We are grateful to the reviewers for her/his positive comments and careful reading of the manuscript. Below we address the comments with our answers in blue. The numbering of pages and lines in our answers refer to the new version of the manuscript. Changes in the manuscript are written in red.

Anonymous Referee #1

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It is relatively easy to obtain detailed size distributions and bulk chemistry of aerosols but in order to understand the sources of particles and their individual chemistry, imaging and analysis of separate particles is required. This has not been a popular form of research because it requires the use of electron microscopes and a very large amount of microscope time to study a representative sample of the aerosol. Interpreting the results also requires experience and wide background knowledge of possible sources of the aerosol.

The paper under review is very valuable because it greatly extends previous work of this type on the summer high-Arctic aerosol using improved techniques and studying a remarkably large number of individual particles. I strongly recommend it for publication, but contribute a few comments that might be useful.

1. Sizing of the aerosol from electron microscope imagery is notoriously difficult and in this case has resulted in acceptable agreement with TDMPS size distributions. Subsequent investigators will want to try to compare their work with that under review. It should therefore be made clear what assumptions were made in sizing particles such as A in figure 4 where no shadow is visible, or B in that figure which shows a thin shadow on the lower edge suggesting that it is a flat crystal. Similarly, in figure 7, were the components of the chain aggregates assumed to be spherical, their volumes summed and the diameter of a sphere with the equivalent diameter calculated? If so, attention should be called to the paper by Rogak et al. (Aerosol Sci. Tech 18, 25-47, 1993) which showed that a mobility analyser bases diameter of such particles on the projected area rather than on the volume. This will affect the comparison of mobility and EM size distributions.

We are aware of this problem and therefore used the projected area of a particle to determine the particle equivalent diameter D_{pa} (the diameter of a circle that comprises the same diameter as the projected particle), see chapter 2.2.4.

2. P.10 line 24. I can't understand why C and O were not detected on blank films of polyvinyl formal. In the supplemental data the carbon signature is strong, so the detector was sufficiently sensitive.

Thank you for pointing out this error. We changed the text to:

P10 lines 23-25. "The EDX spectra of blank grids showed only signals from Pt, the supporting copper TEM grid and carbon and oxygen signals from the Formvar substrate film."

3. Droplet haloes: I don't believe the splash hypothesis is appropriate for low velocity electrostatic collection. In fact I think it is also doubtful for particles of the size of those in figure 10 collected by high velocity impaction. Stratospheric aerosol sampling by an Ames Research Center group (Farlow and Ferry) 40 years ago found that the sulfuric acid particles did not develop haloes if all contact with water vapour was avoided before examination. (Possibly in JGR 82, 4921-4929, 1977 but I don't have the article) It was later confirmed by laboratory experiments (Bigg, Tellus, 38B, 62-66, 1986). A possible explanation is that acid vapour extends outwards from the captured particle as a monolayer (or multiple layers) on the surface. On exposure to water vapour the molecules take up water and coalesce to form tiny droplets.

We agree, halo formation has to be discussed as the result of several factors. We therefore extended the discussion of halo formation as follows:

P16, lines 5-15: “Several authors (Farlow et al., 1977; Bigg, 1986; Bigg and Leck, 2001b) have found that the formation of droplet ring structures from sulphuric acid containing aerosol is a result of humidity, hydrophilicity of the collection surface and impact velocity effects. Bigg and Leck (2001b) observed that a solution of sulfuric acid wets out on a hydrophilic surface but retracts when humidity is reduced, leaving behind small droplets in a symmetrical ring. In our study the sampling procedure led to a drastical reduction in relative humidity, from around 100% at ambient conditions to 20% within the sampling manifold (see chapter 2.1.1) and the aerosol was impacted onto a surface with hydrophilic properties (TEM grid). We will thus assume that the HP originally existed as one particle in the atmosphere that splashed out into the droplet ring structure upon impaction onto the substrate. “

4. P.15, line 23: “the biopolymer networks of marine gels are water solvable”. Solvable means that an answer is available for a problem. If you meant “soluble”, how could they exist as entities in the ocean?

Thank you for pointing that out. We now use “solvated” instead, referring to the IUPAC definition for solvation: “Any stabilizing interaction of a solute (or solute moiety) and the solvent or a similar interaction of solvent with groups of an insoluble material (i.e. the ionic groups of an ion-exchange resin)…”

We changed the text to:
P15, line 17-31: “In seawater the observed size range of gel particles ranges from sovated nanogels (100-200 nm; Bigg et al., 2004) that can further anneal into microgels (> 1000 nm) by interpenetration and entanglement of neighboring nanogels or hydrophobic interaction.”

The manuscript is well-written, the diagrams informative and the references very comprehensive. There are some instances where the spelling or wording differs slightly from conventional English usage and some of these are listed below together with suggested alternatives.

Thank you for thoroughly reading our manuscript. We corrected spelling and wording as suggested below.

p.5, line 21: Longyearbyen, Svalbard

p.5, line 25 and beyond: Since you are reporting completed work it would be more conventional to use the past tense rather than the future tense. E.g., change “will use” to “used”.

p.6, line 2: according to morphological…

p.8, line 19: In order to compare (to) the number…

p.9, line 21: Although wolfram is more logical in view of its symbol, tungsten is the common English usage.

p.10, line 19: were not reliably detected

p.16 line 10: unstable

p.16 line 17: morphology to the

p.20 line 13: is capable of adding

p.20 line 30: In the hope of enhancing

References, p.23, line 5: Ayers, G.P.

p.23 line 8: pouchetii

p.25 line 4: Cambridge

p.30 line 21- 24: Remove hyphens in Ramaswamy, Isaksen, climate and Intergovern-mental

p.31, line 6: atmosphere

Figure 10 caption, line 6: degenerated

Anonymous Referee #2

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The paper presents a hard-earned data set of single particle analysis of samples col- lected in the high Arctic during the summer of 2008. The analysis is used to categorize particles according to their morphological and chemical properties. The most signifi- cant result is that "the particles to be activated into cloud droplets over the Arctic pack ice areas can not be seen as simply organic salts". This result has implications for the modeling of CCN activity and cloud drop formation over the high Arctic. The paper should be published once the concerns outlined below are addressed.

p. 2, line 14: I'm not sure how particles can increase planetary albedo by absorbing sunlight.

We rephrased the sentence to

P2L13. "They alter the planetary albedo both directly by absorbing and scattering sunlight and indirectly …"

p. 4, line 5: Is this meant to be Arctic SURFACE OCEAN DOM?

Corrected

p. 5, line 21: Should be SVALBARD.

Corrected

p. 11, line 25: Why is the size distribution characterized as "bimodal" when, on average, it contains 3+ peaks?

P11, line 24-28. Thank you for pointing out this unclarity. The sentence was rephrased to: "The number size distribution of all imaged aerosol particles exhibited a maximum in the Aitken mode region at 32 nm in diameter and a double peak above 70 nm in the accumulation mode region with maxima at 89 nm and 147 nm with a shoulder to larger diameters at around 335 nm (see Fig. 3, red line)."

Figure 6 caption: I think it should be "unstable", not instable. Also the labeling of the two lines is confusing. In the lower panel there are central particles of HP (red line) and unstable central particles (green line). What line represents the aggregate, aggregate with film and skeletal particles? Also – in this figure and throughout, it would help the reader immensely if legends were added to the plots.

Labels were added to the plot for further clarification.

Figure 9: It is very difficult to tell the orange and red line apart.

The color of the orange line was changed to blue.

p. 15, lines 13 – 20: It is unclear if the descriptions of bonds holding the marine polymer gels together are referring to gels in atmospheric aerosol or in seawater. Assuming seawater (given the Verdugo reference), the size range of nanogels (100 – 200 nm) and microgels (> 1000 nm) are larger than the airbone aggregate particles shown in Figure 9. How can this difference be reconciled?

The paragraph has been rewritten to:

p. 15, lines 16-32: "In seawater the observed size range of gel particles ranges from sovated nanogels (100-200 nm; Bigg et al., 2004) that can further anneal into microgels (> 1000 nm) by interpenetration and entanglement of neighboring nanogels or hydrophobic interaction. Changes in environmental factors like UV-B radiation (Orellana and Verdugo, 2003) or physico-chemical parameters like pH and temperature (Tanaka et al., 1980) lead to inhibition/dispersion or volume change of the gel polymer assemblies. The transport from the ocean water into the atmosphere results in an enhanced exposure of the gel particles to solar UV-B radiation. Together with changes in the physico-chemical environment of the gel particles due to e.g. condensation of acidic gases onto the aerosol droplets the transport into the atmosphere thus might lead to fragmentation and/or shrinking of the gel matter and result in a reduced diameter of atmospheric gel particles compared to gel matter in the ocean (Leck and Bigg, 2005b; Orellana et al., 2011). Embedded in the polymer network is the high content of water (99%) that prevents the network from collapsing (Chin et a., 1998). The biopolymer networks of marine gels are highly surface active and show refractory properties are therefore not expected to evaporate under the electron beam."

p. 17, line 10: Should be IMAGING.
Corrected

p. 17, lines 30 – 33: The dominant particle type was those containing both Na/K and Ca/Mg. Stating a "dominating content of Na/K" or Ca/Mg is not accurate.
Thank you for pointing this out, we corrected a mistake in the figure legend.

Figures 5, 6, and 9: Each of these figures contains some version of the aggregate particle type but each shows different size ranges for that particle type. What is the definition of "airborne aggregate particle" shown in Figure 9 (which resides in the 10 to 100 nm size range) compared to the aggregate particle type shown in Figure 9 (which is in a larger size range)?

Fig. 5 (middle panel) shows the number size distribution of **all gel-type particles** observed with SEM. The SEM images do not allow a differentiation into the subgroups of gel-type particles ("aggregate" particles, "aggregate with film" particles etc.). Gel-type particles were observed above 45 nm and up to 800 nm in diameter.

Fig. 6 (lower panel) shows the number size distributions for **central particles of halo particles**, with the green line representing stable central particles (comprising "aggregate" particles, "aggregate with film" particles and skeletal particles) imaged with TEM, and the red line unstable central particles of halo particles.

Fig. 9 shows the number size distributions of **airborne aggregate particles and their building blocks** at different locations as obtained with TEM. Sizing of *"aggregate"* particles in our study revealed the 10 to 100 nm size range for the building blocks of these particles.

Therefore Figures 5, 6 and 9 show number size distributions of different types of particles that cover different size ranges and thus cannot be readily compared.

How is this reconciled with the statement on p. 19, lines 30 – 33 that says "organic marine gel matter contributes to the particle number concentration . . ..especially at diameters below 60 nm"?
It should be "below 75 nm" instead of "below 60 nm".
Organic marine gel matter (in single particles and gel-type particles) contributes mainly to particle numbers below 75 nm because all other types of particles appear at higher diameters: unstable single particles appear mainly in the accumulation mode (Fig. 6, upper panel) and halo particles (with sulphur-containing satellites) appear above 75 nm (Fig. 5, lower panel).

p. 20, lines 12 – 29: The discussion of the fragmentation of larger particles into smaller particles in the atmosphere due to UV radiation exposure is highly speculative and not supported by direct evidence. The papers cited appear to be based on studies of seawater. What thermodynamically viable mechanism can break apart particles in the 100 - 200 nm size range in the atmosphere? As far as I know, there are no reported observations of such events. (By the way, the Karl et al. (2013) and Tanaka et al. (1980) references, which may provide some insight here, are missing in the list of citations.)
It is correct that UV induced fragmentation of larger gel particles into smaller particles has been studied in seawater, as discussed in chapter 3.3 (p15, line 21-29). According to the current understanding the transport of gel matter from the ocean into the atmosphere occurs through bubble bursting and subsequent formation of small droplets that comprise seawater

and e.g. marine gels (see Introduction, p.4, line 13 ff.). In the atmosphere these droplets can be subject to further condensation of water vapor or other substances, coalescence and incloud processing which all potentially change the physico-chemical conditions within the droplet (Tanaka et al., 1980). The latter in combination with an increased exposure to UV-B radiation in the atmosphere makes it in our view reasonable to discuss fragmentation and/or skrinking as a possible mechanism to produce smaller sized fragments of marine gels (Leck and Bigg, 2010; Karl et al., 2013). This argument is further supported by the finding that spherical subunits in “aggregate”/”aggregate with film” particles and the dense inclusions in “mucus-like” particles appear at diameters down to 10 nm not only in the Arctic but also at different locations at lower latitudes (Fig. 9).

Tanaka et al. (1980) and Karl et al. (2013) were added to the reference list.

Size resolved morphological properties of the high Arctic summer aerosol during ASCOS-2008

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Abstract

The representation of aerosol properties and processes in climate models is fraught with large uncertainties. Especially at high northern latitudes a strong under-prediction of aerosol concentrations and nucleation events is observed and can only be constrained by in situ observations based on the analysis of individual aerosol particles. To further reduce the uncertainties surrounding aerosol properties and their potential role as cloud condensation nuclei this study provides observational data resolved over size on morphological and chemical properties of aerosol particles collected in the summer high Arctic, north of 80° N.

Aerosol particles were imaged with scanning and transmission electron microscopy and further evaluated with digital image analysis. In total 3903 particles were imaged and categorized according to morphological similarities into three gross morphological groups, single particles, gel particles and halo particles. Single particles were observed between 15 nm and 800 nm in diameter and represent the dominating type of particles (82%). The majority of particles appeared to be marine gels with a broad Aitken mode peaking at 70 nm accompanied by a minor fraction of ammonium (bi)sulfate with a maximum in number concentration at 170 nm. Gel particles (11% of all particles) were observed between 45 nm and 800 nm with a maximum in number concentration at 154 nm. Imaging with transmission electron microscopy allowed further morphological discrimination of gel particles in *"aggregate"* particles, *"aggregate with film"* particles and *"mucus-like"* particles.

Halo particles were observed above 75 nm and appeared to be ammonium (bi)sulfate (59% of halo particles), gel matter (19%) or decomposed gel matter (22%) internally mixed with sulfuric acid and/or methane sulfonic acid or ammonium (bi)sulfate with a maximum in number concentration at 161 nm in diameter.

Elemental dispersive X-ray spectroscopy analysis of individual particles revealed prevalence of the monovalent ions Na^+/K^+ for single particles and *"aggregate"* particles and of the divalent ions Ca^{2+}/Mg^{2+} for *"aggregate with film"* particles and "mucus-like" particles. Emanating from those results and in agreement with model studies reported elsewhere we propose a relationship between the availability of a Na^+/K^+ and Ca^{2+}/Mg^{2+} and the length of the biopolymer molecules participating in the formation of the 3D gel networks.

1 Introduction

Aerosol particles have major impacts on the climate of our planet. They alter the planetary albedo both directly by absorbing and scattering sunlight and indirectly by modifying the reflectivity, life-time and extent of clouds (Twomey, 1977; Albrecht, 1989; Solomon et al., 2007). Despite of the shown importance aerosol particles have on clouds their effects still give rise to large uncertainties in climate models (Schimel et al., 1996; Penner et al., 2001; Forster et al., 2007). Detailed model analyses have contributed to an enhanced understanding of the parametric uncertainties in global aerosol models and point towards significant uncertainties arising from an incomplete representation of aerosol processes and emissions in the models (e.g. Lee et al., 2013; Carslaw et al., 2013; Mann et al., 2014). Especially for high northern latitudes a strong under-prediction of aerosol particle concentrations and nucleation events in summer compared to measurements is recognized (Mann et al., 2014) leading to an insufficient representation of cloud condensation nuclei (CCN), the fraction of an aerosol particle population that can activate and form cloud droplets, within the models. Moreover, the microphysical properties of the cloud droplets are strongly related to the size, chemical composition, morphology and state of mixture of the activated CCN. Size resolved data based on the analysis of individual particles are therefore indispensible for an appropriate parameterization of aerosol particles within aerosol models.

The sources of aerosol particles in the Arctic are subjected to large regional and seasonal differences. In late winter/spring a pronounced anthropogenic influence on the Arctic is observed, a phenomenon known as Arctic haze (Shaw, 1995). During that time the Arctic air mass expands southwards towards Eurasia and North America and anthropogenic emissions are transported into the Arctic where they remain for prolonged times (Shaw, 1995; Douglas and Sturm, 2003). The aerosol during periods of Arctic haze is characterised by relatively high concentrations of aged aerosol predominantly in the accumulation mode (Shaw, 1984; Heintzenberg and Leck, 1994; Ström et al., 2003; Engvall et al., 2008; Korhonen et al., 2008). The air masses arriving in summer, however, originate from sectors over the oceans with limited man- made activities and the transport into the Arctic is slower compared to winter conditions (Stohl, 2006). The summer conditions are thus much more pristine and the aerosol shifts from being accumulation mode dominated to be Aitken mode dominated (Heintzenberg et al., 2006; 2015; Engvall et al., 2008).

Over the high Arctic pack ice north of 80° number concentrations of CCN show a large temporal variability, ranging over 2-3 orders of magnitude but usually are below 100 cm^{-3} and occasionally less than 1 cm^{-3} (Lannefors et al., 1983; Bigg et al., 1996; Bigg and Leck, 2001a; Mauritsen et al., 2011; Leck and Svensson, 2015). These relatively low CCN concentrations have a significant impact on the formation of low-level (stratiform) clouds prevalent in the high Arctic summer. Mauritsen et al. (2011) identified a regime with very low CCN concentrations (< 10 cm^{-3}) where cloud formation is limited mainly by the availability of CCN. Such low CCN concentrations occur as a result of weak local aerosol sources and effective wet deposition (Nilsson and Leck, 2002; Held et al., 2011a,b; Heintzenberg et al., 2006; Leck and Svensson, 2015) at the marginal ice zome and over the pack ice.

However, the physical and chemical properties which determine the ability of the summer high Arctic aerosol particles to act as CCN are still not very well understood. Attempts to theoretically predict concentrations of CCN in closure studies resulted in both over- and under-predictions of the observed CCN concentrations (Zhou et al., 2001; Bigg and Leck, 2001a; Lohman and Leck, 2005; Martin et al., 2011; Leck and Svensson, 2015). The most recent closure study by Leck and Svensson (2015) simulated the cloud nucleation process by assuming Köhler theory together with a Lagrangian adiabatic air parcel model that solves the kinetic formulation for condensation of water on size resolved aerosol particles. The authors suggested a larger fraction of the internally/externally mixed water-insoluble particles in the smaller aerosol size ranges and kinetically restricted growth of the activated particles.

The non-water soluble particle fraction was suggested to physically and chemically behave as polymer gels[1] with a dichotomous behavior (low hygroscopic growth factor but a high CCN activation efficiency) in cloud droplet activation as a result of the interaction of the hydrophilic and hydrophobic entities on the structures of the high Arctic polymer gels (Orellana et al., 2011). On average 32% of the Arctic surface ocean DOM assembled as microgels (Orellana et al., 2011), a significantly higher percentage than reported for other ocean regions (10%; Chin et al., 1998; Verdugo et al., 2004). All together these findings strongly supported the previously unverified hypothesis of a link between cloud formation and polymer gels in the surface microlayer (SML, <1000 μm thick at the air-sea interface) of the high Arctic open leads (Bigg et al., 2004; Leck and Bigg, 1999; Leck et al., 2002; Leck and Bigg, 2005b; Bigg and Leck, 2008; Leck and Bigg, 2010).

The transport of marine gels into the atmosphere is thought to happen via the burst of air bubbles at the air-sea interface. Air bubbles rising within the water column scavenge surface-active organic matter especially from the surface microlayer to their outer walls (Wotton and Preston, 2005). Bursting of the bubbles at the water surface produces small jet and film drops containing organic surface-active compounds, debris of phytoplankton, bacteria, viruses and sea salt (Blanchard and Woodcock, 1957; Blanchard, 1971, Blanchard and Syzdek, 1988; Gershey, 1983; O'Dowd et al., 1999) which are transported further up into the atmosphere through turbulent mixing processes. However, studies of individual particles by Bigg and Leck (2001; 2008); Leck et al., (2002); Leck and Bigg (2005a; 2005b) over the perennial ice have failed to find evidence of sea salt particles of less than 200 nm in diameter. In the Arctic breaking waves as a source of bubbles are rare due to low wind speeds and short fetches between the ice floes (Tjernström et al., 2012). Even in the absence of wind-driven breaking waves a recent study has now confirmed both the presence and temporal variability of a population of bubbles within the open leads (Norris et al., 2011). The considered mechanisms for bubble formation and mixing were induced by changes in gas saturation. Other possible bubble formation mechanisms are respiration from algae and phytoplankton (Medwin, 1970; Johnson and Wangersky, 1987) and the release of trapped air from melting ice (Wettlaufer, 1998).

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[1] Phytoplankton and bacteria in surface seawater produce varying amounts of mucus- or gel-like matter comprised of biopolymers like proteins, polysaccharides or lipids that form 3-dimensional networks inter-bridged with divalent ions, preferably Ca^{2+} and Mg^{2+}. This type of supramolecular organisation is referred to as marine gels. (Verdugo, 2012 gives a review).

Due to the remoteness and the harsh conditions in the high Arctic the number of aerosol studies from this region is limited; the data available rely on four expeditions onboard the Swedish icebreaker *Oden* during the summers of 1991, 1996, 2001 and 2008 (Leck et al., 1996; 2001, 2004; Tjernström et al., 2014). These expeditions took advantage of the pristine conditions during the Arctic summer when the Arctic is to a great extent separated from air masses from polluted mid-latitudinal sources which provided the unique opportunity to study aerosol particles from predominantly natural sources. All other Arctic studies on aerosol chemical composition, morphology and state of mixture were either performed during winter/spring when transport of polluted aerosol from lower latitudes into the high Arctic is strong (e.g. Hara et al., 2003; Xie et al., 2007; Winiger et al., 2015) and/or they were located further south, outside the pack ice area, missing potential aerosol sources from the pack-ice area and at the same time including anthropogenic pollutions, e.g. studies from Svalbard (Geng et al., 2010; Chi et al., 2015).

To further reduce the uncertainties surrounding the CCN properties that promote /suppress cloud droplet formation over the pack ice area an investigation of size, chemical composition, morphology and state of mixture on the level of individual aerosol particles is required. The present study will make use of aerosol particles collected during the most recent icebreaker expedition under the name ASCOS (Arctic Summer Cloud and Ocean Study) 2008. The Swedish icebreaker *Oden* departed from Longyearbyen on Svalbard on 2 August and returned on 9 September 2008. After traversing the pack-ice northward the icebreaker was moored to an ice floe and drifted passively with it around 87° N between 12 August and 1 September (Tjernström et al., 2014). We used electron microscopy (scanning electron microscopy (SEM) and transmission electron microscopy (TEM)) to image aerosol particles at high resolution, and subsequent digital image analysis to objectively assess size and morphology of the particles on an individual basis. Earlier studies north of 80° focused rather on a qualitative description of the aerosol in the high Arctic (Leck and Bigg, 2005, 2008, 2010; Bigg and Leck, 2001b, 2008) complemented with bulk chemical analyses (Leck et al., 2002; 2013; Leck and Svensson, 2015; Lohman and Leck, 2005).

By individually screening close to 4000 aerosol particles collected during the ice-drift with SEM and subsequent digital mapping we firstly gained size resolved information on the aerosol population as a whole. The obtained number size distribution was compared with measurements from an independent method (Tandem Differential Mobility Particle Sizer, TDMPS) to verify that a representative fraction of the aerosol population was captured with SEM. Secondly, we sorted all mapped particles according to morphological differences and a separate number size distribution for each of the morphological types was obtained. Thirdly, to obtain deeper insights into the morphological features of the collected particles and to simultaneously assess their elemental composition with EDX spectroscopy investigated a subpopulation of aerosol particles in TEM at very high resolution.

2 Methods for sampling of airborne aerosol particles during ASCOS

2.1 Collection of airborne particles

2.1.1 The sampling inlet

A PM_{10}-inlet (9 cm inner diameter) was deployed at ambient conditions (85 – 100 % relative humidity (RH) and temperatures around 0 °C) to eliminate particles with diameters > 10 micrometer in equivalent aerosol dynamic diameter (EAD) from the sampled air. To optimise the distance from the sea surface and the ship's superstructure the inlet was located forward ~ 25 m above the sea surface and 3 m above the roof of the laboratory container on the 4th deck of the icebreaker. Direct contamination from the ship was excluded by using a pollution controller, located directly after the inlet pipe that passed through the roof of the container. Provided that the wind was within ± 70° of the direction of the bow and stronger than 2 ms^{-1}, no pollution reached the sample inlets (Leck et al., 1996). Directly downstream from the pollution sensor the electrostatic precipitator and the TDMPS were connected to the inlet with short stainless steel tubes (length ca. 1 m). To ensure that the sampling conditions and losses were the same for both instruments, the inlet take-offs for the two samplers were placed closely together. The temperature in the container was kept at 20 °C which resulted in a RH of 20% in the secondary lines during sampling. See Leck et al. (2001) for more details of the set-up for the sampling of aerosol particles.

Volatile compounds on particle surfaces and weakly bound water molecules were probably lost during the sampling procedure. In the Arctic the concentration of volatile compounds is generally lower than at lower latitudes (Bates et al., 1987) and losses due to evaporation can thus be considered very small.

2.1.2 The electrostatic precipitator

Using the electrostatic precipitator the aerosol particles were collected directly onto 3 mm copper 300 mesh Formvar-coated TEM grids (TED PELLA Inc.; Dixkens and Fissan, 1999; Leck and Bigg, 2008). Formvar-coated grids were chosen because of the hydrophilic and thus polar nature of the Formvar film (Rocha et al., 2005). The aerosol particles were charged at the inlet of the precipitator by a ^{63}Ni beta-emitting radioactive source and precipitated by a 12 kV cm^{-1} electric field between the inlet and the collecting grid surface. The flow rate was kept very low (0.17 mL s^{-1}) in order to collect particles up to ~1 µm in diameter. The collection efficiency of the electrostatic precipitator was intercompared with a TSI 1236 Nanometer Aerosol Sampler (^{63}Ni beta-emitting radioactive source and sample flow of 1 Lm^{-1}) mounted side-by-side with the electrostatic precipitator. Both collected a small, but statistically significant number of particles < 25 nm in diameter. The precipitator took samples for 6 to 12 hrs. Before and after sampling the grids were placed within a grid holder box in a sealed plastic bag, together with silica gel packets, and stored in a desiccator at a constant temperature of 20 °C in a clean room before they were investigated.

2.1.3 The TDMPS-sampling system

The TDMPS-sampling system to measure the number size distributions of dry (20% RH) sub-micrometer particles used pairs of differential mobility analyzers (DMAs). The TSI 3010 counters in the DMAs were size and concentration calibrated against an electrometer and the TSI 3025 counters for particle sizes below 20 nm diameter according to Stolzenburg (1988). This set up yielded a complete number size distribution from 3 nm to 800 nm diameter scanned over 45 size channels every 10 - 20 min. Further details of the TDMPS system can be found in Heintzenberg and Leck (2012). NIST (National Institute of Standards Technology) traceable calibration standards of polystyrene latex spherical particles were used to determine error in determination of the mobility diameter to ± 5 % (Wiedensohler et al., 2012).

In order to compare the number size distribution obtained from the precipitator samples (section 2.1.2) with those simultaneously recorded by the TDMPS we assumed median particle number diameters for each of the 45 TDMPS size channels. The particle diameters were then merged to form a complete set of diameters across the TDMPS measuring interval.

2.2 Image recording and elemental analysis

2.2.1 Imaging with scanning electron microscopy (SEM)

The samples were investigated with a high-resolution SEM (JEOL JSM-7401) under high vacuum conditions, at less than 9.63 x 10-5 Pa (Stevens et al., 2009). A detailed description of the setup of the scanning electron microscope can be found in Hamacher-Barth et al. (2013). The Gentle Beam mode of the microscope was used to minimalize radiation damage of the aerosol particles, avoid surface charge-up and to demagnify the electron beam diameter (Michael et al., 2010). Correction for stigmatism and focusing of the electron beam was done every time before imaging an aerosol particle. The grey scale (contrast and brightness) was adjusted automatically before recording an image.

The imaging of the aerosol particles aimed to account for an uneven distribution of the particles on the TEM grid and to capture a representative fraction of the aerosol particles. In brief, particles were imaged at a magnification of 40.000 on the TEM grid squares, along a diagonal from the center of the grid to the edge on 6 to 8 squares of the TEM grid. Each square was screened systematically to capture a representative fraction of the aerosol population. For a detailed description of the screening procedure see Hamacher-Barth et al. (2013).

2.2.2 Imaging with transmission electron microscopy (TEM)

To image the samples with TEM they have to be coated by a thin metal layer. Evaporation of a heavy metal thin coating at an oblique angle onto the sample increases the mass contrast and accentuates the topography of the aerosol particle by producing a shadow (William and Carter, 2006). Furthermore shading has the advantage that the metal cover protects the aerosol particles against heating by the electron beam during examination, especially at high magnifications. It is also advantageous that in case of any evaporation from the aerosol particle the metal replica of the aerosol particle is still visible.

The aerosol particles were shaded with platinum (Pt) at an angle of arctan(0.5) = 26° (Okada, 1983) in a vacuum chamber at 10^{-6} mbar. Pt was evaporated from a Pt wire (∅ 0.2 mm, 20 mm length). The Pt wire was drawn around a tungsten (W) wire and evaporated clusters of Pt atoms when the W wire was heated up electrically by a 85 mA current for 30 sec. The shading procedure produces a layer of Pt particles of 1-2 nm in diameter on the TEM grid.

After shadowing the TEM grids were examined in TEM using a JEOL JEM-2100 high-resolution instrument, equipped with a LaB_6 filament and a Si/Li detector crystal. The TEM grid containing the aerosol particles was mounted on a sample holder made of Beryllium to avoid background signals from the sample holder material in the EDX measurements (see chapter 2.2.3). A CCD camera (Gatan SC1000 Orius, 11 Megapixel) in bottom mount position was used to image the aerosol particles. Images were taken at high vacuum, less than 35 x 10^{-5} Pa and at an accelerating voltage of 100 kV.

Particles were imaged on TEM grid squares along a diagonal from the center of the grid to the edge on 6 to 8 squares. To avoid imaging of particles that were damaged by prior imaging with SEM an area of the grid was chosen which was not exposed to any electron beam at high magnifications before. Screening each square for individual particles was done at a magnification of 30.000, and images were taken at magnifications between 25.000 and 80.000.

2.2.3 Elemental X-ray spectroscopy

The elemental analyses were performed using an energy dispersive X-ray detector JED-2300 attached to the JEM-2100 TEM. In order to avoid time consuming realignment of the electron beam and focusing procedures the EDX-analyses were also performed at an accelerating voltage of 100 kV. The energy range measured was 0-20 keV, counting rate was typically 1053 counts/sec^{-1}, life time 30 sec, real time 33.00 sec and dead time 10 %. Generally EDX spectroscopy allows the detection of elements ≥ Be as their photon energies are above 100 eV and thus lie within the X-ray region of the electromagnetic spectrum (Egerton, 2008). Nevertheless the detection of light elements like C, N, and O that are typical for organic compounds can be difficult on a Formvar-coated copper grid since the signal intensity can be biased by attenuation of the X-ray signal through absorption by the adjacent copper grid. For this reason these elements were not reliably detectable and are thus not part of this study.

Blank grids shadowed with platinum were used to identify the background noise and signals from the TEM grid including copper from the grid and the Formvar film and the Pt shadowing. The EDX spectra of blank grids showed only signals from Pt, the supporting copper TEM grid and carbon and oxygen signals from the Formvar substrate-film.

2.2.4 Digital image analysis

Images taken with SEM at a magnification of 40.000 were evaluated using an optimized commercial image processing software (Aphelion™ Dev 4.10). In brief, the maximal intensity of the neighboring background of each aerosol particle was determined. Using exactly the same image but including the aerosol particle allowed the separation of the particle and measurement of the particle area in pixels (Hamacher-Barth et al., 2013).

The particle size was calculated according to Eq. (1)

$$D_{pa} = 2\sqrt{Area/\pi} \qquad (1)$$

with D_{pa} as the particle equivalent diameter, which is the diameter of a circle that comprises the same area as the aerosol particle projected onto a two-dimensional surface (Allen, 1997; Hinds, 1999). The value for the area is calculated from the number of pixels counted for each particle. A number size distribution of the aerosol sample was obtained using MATLAB 2011a and the freely available software package EasyFit.

3 Results and discussion

To verify that a representative fraction of the aerosol population has been captured with SEM we firstly calculated a number size distribution of all aerosol particles and compare it with measurements from TDMPS. Secondly we sorted all particles imaged according to morphological similarities into three gross groups, named: single particles (SP), gel-like particles (GP) and halo particles (HP), shown in Fig. 2. Thirdly, to obtain more subtle insights into the morphological features of the collected aerosol particles and simultaneously assess their elemental composition we investigated a subpopulation of the aerosol particles with TEM and EDX spectroscopy at very high resolution.

3.1 Total number size distributions

In order to derive an overall number size distribution we imaged in total 3909 aerosol particles at a magnification of 40,000 with SEM. The number size distribution of all imaged aerosol particles exhibited a maximum in the Aitken mode region at 32 nm in diameter and a double peak above 70 nm in the accumulation mode region with maxima at 89 nm and 147 nm with a shoulder to larger diameters at around 335 nm (see Fig. 3, red line). Hamacher-Barth et al. (2013) used the same image mapping method as used in this study and determined the error of sizing for polystyrene latex spheres of several diameter sizes between 20 nm and 900 nm was determined. The error values are displayed in Fig. 3, red arrows. For the TDMPS number size distribution we assumed an error in determining the mobility diameter of 5% across the whole measuring interval (Wiedensohler et al., 2012).

The two approaches show an overall good agreement between their number size distributions with a similar modal structure with an Aitken mode below 80 nm and an accumulation mode at higher diameters. The reduced particle number concentration in the Aitken mode seen by SEM was probably caused by their partly weak contrast to the Formvar film, which either resulted in an underestimation of the size or that the particles remained undetected. The accumulation mode was separated into a double peak with particle number maxima at 89 nm and 147 nm in SEM and 106 nm and 158 nm in diameter in TDMPS. The aerosol particles at diameters > 100 nm often showed a patchy and inhomogeneous appearance which might have lead to an underestimation of their size and the observed shift to smaller diameters in SEM, at 147 nm compared to 173 nm in TDMPS and broadening of the maximum at 335 nm.

In general the number size distributions determined for particle sizes larger than 20 nm in diameter showed the typical modal features of aerosol collected in the high Arctic summer boundary layer (Covert et al., 1996; Heintzenberg et al., 2006) with an Aitken mode between 26 nm and 80 nm and the multimodal accumulation size range between 80 nm and 1000 nm (Heintzenberg and Leck, 2012) with the so called Hoppel minimum around 80 nm inbetween (Hoppel, 1986).

3.2 Single particles

Single particles (SP) seen by SEM appeared as single entities that mostly contrasted sharply and thus could be easily separated from their Formvar background for diameters > 40 nm. At smaller diameters, however, the contrast to the backgroud was often weak and probably resulted in an underestimation of particle size or non-detection of particles. Imaged examples of SP are shown in Figure 4. Of the 3909 particles that were mapped SP were the overall dominating type of particles, 82% of the total aerosol particles were attributed to this group (Table 1). They were observed over the whole size range, between 15 nm and 800 nm in diameter with a broad Aitken mode peaking at 64 nm accompanied by a less pronounced peak at 27 nm. The majority of SP (80%) appeared in the Aitken mode size region and below 80 nm in diameter (Table 1). In the accumulation mode size range 18% of SP appeared between 80 and 200 nm with a maximum at 106 nm in diameter and the remaining 2% of the SP were detected in diameter sizes (Table 1) > 200 nm (Fig. 5, upper panel). We observed that 35% of the SP partly evaporated under the SEM electron beam but retained their outer shape on the timescale of minutes. Also at a higher magnification using TEM the same behavior was seen for 30% of the particles. We tentatively assigned these particles to be ammonium (bi)sulfate particles. We were guided by the results published by Heard and Wiffen (1969) and Bigg and Leck (2001b) where particles with the same morphological features and instability under the electron microscope were made up by ammonium sulfate, bisulfate or methane sulfonate mixtures. The presence of ammonium sulfate or bisulfate particles would be supported by the fact that ammonia has been reported to be the predominant base in the remote marine troposphere (Söderlund, 1982) that undergoes primarily acid-base reactions with non-seasalt H_2SO_4, an oxidation product of biogenic dimethyl sulfide, DMS (Quinn et al., 1987). Leck and Persson confirmed the presence of ammonia bisulfate particles both along the marginal ice edge and over the inner parts of the pack ice. Over remote marine locations at lower latitudes Meszaros and Vissy (1974) observed, by means of electron microscopy, ammonium bisulfate concentrations up to 38%, on average 24%, with the highest particle concentrations between 100 nm and 1 um in diameter. In the literature chemical tests have also been used to identify ammonium and sulfate in samples investigated by TEM (Bigg and Leck, 2001b). Such tests were not implemented during this study since the use of chemicals would have added additional mass onto the particles. This would have altered the size and the morphology of the particles and hampered the investigation of the aerosol particles with TEM and EDX spectroscopy.

The presence of biogenic nitrate as a counter ion to ammonium can be considered rather unlikely since the formation of ammonium nitrate happens only after all sulfate has been neutralized (Kuhn et al., 2010). Nitrate concentrations from impactor measurements during ASCOS show nitrate values that are one order of magnitude lower than sulfate concentrations at the same time, usually below 0.1 $nmolm^{-3}$ (*C. Leck pers. comm., 2015*). Moreover ammonium nitrate does not evaporate and is stable under the electron beam (Rao et al., 1989). To minimize biases due to evaporative losses and beam damage the ammonium sulfate particles were imaged as quickly as possible. Figure 6 (upper panel) shows the number size distribution of the ammonium sulfate particles derived from the TEM images with a maximum at 172 nm in the accumulation mode.

The remaining 65% of the imaged particles (Fig. 5, upper panel) were stable under the heat of the electron beam and showed no sign of evaporation or changes in morphology. Some of those particles appeared as skeletal structures (Fig. 4B) that collapsed and merged to an unstructured flat appearance after exposure times to the electron beam significantly longer than the justified time for imaging of the particles. None of the SP particles showed an apparently crystalline appearance that could be attributed to sea salt or any other inorganic crystalline matter.

3.3 Gel-like particles

Aerosol particles classified as gel-like particles (GP) using SEM showed an amorphous texture with an inhomogeneous distribution of pixel intensity. Their diffuse structure and weak contrast to the Formvar-film suggested that these particles predominantly contain light elements like C, H, N and O, which are typical components of organic matter. The contrast between the particles and the Formvar-film provides (indirect) information about the elemental composition of the aerosol particle since the number of the detected secondary electrons increases with increasing atomic number of the elements present in the aerosol particle (Zhou et al., 2006) suggesting that the aerosol particles under investigation are built up by matter of biological origin. The potential similarity in chemical composition between the GP and the Formvar-film might have lead to an underestimation of the particle size which resulted in the shift of the higher accumulation mode peak at 173 nm in TDMPS to 147 nm in the total number size distribution (Fig. 3).

GP appeared in the Aitken mode at diameters above 45 nm but were most frequently observed in the accumulation mode with a maximum at 174 nm, covering all sizes up to 800 nm (Fig. 5, middle panel). In total 11% of the 3909 particles that were imaged were classified as GP of which 24% were observed in the Aitken mode > 45 nm, 49% appeared in the accumulation mode between 80 nm and 200 nm and 27% were observed > 200 nm (Table 1).

Particles classified as GP were further evaluated with TEM. The higher resolution of the TEM images revealed better insights into the morphology of the particles and the GP could be further divided into subgroups (see Fig. 2). 14% of the particles consisted of a conglomeration of smaller spherical subunits that were welded together and formed small chains or agglomerates (Fig. 7A, B). Those particles were named *"aggregate"* particles. 29% of the gel particles appeared as "*aggregate with film"* particles where *"aggregate"* particles were covered with a diffuse and nearly electron-transparent film that partly obscured the underlying subunits and produced a more smooth appearance compared to the bare *"aggregate"* particles (Fig. 7 C, D and E). However, the majority of GP, 57%, showed a "*mucus-like"* texture that was many times widely outspread on the Formvar-film (Fig. 8 A, B), partly in long drawn-out structures (Fig. 8 C) or with small electron dense inclusions (Fig. 8 D).

The individual subunits of *"aggregate"* particles and the dense spots in *"mucus-like"* particles exhibit diameters between 11 nm and 109 nm with a maximum in number size distribution at 39 nm and a smaller maximum at 28 nm. Fig. 9 compares the size distributions of *"aggregate"* components from this study (red line) with those from previous studies in the high Arctic and at lower latitudes (Leck and Bigg, 2005a; 2008; 2010). Similarity with previous studies outside and within the pack ice (Leck and Bigg, 2005b; Orellana et al., 2011, same period as this study) strongly suggests the presence of airborne marine gels. Entanglements, ionic or hydrophobic interactions and/or hydrogen bonds stabilize the three-dimensional biopolymer networks of the marine polymer gels, with electrostatic bonds involving Ca^{2+} or Mg^{2+} ions being the most dominating (Verdugo, 2012; Orellana and Leck, 2015). In seawater the observed size range of gel particles ranges from sovated nanogels (100-200 nm; Bigg et al., 2004) that can further anneal into microgels (> 1000 nm) by interpenetration and entanglement of neighboring nanogels or hydrophobic interaction. Changes in environmental factors like UV-B radiation (Orellana and Verdugo, 2003) or physico-chemical parameters like pH and temperature (Tanaka et al., 1980) lead to inhibition/dispersion or volume change of the gel polymer assemblies. The transport from the ocean water into the atmosphere results in an enhanced exposure of the gel particles to solar UV-B radiation. Together with changes in the physico-chemical environment of the gel particles due to e.g. condensation of acidic gases onto the aerosol droplets the transport into the atmosphere thus might lead to fragmentation and/or shrinking of the gel matter and result in a reduced diameter of atmospheric gel particles compared to gel matter in the ocean (Leck and Bigg, 2005b; Orellana et al, 2011). Embedded in the polymer network is the high content of water (99%) that prevents the network from collapsing (Chin et a., 1998). The biopolymer networks of marine gels are highly surface active and show refractory properties are therefore not expected to evaporate under the electron beam.

3.4 Halo particles

Besides SP and GP we observed particles with a halo-like appearance (halo particles, HP) on the TEM grid where a relatively large central particle was surrounded by a droplet ring structure of numerous smaller particles (for examples see Fig. 10).

Several authors (Farlow et al., 1977; Bigg, 1986; Bigg et Leck, 2001b) have found that the formation of droplet ring structures from sulphuric acid containing aerosol is a result of humidity, hydrophilicity of the collection surface and impact velocity effects. Bigg and Leck (2001b) observed that a solution of sulfuric acid wets out on a hydrophilic surface but retracts when humidity is reduced, leaving behind small droplets in a symmetrical ring. In our study the sampling procedure led to a drastical reduction in relative humidity, from around 100% at ambient conditions to 20% within the sampling manifold (see chapter 2.1.1) and the aerosol was impacted onto a surface with hydrophilic properties (TEM grid). We will thus assume that the HP originally existed as one particle in the atmosphere that splashed out into the droplet ring structure upon impaction onto the substrate.

HP comprised 7% of the total number of aerosol particles (Table 1) and appeared at diameters above 75 nm and thus mainly in the accumulation mode. Number maxima were found at at 161 nm and 293 nm, respectively (Fig. 5, lower panel, left). The very weak contrast of the satellite particles against the Formvar background (Fig. 3) probable shifted the particle number size distribution towards smaller sizes to some extent.

Imaging with TEM allowed a more detailed investigation of the HP and revealed three morphologically different types of the central particle. Two of the particle types consisted predominantly of particles with skeletal structures and of particles in the form of *"aggregates"* or *"aggregate with film"*. The third group consisted of particles that were in opposite to the former particle types unstable under the electron beam (Fig. 2). Central particles of skeletal structures or *"aggregate"*/*"aggregate with film"* made up for 19% and 22%, respectively of the HP examined. Examples of both particle types are shown in Figs. 10(A) and 10(B). The majority of central particles (59%), however seemed to partly evaporate during the imaging process, leaving more transparent structures behind, similar to the SP described in chapter 3.2. We sized the central particles individually in order to compare them with particles of similar morphology to the SP or GP. The number size distribution of the *"aggregate"*,

"aggregate with film" and skeletal particles is shown in Fig. 6(B), green line, with a maximum at 270 nm diameters, compared to the maximum at 171 nm (Fig. 6(B), red line) resulting from sizing the heat sensitive central particles under the electron beam.

The satellites (particulates or droplets) exhibited varying morphologies. Sometimes numerous small satellites surrounded the central particle in a symmetrical ring (Fig. 10(A) whereas in other cases the satellite droplets were larger but fewer (Fig. 10(B), (C)). In the literature three types of compounds have been described to form satellites when airborne aerosol particles impact on a collection substrate: sulfuric acid (Ayers, 1978; Ferek et al., 1983), ammonium sulfate and bisulfate (Bigg, 1980; Busek and Pósfai, 1999) and methane sulfonic acid, MSA, (Bigg et al., 1974). Sulfuric acid exhibits a distinctive morphology: a central particle surrounded by a droplet-halo of numerous smaller satellites. Neutralization of sulfuric acid by ammonium or a high content of methane sulfonic acid produces a halo of larger and fewer droplets (Bigg and Leck, 2001a). The morphology of the droplet-halos we observed in this study points towards the presence of sulfuric acid, often in a mixture with ammonium sulfate or bisulfate and/or methane sulfonic acid. As discussed in section 3.2 these sulfur-containing components have not only been reported to be present over the Arctic pack ice area in summer (Bigg and Leck, 2001a) but also to frequently occur in the remote marine atmosphere (Barnard et al., 1994; Capaldo and Pandis, 1997; Kettle et al., 1999). The observed number size distribution for all HP (Fig. 5, lower panel) is in agreement with results from the high Arctic reported by Hillamo et al. (2001) which observed the first maximum in sulfate containing aerosol particles at diameters > 80 nm and in ammonium and MSA containing particles at diameters > 100 nm.

3.5 EDX measurements

To determine the elemental composition of the aerosol samples an EDX spectrometer coupled to TEM was used. EDX spectra of 103 aerosol particles were recorded in conjunction with the imaging process. Molecular dynamics studies on polysaccharides by Li et al. (2013) and Sun et al. (2014) have shown that not only the divalent ions Ca^{2+} and Mg^{2+} but also the monovalent ions Na^+ and K^+ can stabilize the three-dimensional biopolymer gel networks. Inspired by these results we focused on the detection of the alkali ions Na^+ and K^+ and the divalent ions Ca^{2+} and Mg^{2+} in the gel-type particles. In the following we will refer to Na^+ and K^+ as Na^+/K^+ and Ca^{2+} and Mg^{2+} as Ca^{2+}/Mg^{2+}.

The analysis revealed the following characteristics: Na^+/K^+ was detected in 91% of the SP, 13% of these particles contained exclusively Na^+/K^+ whereas 78% contained both types of metal ions, Na^+/K^+ and Ca^{2+}/Mg^{2+} with the latter only in minor quantities (Fig. 11(A)); examples of EDX spectra for the different types of particles are shown in Fig. S1. The *"aggregate"* particles contained exclusively Na^+/K^+ in 20% of the particles and predominantly Na^+/K^+ and minor contents of Ca^{2+}/Mg^{2+} in 80% of the particles (Fig. 11(B)). For the particle types *"aggregate plus film"* and *"mucus-like"* particles, however, a clear dominance of Ca^{2+}/Mg^{2+} was detected. 17% of the *"aggregate plus film"* particles contained only Ca^{2+}/Mg^{2+} and 67% of the particles contained Ca^{2+}/Mg^{2+} accompanied by minor contents of Na^+/K^+ (Fig. 11(C)). *"Aggregate plus film"* particles thus contained to 86% Ca^{2+}/Mg^{2+} as the dominating type of ions. *"Mucus-like"* particles contained to 11% only Ca^{2+}/Mg^{2+} and up to 86% Ca^{2+}/Mg^{2+} accompanied by minor contents of Na^+/K^+. 97% of the type *"mucus-like"* particles thus contained Ca^{2+}/Mg^{2+} as the dominating type of metals. In summary, we observed a gradual transition from particles with a dominating content of Na^+/K^+ to particles with a dominating content of Ca^{2+}/Mg^{2+} moving from SP over *"aggregate"* particles and *"aggregate with film"* particles to *"mucus-like"* particles. We therefore hypothesise a connection between the morphology of the particles and the respective dominating crosslinking ion within the polymer 3-dimensional network of the marine gels. Li et al. (2013) compared polysaccharides with 3 and 4 repetition units of molecular weights of 1.9 kDa and 2.5 kDa respectively as representations for organic matter in seawater (Verdugo, 2004). Their results showed that the assembly of the longer polysaccharide chains seems to be accelerated in the presence of Ca^{2+} whereas the presence of Na^+ has a positive effect on the assembly of shorter polysaccharide chains. Considering the observed morphology of the aerosol particles that are built up by marine gel matter a high content of Ca^{2+}/Mg^{2+} could facilitate the formation of fluffy and less compact *"mucus-like"* gel matter whereas the presence of Na^+/K^+ favoured a more compact structure of type *"aggregate"* and SP.

Halo particles with a center of gel or fraction of a gel showed a high content of Na^+/K^+: 50% of the particles contained those metals exclusively whereas another 25% contained mainly Na^+/K^+ with smaller amounts of Ca^{2+}/Mg^{2+} (Fig. 12). The high content of alkali metal ions in those particles suggested that they originated from SP or fragmented *"aggregate"* particles, which were exposed to processes that lead to condensational growth of the original gel particles.

4 Summary and conclusions

Aerosol particles collected in the summer high Arctic north of 80° were individually and objectively investigated with electron microscopy and subsequent image mapping. This enabled a division of the aerosol particles into three size resolved gross morphological groups, single particles (SP), gel particles (GP) and halo particles (HP). Single particles (SP) dominated the aerosol population in terms of numbers and made up 82% of all particles; they were observed over the whole sub-micrometer size range and clearly dominated the Aitken mode. The majority of SP (65%) was stable under the electron microscope and showed no signs of evaporation or morphological changes during imaging. These particles with refractory properties appeared over the whole size range of particles observed whereas the remaining 35% of SP appeared to be heat instable, evaporated partly and were predominantly observed in the accumulation mode. GP were observed at diameters > 45 nm predominantly in the accumulation mode with a maximum in number at 154 nm and contributed with 11% to the total particle number. The GP exhibited various morphological features and appeared as *"aggregate"* particles (14%) and as *"aggregate with film"* particles (29%) but the majority, 59% was made up by *"mucus-like"* particles. 70% of the GP in our study appeared to be smaller than 100 nm in diameter, and 90% were smaller than 200 nm.

HP appeared mainly in the accumulation mode at diameters > 60 nm with a maximum in number at 161 nm and contributed up to 7% to the total particle number mapped. The majority of HP consisted of heat instable particles, probably ammonium bisulfate (59% of all particles), internally mixed with sulfur containing compounds (sulfuric acid, ammonium bisulfate, methane sulfonic acid). The remaining fraction was made up by *"aggregate"* particles (19%) and decomposed or fragmented gel matter (22%) internally mixed with sulfur containing compounds.

Electron dispersive X-ray (EDX) spectroscopy revealed a gradual transition in the content of Na^+/K and Ca^{2+}/Mg^{2+} between different particle morphologies. SP and *"aggregate"* particles preferentially contained Na^+/K^+ whereas *"aggregate with film"* particles and *"mucus-like"* particles contained mainly Ca^{2+}/Mg^{2+} with minor contents of Na^+/K^+. Supported by model studies (Li et al., 2013; Sun et al., 2014) we hypothesize that a correlation exists between particle morphology and the prevalence of the ions Na^+/K^+ and/or Ca^{2+}/Mg^{2+} were the prevalence of Ca^{2+}/Mg^{2+} facilitates the formation of large organic assemblies of GP type whereas a lack of Ca^{2+}/Mg^{2+} and a prevalence of Na^+/K^+ prohibit the formation of large assemblies leading to smaller entities of SP type.

The so far generally insufficient understanding of the size resolved aerosol composition and especially the role of organic compounds, their morphology and state of mixture had hampered a detailed understanding of the of the processes that lead to the activation of the high Arctic aerosol particles and thus their role in the formation of cloud droplets (Leck and Svensson, 2015; Martin et al., 2011; Zhou et al., 2001; Leck et al., 2002). One evident outcome from this study is that the aerosol particles to be activated into cloud droplets over the Arctic pack ice areas cannot be seen as simply inorganic salts. None of the aerosol particles showed an apparently cubic or otherwise crystalline appearance that could be attributed to sea salt particles. Instead the results from this study clearly show that organic marine gel matter significantly contributes to the particle number concentration over the whole sub-micrometer size range but especially at diameters below 60 nm.

A parallel study conducted during the ASCOS campaign (Orellana et al., 2011) demonstrated that airborne aerosol particles contain hydrophobic moieties on their surface that play an important role for gel formation (Maitra et al., 2001) and increase the rate of gel assembly (Ding et al., 2008). The interaction of the hydrophilic and hydrophobic entities on the structure of the polymer gels likely will influence the water vapor pressure and decrease the surface tension of the cloud droplets to be formed (Leck and Svensson, 2015; Ovadnevaite et al., 2011).

Water-soluble particles like ammonium sulfate were present mainly in the accumulation mode at diameters above 100 nm. Growth of the sub-Aitken particles probably resulted from deposition of acids/organic vapors on polymer gel particles and produced HP or sulfur containing particles with hygroscopic properties typical for a gel nucleus covered by a sulfate-methane sulfonate-ammonium complex. At the same time the fragmentation of larger particles is capable of adding numbers into the Aitken mode (Leck and Bigg, 1999; 2010; Karl et al., 2013). Orellana and Verdugo (2003) and Orellana et al. (2011) observed the sensitivity of marine gels to changes in the physicochemical environment (pH and T) and the fragmentation of gel matter into smaller entities as a result to UV radiation exposure. Acidic compounds typically found in the marine atmosphere like sulfuric acid and dimethyl sulfide (DMS) induced volume collapse of the swollen hydrated polymer gel network into a condensed and more compact form (Tanaka et al., 1980; Leck and Bigg, 2010;

Orellana et al., 2011). Condensation of sulfur acidic compounds and in-cloud processing of the marine gels in the atmosphere during their passage over the pack-ice and continuous exposure to UV radiation due to the length of the polar day in summer could produce smaller sized fragments of marine gels similar to the spherical subunits observed in *"aggregate"/"aggregate with film"* particles and the dense inclusions in *"mucus-like"* particles. Since SP showed a maximum in number concentration in the same size range, at 27 nm, it cannot be excluded that fragmentation of gel matter or pH induced collapse of the gels lead to the formation of smaller entities and by that providing a mechanism to produce SP and to add particle numbers to the Aitken mode.

In hope of enhancing our understanding on CCN properties promoting /suppressing cloud droplet formation over the pack ice area in summer and at the same time meet the demand for observational data for the evaluation of climate models, this study has presented critical size resolved data on particle morphology, chemical composition and state of mixture based on the analysis of individual particles.

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	15-80 nm	80-200 nm	> 200 nm	Sum (% of total)
Single particles (% of total SP)	2609 (80%)	573 (18%)	57 (2%)	3239 (82 %)
Gel particles (% of total GP)	97 (24%)	198 (49%)	108 (27%)	403 (11 %)
Halo particles (% of total HP)	9 (3%)	95 (36%)	163 (61%)	267 (7 %)
Total number of particles				3909 (100%)

Table 1. Numbers and percentage of total for single particles (SP), gel particles (GP) and halo particles (HP) imaged with SEM and used for calculating number size distributions.

	No Na^+/K^+, no Ca^{2+}/Mg^{2+}	Ca^{2+}/Mg^{2+}	Na^+/K^+	Ca^{2+}/Mg^{2+} and Na^+/K^+
Single particles	4 %	4 %	13 %	78 % (Na^+/K^+)
"Aggregate" particles	-	-	20 %	80 % (Na^+/K^+)
"Aggregate with film" particles	-	17 %	17 %	67% (Ca^{2+}/Mg^{2+})
"Mucus-like" particles	-	11 %	3 %	86 % (Ca^{2+}/Mg^{2+})
Halo particles	25 %	-	50 %	25 % (Na^+/K^+)

Table 2. Fraction of particles containing the ions Na^+/K^+ or Ca^{2+}/Mg^{2+}, or both, Na^+/K^+ and Ca^{2+}/Mg^{2+}, or neither Na/K nor Ca^{2+}/Mg^{2+} in single particles, *"aggregate"* particles, *"aggregate with film"* particles, *"mucus-like"* particles and halo particles. The ions written in brackets in the last column indicate the prevalent type of ion in the respective type of particle.

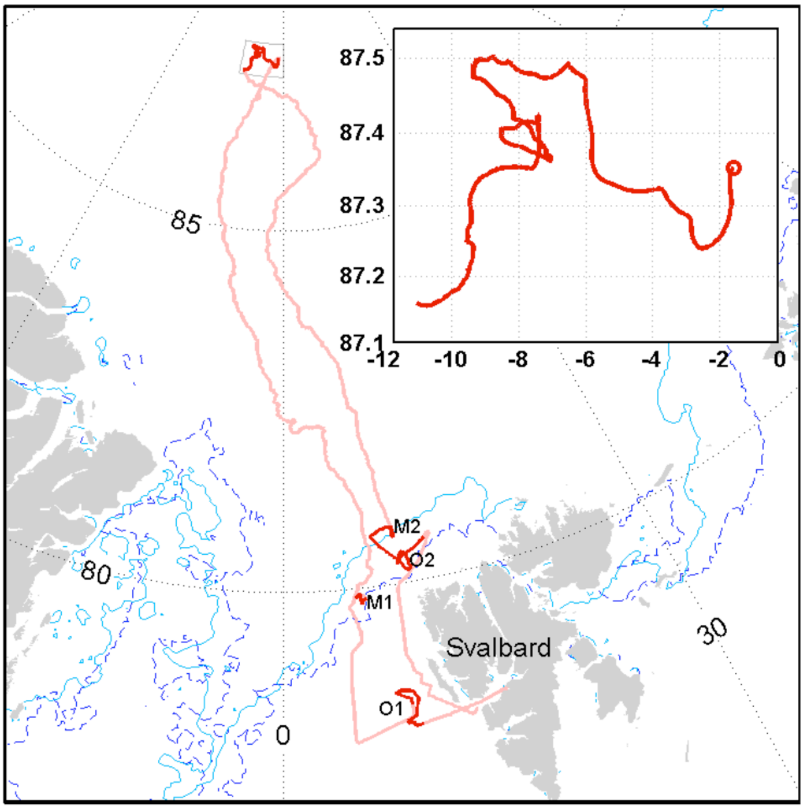

Figure 1. Track of the icebreaker *Oden* in the Arctic (pink). The path during the ice-drift is shown in the insert (red line); the circle indicates the start of the ice-drift, the ice edge (thin blue line) was passed on 12 August 2008.

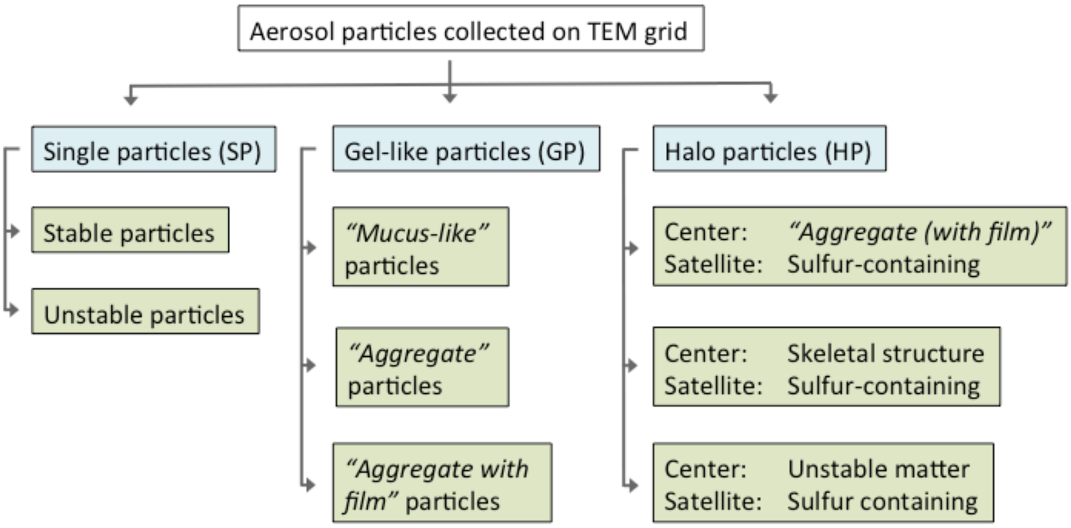

Figure 2. Scheme of the aerosol particle types collected on Formvar grid; the particles observed with SEM are shaded in light blue, particles observed in TEM are shaded in light green.

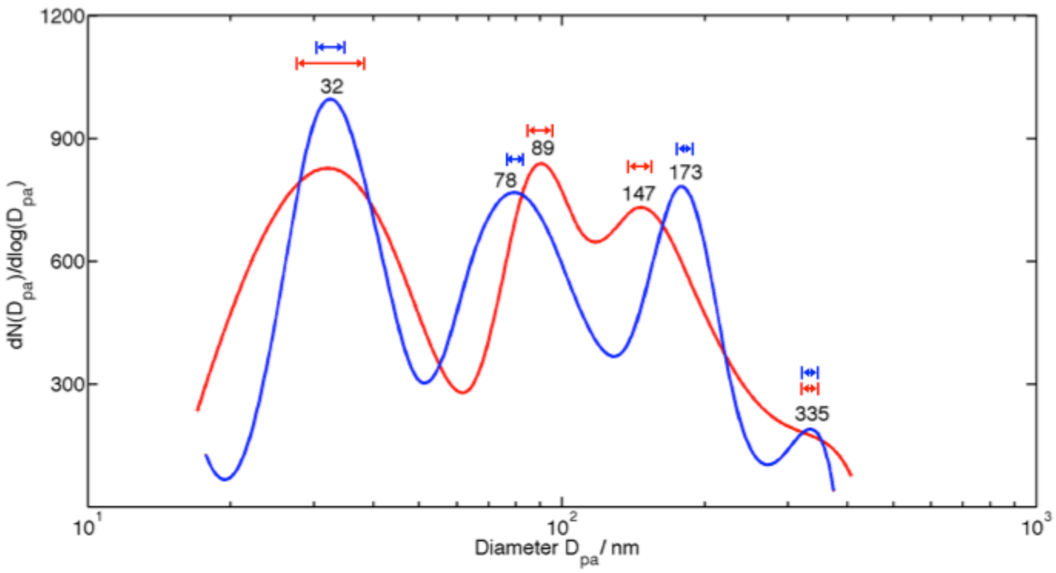

Figure 3. Number size distribution of the total aerosol collected for this study; red line: SEM derived particle number distribution, error bars represent the error size determination retrieved from calibration measurements described in Hamacher-Barth et al. (2013); blue line: number size distribution from simultaneous TDMPS measurements, errors bars represent 5 % uncertainty of the data (Wiedensohler et al., 2012).

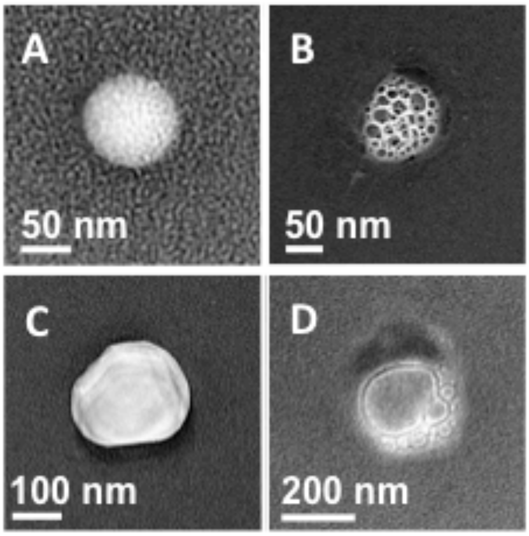

Figure 4. Examples for single particles (SP) observed with TEM. (A) a particle stable under the beam of the electron microscope. (B) particle with a skeletal structure. (C) a particle stable under the electron beam. (D) an example for a particle that is unstable under the electron beam.

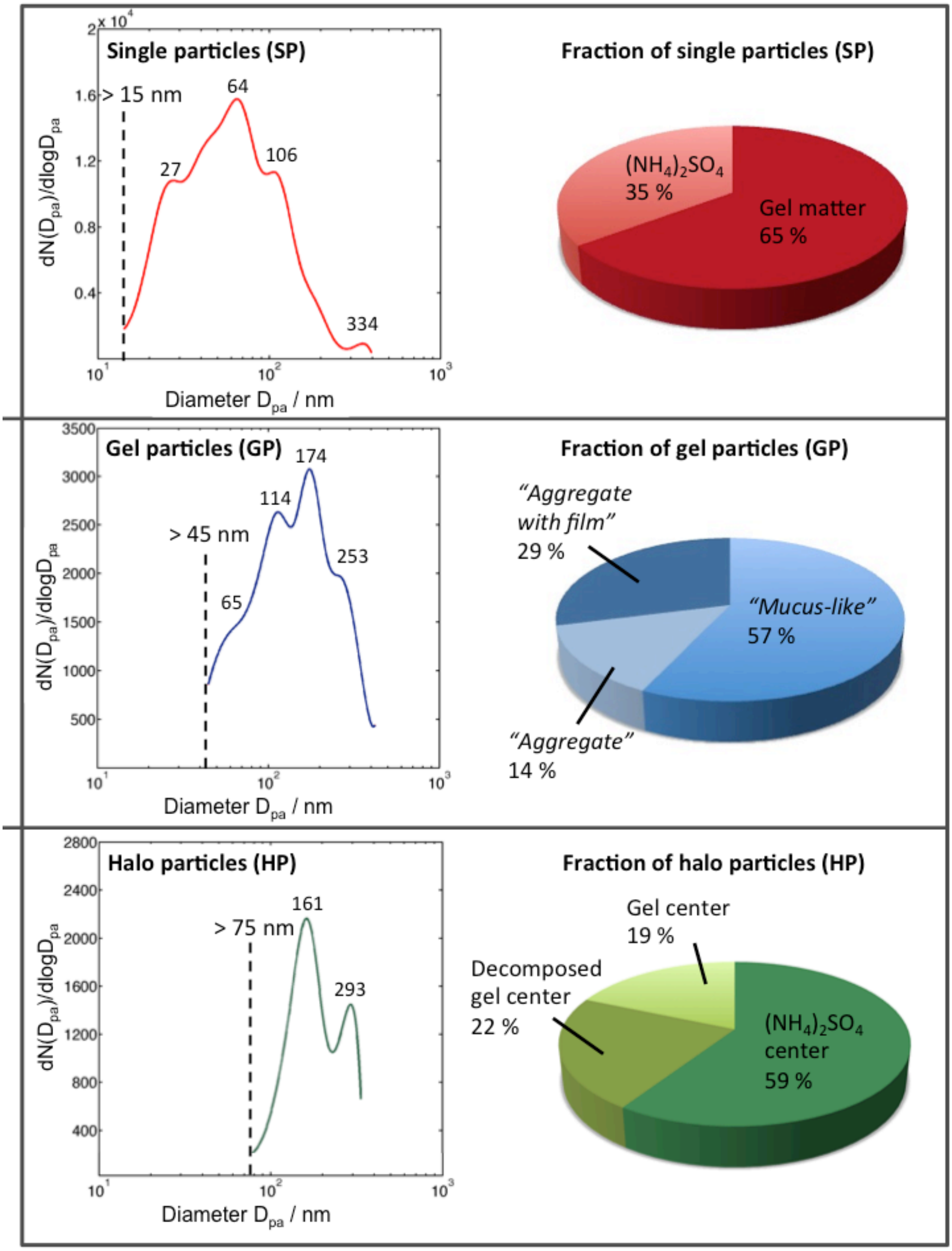

Figure 5. SEM number size distribution of the particle types (single particles, gel-like particles and halo particles) evaluated for this study (to the left) plus the fraction of the different subgroups of particles derived from TEM (to the right). The dashed line in each figure marks the lowest diameter at which the respective particle type appears.

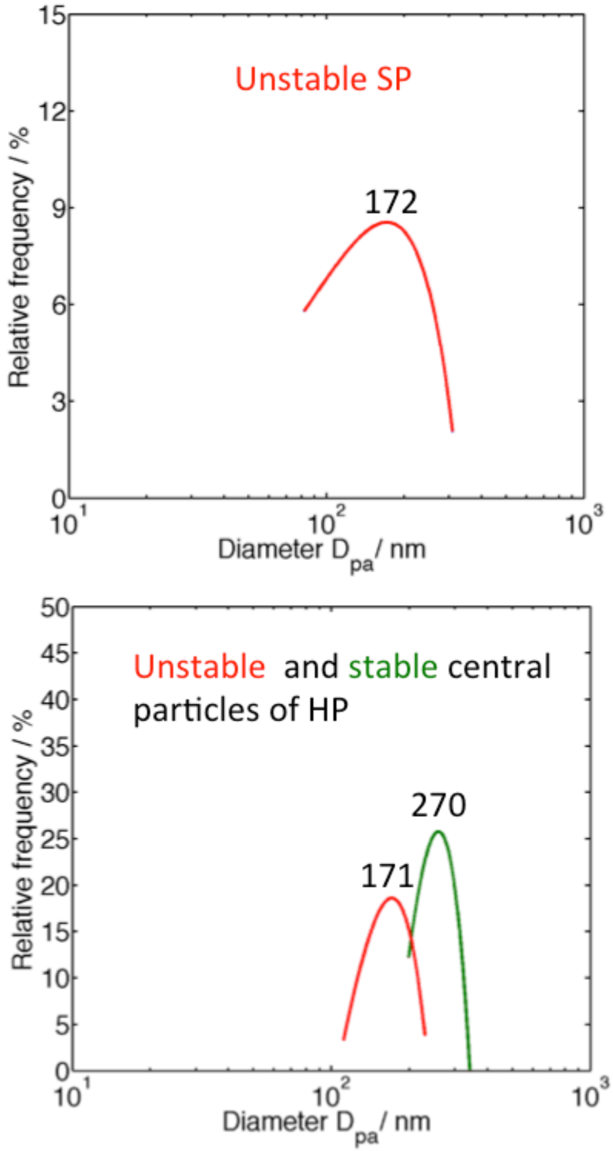

Figure 6. Number size distributions obtained from TEM images. Upper panel: unstable SP. Lower panel: central particles of HP; red line: unstable central particles, green line: stable central particles comprising *"aggregate"*, *"aggregate with film"* and skeletal particles.

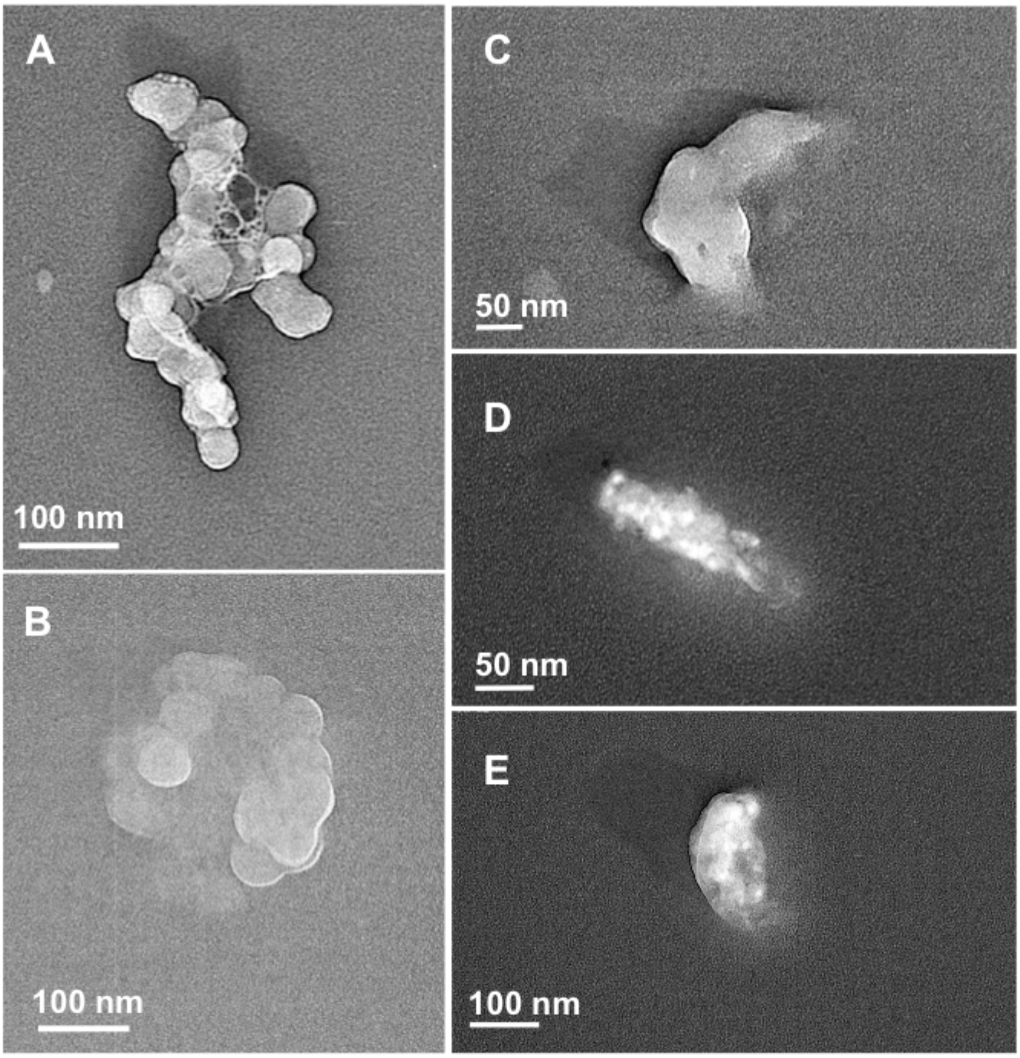

Figure 7. Examples for particles built up by aggregated subunits, observed with TEM. (A), (B) consist of pure aggregates (*"aggregate"* particles). (C), (D) and (E) aggregate particles covered with a thin film of gel *("aggregate with film"* particles).

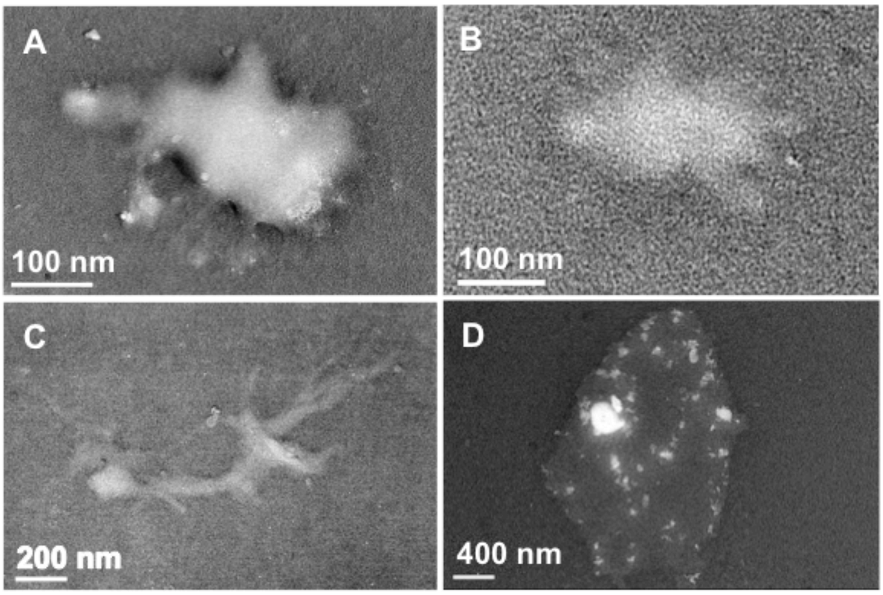

Figure 8. Examples for *"mucus-like"* particles observed with TEM. (A) mucus matter with small dense inclusions, partly outdrawn on the Formvar film. (B) mucus matter, outdrawn on the Formvar film. (C) mucus matter, extensively outdrawn on the formvar film. (D) mucus matter with numerous dense inclusions.

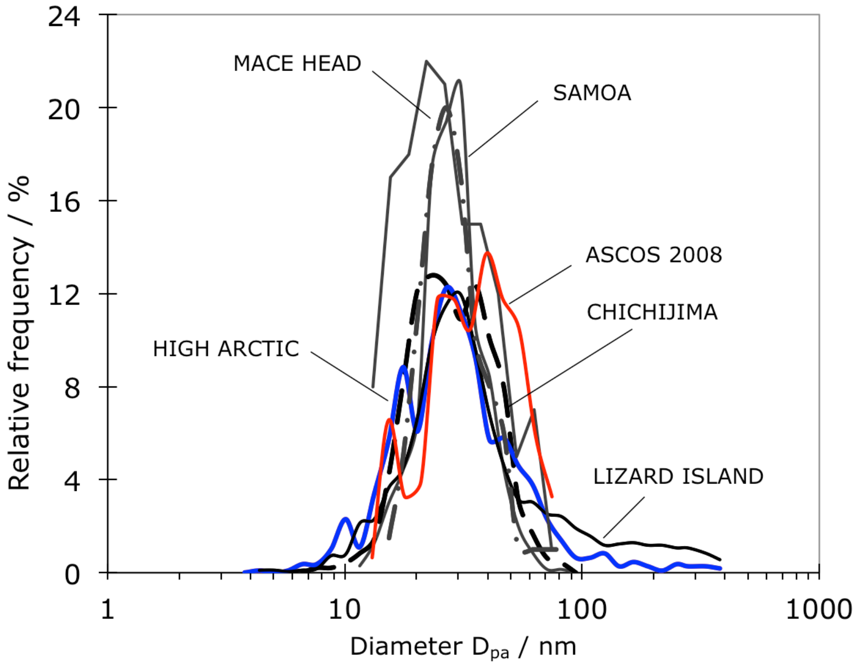

Figure 9. Number size distributions of airborne aggregate particles and their building blocks at different locations: Mace Head (53°N, 10°W), Lizard Island (14.6°S, 145.5 °E), American Samoa (14 °S, 172 °W), Chichijima (27 °N, 142 °E), High Arctic (AOE-2001, between 88.9 °N and 88.2 °N; blue line), and ASCOS 2008 (between 87 °N, 1°W and 87 °N, 11 °W, red line). All particles were assumed to be spherical in shape (from Bigg and Leck (2008), modified).

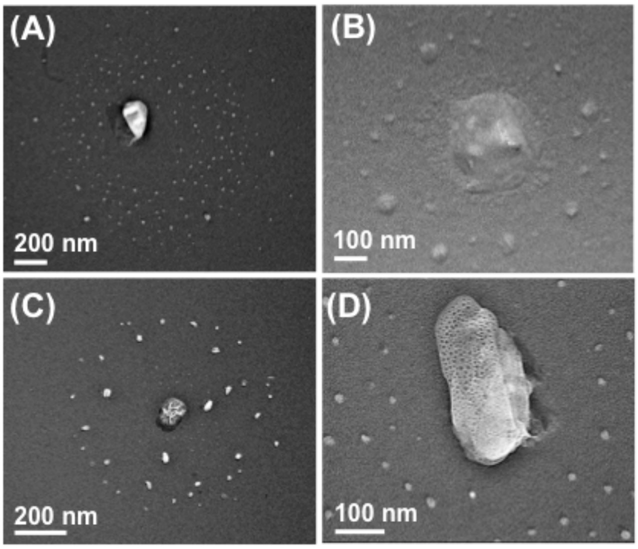

Figure 10. Examples for Halo Particles observed with TEM. (A) a central *“aggregate”* particle surrounded by satellite particles of sulfuric acid and a smaller amount of methane sulfonic acid. (B) central *“aggregate with film”* particles, surrounded by satellite particles of sulfuric acid and methane sulfonic acid. (C) central particle formed by ammonium sulfate, satellite particles formed by methane sulfonic acid, probably mixed with sulfuric acid. (D) central particle of degenerated gel, surrounded by methane sulfonic acid mixed with sulfuric acid.

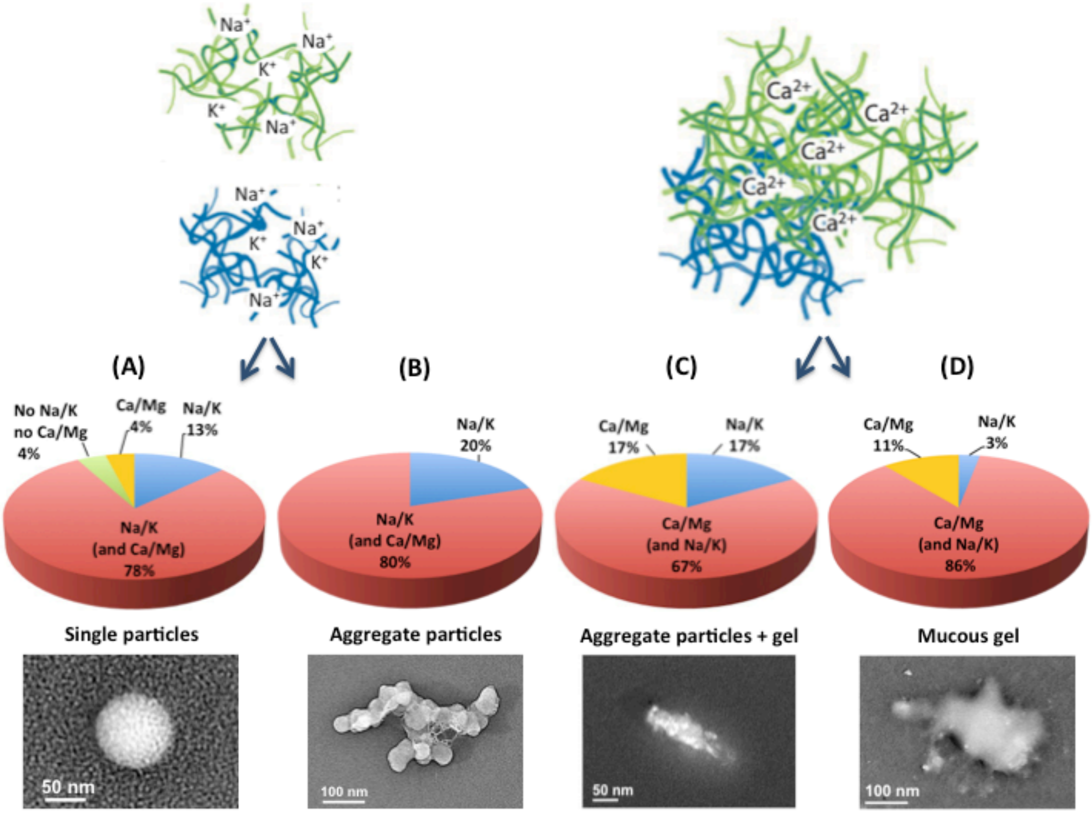

Figure 11. Fraction of particles containing the following ions: Na^+/K^+ (blue), Ca^{2+}/Mg^{2+} (yellow), Na^+/K^+ and minor contents of Ca^{2+}/Mg^{2+} (red), and neither Na^+/K^+ nor Ca^{2+}/Mg^{2+} (green). (A) Single particles comprised of gel matter. (B) *"mucus-like"* particles. (C) *"aggregate"* particles. (D) *"aggregate with film"* particles.

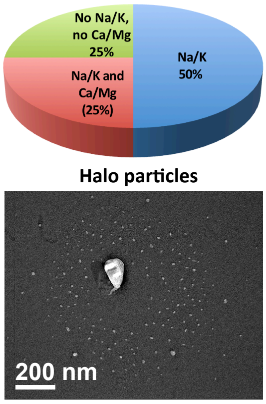

Figure 12. Fraction of HP containing the following ions: Na^+/K^+ (blue), Na^+/K^+ and Ca^{2+}/Mg^{2+} (red), and neither Na^+/K^+ nor Ca^{2+}/Mg^{2+} (green).

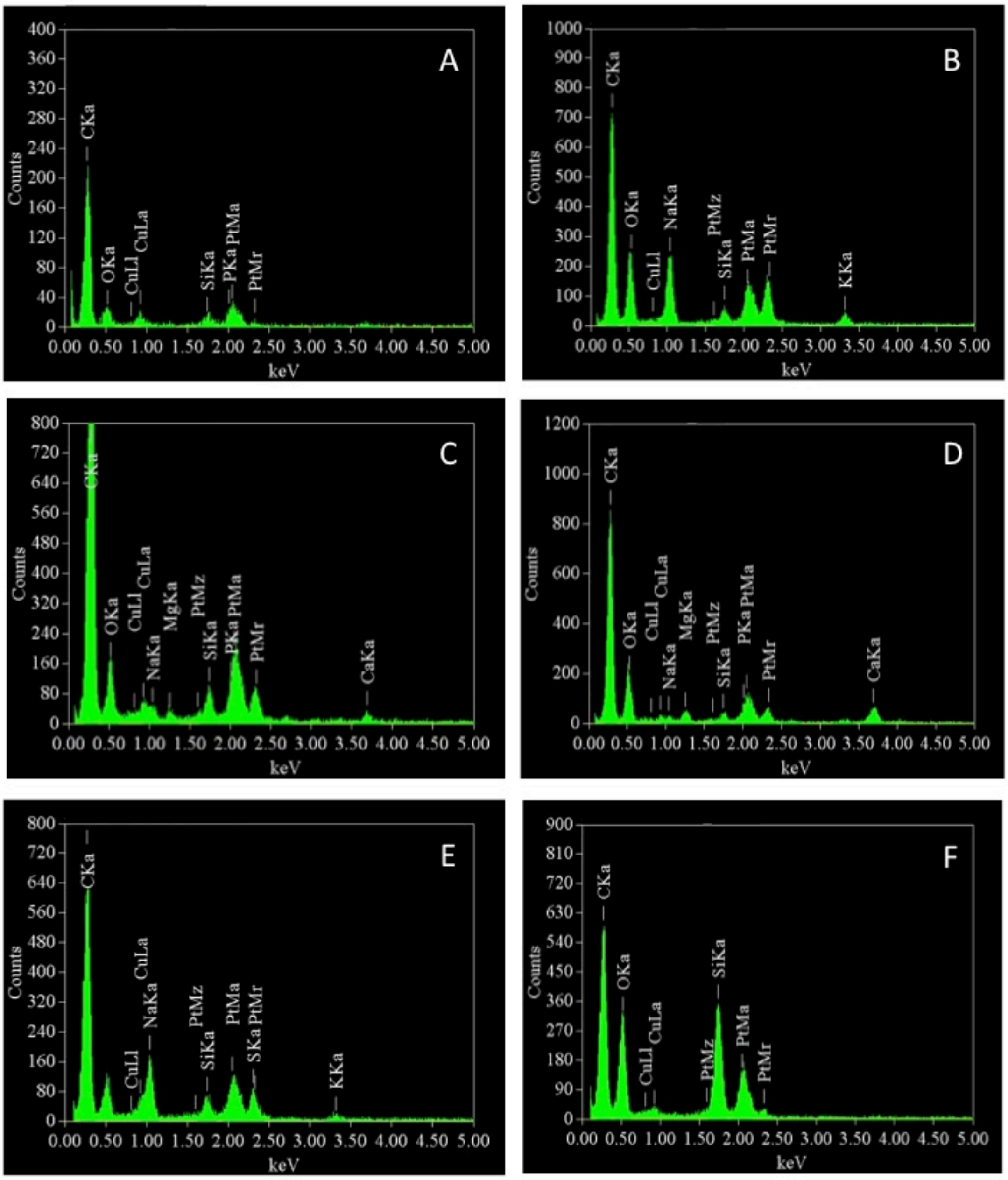

Figure S1: Examples of EDX spectra of aerosol particle investigated in this study. (A) single particle containing neither Na^+/K^+ nor Ca^{2+}/Mg^{2+}. (B) *"aggregate"* particle containing Na^+/K^+. (C) *"aggregate with film"* particle containing Na^+ and minor contents of Ca^{2+}/Mg^{2+}. (D) *"mucus-like"* particle containing Ca^{2+}/Mg^{2+} and minor contents of Na^+. (E) halo particle containing Na^+/K^+ and S probably in the satellite particles. (F) blank spectrum taken from a Pt-shadowed TEM grid.