Bigg, K. and Hillamo, R. 2002. Chemical composition and sources of the high Arctic aerosol relevant for cloud formation. *J. Geophys. Res.* **107**, doi:10.1029/2001JD001463.
- Leck, C. and Persson, C. 1996a. The central Arctic Ocean as a source of dimethyl sulfide: seasonal variability in relation to biological activity. *Tellus* **48B**, 156–177.
- Leck, C. and Persson, C. 1996b. Seasonal and short-term variability in dimethyl sulfide, sulfur dioxide and biogenic sulfur and sea salt aerosol particles in the arctic marine boundary layer, during summer and autumn. *Tellus* **48B**, 272–299.
- Lohmann, U., Broekhuizen, K., Leaitch, R., Shantz, N. and Abbatt, J. 2004. How efficient is cloud droplet formation of organic aerosols? *Geophys. Res. Lett.* **31**, doi:10.1029/2003GL018999.
- Lohmann, U. and Lesins, G. 2002. Stronger constraints on the anthropogenic indirect aerosol effect. *Science* **298**, 1012–1016.
- Narukawa, M., Kawamura, K., Li, S.-M. and Bottenheim, J. W. 2002. Dicarboxylic acids in the Arctic aerosols and snowpacks collected during ALERT 2000. *Atmos. Environ.* **36**, 2491–2499.
- Nilsson, E. D. 1996. Planetary boundary layer structure and air mass transport during the International Arctic Ocean Expedition 1991. *Tellus* **48B**, 178–196.
- Phinney, L., Lohmann, U. and Leaitch, W. R. 2003. Limitations of using an equilibrium approximation in an aerosol activation parameterisation. *J. Geophys. Res.* **108**, doi:10.1029/2002JD002391.
- Pruppacher, H. R. and Klett, J. D. 1997. *Microphysics of Clouds and Precipitation*. Kluwer Academic, Norwell, MA.
- Russell, L., Maria, S. F. and Myneni, C. B. 2002. Mapping organic coatings on atmospheric particles. *Geophys. Res. Lett.* **29**, doi:10.1029/2002GL014874.
- Seinfeld, J. H. and Pandis, S. N. 1997. *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*. Wiley, New York.
- Shantz, N. C., Leaitch, W. R. and Caffrey, P. 2003. Effect of organics of low solubility on the growth rate of cloud droplets. *J. Geophys. Res.* **108**, doi:10.1029/2002JD002540.
- Shulman, M. L. 1995. Influence of Atmospheric Organic Compounds on Cloud Microphysics. PhD thesis. University of Washington, Seattle, WA.
- Sorjamaa, R., Raatikainen, T. and Laaksonen, A. 2004. The role of surfactants in Köhler theory reconsidered. *Atmos. Chem. Phys. Discuss.* **4**, 2781–2804.
- Tang, I. N. 1997. Thermodynamic and optical properties of mixed-salt aerosols of atmospheric importance. *J. Geophys. Res.* **102**, 1883–1893.
- Tang, I. N. and Munkelwitz, H. R. 1994. Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance. *J. Geophys. Res.* **99**, 18 801–18 808.
- Tang, I. N., Tridico, A. and Fung, K. H. 1997. Thermodynamic and optical properties of sea salt aerosols. *J. Geophys. Res.* **102**, 23 269–23 275.
- Zhou, J., Swietlicki, E., Berg, O. H., Aalto, P. P., Hämeri, K. and co-authors 2001. Hygroscopic properties of aerosol particles over the central Arctic Ocean during summer. *J. Geophys. Res.* **106**, 32 111–32 123.