

# Multidisciplinary research on biogenically driven new particle formation in Svalbard (SVALBAEROSOL)

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## 1. Introduction

### 1.1 Arctic change, clouds and climate

The climate and environment in the Arctic are changing faster than anywhere else on this planet (e.g. Mauritsen 2016). The warming climate is reflected in the decrease in snow cover, thawing of permafrost, changes in flora and fauna and decay and thinning of Arctic sea ice (e.g. Overland and Wang 2013; Stroeve and Notz 2018). Sea ice loss further accelerates warming since the Arctic sea ice plays an important climatic role by reflecting solar light back into space. There is a positive feedback: when the ice melts, solar radiation is absorbed into and thereby heats the (darker) seawater and leads to increased melting. Melting of sea ice and other climate change effects influence also the marine ecosystem, including phytoplankton and their productivity (Wassmann and Reigstad 2011). As phytoplankton are also emitting biogenic vapours into the atmosphere (Levasseur 2013, Galí et al 2019), these changes may have consequences to atmospheric chemistry, secondary aerosol formation and clouds. An increase in phytoplankton productivity may thus lead to another feedback (negative or positive) that could mitigate or accelerate Arctic warming. The idea of increasing phytoplankton productivity with increasing temperature leading to a negative feedback via perturbations of cloud properties was first presented by Charlson et al. (1987). This so-called CLAW-hypothesis has also been strongly criticized (Quinn and Bates 2011). However, the Arctic system is highly complex and the sign of the feedback depends on many more variables (see below). Nevertheless, much more data are required before final conclusions on these mechanisms can be drawn.

Low-level clouds above Arctic sea ice and open waters play an important climatic role that is connected to the characteristics of the sea ice. Above highly reflecting ice surfaces, low-level clouds decrease the radiative cooling of the surface which keeps the ice warmer than it would be without clouds. This process reverses above dark surfaces, such as open seawater, where the reflectance of solar radiation by clouds cools the surface whenever the radiation intensity is sufficient (Tjernström et al. 2014). The formation of clouds depends on the prevailing meteorological conditions, but the optical properties of clouds are determined by both their micro- and macro-physical characteristics. The optical properties of clouds depend, among other variables, on the amount and properties of cloud condensation nuclei (CCN), which are aerosol particles with diameters larger than 20 nm. Cloud droplets are formed by water condensation on CCN. If the CCN concentrations are high, little water remains for each droplet leading to small but numerous cloud droplets, which makes the cloud highly reflective (Twomey et al. 1974). Small droplet size also increases the lifetime of the cloud (Albrecht et al. 1989). The sign and magnitude of any cloud feedback depends not only on aerosol properties and CCN concentrations but also on the height and geographical location of the cloud, time of the year and day, availability of water vapour, surface albedo

etc. Arctic clouds, in general, produce a cooling effect at the surface only in the summer while warming the Arctic surface for the rest of the year (Alterskjaer et al. 2010; Sedlar et al. 2011; Doscher et al. 2014; Intrieri et al. 2002; Shupe and Intrieri 2004). Addition of cloud nuclei can thus lead to cooling or warming of surface temperatures and therefore the overall effects of aerosol – cloud interactions in the Arctic currently remain highly uncertain. This report does not aim at describing the details of aerosol – cloud – climate interactions. However, these interactions and associated feedbacks – including those driven by sea ice loss – cannot be reliably solved, unless the mechanisms of how these CCN end up in the Arctic atmosphere are known. So, what is known?

## **1.2 Aerosols**

Atmospheric aerosol particle diameters range from nanometers to micrometers. When particles are in the few nanometers scale, supersaturated water vapor cannot condense on them. When particles are larger than ~20 - 100 nm, water vapor (RH>100%) may condense on them, thereby growing the particles into cloud droplets. The lower end of the size range of CCN is not fixed, as it depends on atmospheric humidity and particle chemical composition as well as on concentration (availability) of potential CCN. In the clean Arctic environment particles as small as ~20 nm may act as CCN (Beck et al. unpublished data).

The sources of polar CCN are both natural and anthropogenic. In the High Arctic, anthropogenic particles are long-range transported from Europe, North America and East Asia (Stohl 2006). The main source of natural aerosols is the ocean. Marine aerosols constitute one of the most important natural aerosol systems, which contributes significantly to the Earth's radiative budget and biogeochemical cycling (O'Dowd and de Leeuw 2007). The primary particles released from the sea surface (as sea spray) mainly consist of sea salt by mass but contain also biogenic organic matter. The secondary marine aerosol is suggested to originate from phytoplankton-emitted dimethyl sulphide (DMS). Over ice covered oceans, secondary aerosol formation is connected also to iodine emissions. The role of oceanic biota in modifying marine aerosol formation remains one of the most important questions in estimating the climate forcing by aerosols (O'Dowd and de Leeuw 2007). In the Arctic, around the Svalbard Archipelago, frequent new particle formation (NPF) events have been linked to biogenic precursors released by open water and melting of sea ice regions (Dall'Osto et al. 2017). NPF from gas phase vapours is an important topic, since up to 90% of Arctic CCN are suggested to belong to this fraction (Merikanto et al. 2009). Anthropogenic pollution, mainly SO<sub>2</sub>, may contribute to new particle production especially in the early spring during the transition from the Arctic haze period to clean, natural conditions. However, in this report we will limit our assessment to non-anthropogenic biogenic processes.

### 1.3 New particle formation (NPF) mechanisms in the Arctic

Atmospheric NPF is, in general, connected to a) emission of several precursor vapours, b) ionization of air by radon or galactic cosmic radiation, c) adiabatic cooling of air masses during updraft leading to increased supersaturation of precursor vapours and d) the surface area of pre-existing aerosols which serve as a sink for precursor vapours needed for new particle formation. NPF starts with homogeneous nucleation of vapours where gas phase molecules stick to each other, or heterogeneous ion-induced nucleation of vapours where gas phase vapours condense on top of an air ion (usually  $\text{HSO}_4^-$  - ion) due to ion-dipole interactions. In presence of sufficient amounts of supersaturated vapours, these approx. 1 nm clusters can grow up to CCN sizes in time scales of hours to days. While growing, these small particles suffer from continuous threat to be scavenged by pre-existing larger aerosol particles and therefore only a small fraction of the formed clusters ever reaches the CCN size. CCN formation is therefore highly sensitive to the availability of condensing vapours, as well as the surface area of pre-existing particles.

To understand the present and predict the future CCN concentrations and properties, the exact secondary aerosol formation pathways must be known. In many mid- or low latitude continental environments, secondary aerosol formation is likely driven by a cocktail of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) (Kulmala et al. 2013), ammonia ( $\text{NH}_3$ ) (Kirkby et al. 2011), amines (Almeida et al. 2013, Yao et al. 2018), and highly oxidized organic molecules (HOM) (Ehn et al. 2014) from natural or anthropogenic VOC (Volatile Organic Compound) sources. In coastal areas, local aerosol formation from iodine oxyacids, especially iodic acid  $\text{HIO}_3$  originating from macroalgae iodine emissions, produces vast concentrations of new particles (Sipilä et al. 2016). But what is known about Arctic polar aerosol formation?

#### 1.3.1 Arctic aerosol formation and the role of phytoplankton DMS and bird colony $\text{NH}_3$

One of the first datasets on Arctic aerosol size distributions was recorded in late summer and early autumn 1991 during the International Arctic Ocean Expedition (IAOE-91) onboard the Swedish icebreaker Oden (Wiedensohler et al. 1996; Covert et al. 1996). Those datasets are the first to report the existence of a “nucleation” mode aerosol (<20 nm) indicating active NPF in the Arctic atmosphere. These studies also connect the appearance of these nucleation mode particles to oceanic emissions, potentially DMS. Since then several reports on observations of NPF have been published.

Giardi et al. (2016) used data collected at the Grubebadet laboratory in Ny-Ålesund and found NPF to be frequent during spring and summertime. While in early spring, anthropogenic sulphur was observed in bulk aerosol, late spring and early summertime observations of aerosol phase methane sulphonate (MSA) suggested a strong influence of biogenic marine DMS emissions (MSA is a proxy for DMS, the oxidation of which leads to

the formation of  $\text{H}_2\text{SO}_4$ ) in NPF or at least in particle growth to detectable sizes.

The role of DMS in secondary aerosol and NPF is generally well established. Ghahremaninezhad et al. (2016) performed measurements in the Arctic ocean and concluded that fine particles were mainly made of sulphate of biological origin showing the critical role of marine organisms, e.g. phytoplankton, for the formation of new particles in the summertime Arctic. Mungal et al. (2017) measured fluxes of DMS in the summertime Arctic (Baffin Bay between Greenland and Canada). As a result of air mass and chemical transport modelling, they concluded that though marine sources were dominant, there is a possibility that non-marine sources (e.g. lakes, melt ponds and tundra) could make additional contributions to atmospheric DMS concentrations. Further DMS data both from the atmosphere and from the sea water with larger spatial and temporal resolution are needed to resolve this issue. Park et al. (2017) analyzed atmospheric DMS concentrations, aerosol particle size distribution and aerosol chemical composition in Ny-Ålesund, Svalbard. They showed that the formation of submicron (secondary) aerosols was strongly correlated with the atmospheric DMS mixing ratio during the phytoplankton bloom period.

Besides availability of aerosol precursor vapours or gases, such as DMS, the formation of new particles is strongly connected to properties of pre-existing aerosols. Data collected from Alert (Nunavut, northern Canada) shows that NPF is frequent in the summertime Arctic and associated with a low condensation sink (pre-existing aerosol surface) (Leaith et al. 2013). Tunved et al. (2013), based on data taken at the Zeppelin station, Ny-Ålesund, also showed that NPF events associated with marine air masses are a rather common phenomenon in the Arctic during summer, which result from both photochemical production of particle precursor vapours and low condensation sinks. Furthermore, Croft et al. (2016) confirmed that NPF during summer time in the Arctic is associated with efficient wet removal of larger pre-existing aerosol allowing the condensable vapour concentrations to reach the levels needed for efficient NPF and growth. Authors call for further research on cloud scavenging and wet removal of aerosols as well as NPF to reduce uncertainties in aerosol-cloud-climate coupling in the Arctic.

Dall'Osto et al. (2017) investigated the role of sea ice extent NPF by analysing 11 years of aerosol size distribution data from the Zeppelin observatory next to Ny-Ålesund. They found that NPF occurred in 18% of the days with a peak of 51% during the summer months. They suggested that these events are connected to biogenic precursor gases released from regions with open water and/or melting sea ice. They also showed that NPF is anti-correlated with sea ice extent, suggesting the open ocean as a primary source of new particle precursor gases. Furthermore, they demonstrate a more than 20% increase in CCN concentrations due to NPF and suggest that melting sea ice via accelerated new particle and CCN formation may have already accelerated Arctic warming (i.e. they assume positive feedback). In a follow-up work, Dall'Osto et al. (2019) analysed simultaneously collected

data from Zeppelin and two additional high Arctic sites during a 3-year period (2013–2015) – Gruebadet in Ny-Ålesund and Villum Research Station at Station Nord, Greenland. Their analysis shows that NPF occurred in 16% - 32% of the days. The authors suggest that lower ultrafine aerosol concentrations at the Greenland site in comparison to the Svalbard sites are indicative of less efficient NPF due to longer time periods of consolidated pack ice in Greenland. Conclusions regarding the role of sea ice in suppressing aerosol formation are highly convincing but authors still state that it is imperative to continue strengthening international scientific cooperation to address these research questions beyond a singular station or measurement events. Data collected from Alert, Nunavut, northern Canada also shows that NPF is frequent in the summertime Arctic and associated with a low condensation sink (Leaith et al. 2013). The authors show that NPF is connected with the presence of MSA, which points toward emissions of DMS, and possibly other organic precursors as a primary driver of NPF.

Leaith et al. (2013) assessed the increase in CCN and cloud droplet number concentrations (CDNC) due DMS-related new particle formation. They show that increases in CDNC can be as high as 23–44  $\text{cm}^{-3}$ , which would remarkably modify the Arctic summer shortwave cloud albedo. Their study unambiguously shows that secondary aerosol formation is a highly important phenomenon in the clean summertime Arctic environment. All in all, DMS clearly seems to be important for Arctic aerosol formation, CCN concentrations and cloud properties. But how?

In the atmosphere, DMS is oxidized by OH-radicals to MSA and  $\text{SO}_2$ .  $\text{SO}_2$  further reacts with OH to produce  $\text{H}_2\text{SO}_4$ , which is known to be responsible for particle formation in multiple environments over the globe.  $\text{H}_2\text{SO}_4$  molecules, however, do not stick to each other and any clusters would evaporate immediately, therefore stabilizing compounds are required for nucleation. Water can stabilize nucleating clusters in cold temperatures (Kirkby et al. 2011) relevant for the upper troposphere, but unlikely in close to zero degrees Celsius temperatures of summertime Arctic. Ammonia, on the other hand, would stabilize small clusters far better than water and minute, sub-100 pptv concentrations can enhance the rate of NPF by several orders of magnitude (Kirkby et al. 2011; Dunne et al. 2016). Ammonia measurements in the concentrations required to catch the particularly low Arctic levels are, however, almost non-existent. Wentworth et al. (2016), measured ammonia in Baffin Bay and the eastern Canadian Arctic Archipelago and found concentrations between 40 - 870 pptv. Such concentrations would be sufficient to enhance particle formation rates by a factor of approx. 100 (40 pptv) – up to over 1000 (870 pptv) in  $\text{H}_2\text{SO}_4$ -limited conditions ( $\text{H}_2\text{SO}_4 < \text{few } 10^7 \text{ molecules cm}^{-3}$ ), which is the case in most parts of the world (in Antarctica, the closest point of comparison, the maximum recorded values are in the range of  $2 \times 10^7 \text{ molecules cm}^{-3}$ , Jokinen et al. 2018). Wentworth et al. (2016) suggest sea-bird colonies as a primary source of ammonia. Simulations that account for colonies suggest ammonia concentrations from few pptv to few hundreds of pptv that contribute strongly to new

particle and CCN formation around the Svalbard archipelago (Croft et al. 2016). However, due to sparseness of data and difficulties related to ammonia measurement techniques, a proper assessment would require more data on ammonia concentrations with better spatial and temporal resolutions around the whole Arctic.

Another open question concerns the role of MSA in the formation and growth of sub-CCN aerosols. MSA is found in bulk aerosol samples (e.g. Park et al. 2017), but analysis of bulk hardly tells anything about the composition of particles in the sub-50 nm size range. As the measurements of chemical composition of Arctic low concentrations of sub-50 nm particles are either extremely challenging or impossible, concurrent measurements of gas phase MSA and particle growth rate, or the measurement of aerosol hygroscopicity or volatility would provide indirect evidence of whether MSA contributes to the growth of small particles or not.

### 1.3.2 Phytoplankton, DMSP production and DMS emissions

Arctic DMS (dimethylsulphide) emissions increased by 33% in the past decade (Galí et al. 2019). This trend is mostly explained by the reduction in sea-ice extent and the extrapolation to an ice-free Arctic summer could imply up to 3.6-fold increase in DMS emissions compared to present emissions (Galí et al. 2019). Such a change, if reflected in  $\text{H}_2\text{SO}_4$  and MSA concentrations, would largely influence new particle and CCN production in the Arctic. DMS, which represents the main source of biogenic sulphur emissions (Liss et al. 1997), is produced by the degradation of dimethylsulfoniopropionate (DMSP). DMSP itself is produced by marine algae for osmoregulation, and may also have other important cellular functions (e.g. as an antioxidant or cryoprotectant; Sunda et al. 2002; Stefels et al. 2007). DMSP is released from the algae primarily as a result of grazing or virus-induced lysis of the cells, and cleaved to DMS via bacterial degradation (Curson et al. 2011). After its release, DMS is consumed by bacteria, depending on the degradation pathway either via the release of DMS or the usage of both carbon and sulphur (Kiene et al. 2000). Thus, the interplay of microbial production and consumption rates together with air-sea exchange processes influence the measurable DMS and DMPS concentrations in seawater.

A number of studies have shown the general correspondence of DMS/DMSP and chlorophyll-a in the marine environment (Challenger and Simpson 1948; Trevena and Jones 2006 and 2012; Uhlig et al. 2019; Jarníková et al. 2018). However, not all marine algae are capable of producing DMSP and production varies between taxonomic groups. Dinoflagellates as well as prymnesiophytes (e.g. the important colony-forming *Phaeocystis* spp.) producing the highest, and diatoms as well as prasinophytes (e.g. the picoplankter *Micromonas* spp.) producing rather low amounts of DMSP (Keller et al. 1989; Stefels et al. 2007). In polar regions, also sea ice algae make an important contribution (Kirst et al. 1991; Uhlig et al. 2019). The quantification of the contribution of different marine algae and their

associated bacteria to DMSP and DMS emissions are key in understanding the factors affecting DMS emissions in the Arctic. Despite differences between taxonomic groups, also physiological adjustments have an impact on microalgal DMSP production. As reviewed by Stefels et al. (2007), potential stressful conditions such as a strong increase in salinity or irradiance or very cold temperatures have been found to increase cellular DMSP levels in different phytoplankton, while effects of nutrient limitation are complex and still not fully understood. Therefore, impacts of the multiple drivers that are concurrently changing under climate change are not straight-forward to predict. There is evidence that DMS production by phytoplankton decreases with ongoing ocean acidification (Husserr et al. 2017) even though Arctic phytoplankton species composition and primary production have been shown to be rather resistant towards acidification (Hoppe et al. 2018). Understanding how the interplay of processes affecting the timing, taxonomic composition and physiological state of phytoplankton blooms around Svalbard (Hegseth et al. 2019; Hoppe et al. (unpublished data)) will affect DMS emissions and aerosol formation will require coordinated oceanographic, biological and atmospheric observations. The Ny-Ålesund research station provides ideal conditions for such an endeavour.

### 1.3.3 Recent update: Iodine emissions and aerosol formation

Besides DMS, iodine emissions have been recently identified as a source of aerosol precursor vapours. Iodine chemistry in general plays important roles in atmospheric chemistry, including ozone and mercury depletion in the polar troposphere (Saiz-Lopez and von Glasow 2012; Simpson et al. 2015). Very recently, Sipilä et al. (2016) measured high concentrations (up to  $10^8$  molecules  $\text{cm}^{-3}$ ) of iodic acid ( $\text{HIO}_3$ ) in spring time northern Greenland (Villum Research station) associated with NPF events. By direct measurements of the chemical composition of the nucleating clusters, they suggested that particle formation proceeds via sequential addition of  $\text{HIO}_3$  molecules, i.e. homogenous unimolecular nucleation of  $\text{HIO}_3$ , possibly followed by subsequent conversion to  $\text{I}_2\text{O}_5$  in clusters and recycling of water. However, the exact formation pathways of  $\text{HIO}_3$  in the atmosphere are not known, and neither are the iodine-containing precursors. The primary candidate here is  $\text{I}_2$ , which is photolyzed to two iodine radicals which subsequently react with ozone, leading to the formation of IO. Pathways from IO to  $\text{HIO}_3$  are under intensive research with no conclusion yet. But where does iodine come from?

Due to limited knowledge, we now need to have a wider perspective to understand the possible sources and focus not only on the Arctic but both polar areas. Studies have shown that inorganic iodine compounds (i.e. iodide monoxide (IO) and molecular iodine ( $\text{I}_2$ )) are abundant in the ice-covered polar regions; especially during spring. Saiz-Lopez et al. (2007a) measured a peak of 20 ppt of IO during the springtime in Halley station, Antarctica. Satellite observations confirmed the presence of widespread IO, with the highest concentration observed over the ice-covered seas around Antarctica (Saiz-Lopez et al. 2007b; Schönhard



et al. 2012; Atkinson et al. 2012). Atkinson et al. (2012) suggested that  $I_2$  is most likely the precursor for IO, as they concurrently observed significant levels of  $I_2$  (up to 31 ppt) above the surface snow and sea ice in Antarctica. In the Arctic, Mahajan et al. (2010) reported IO concentrations up to 3.4 ppt at a sea ice edge site in Hudson Bay, Canada and Raso et al. (2017) measured 0.3-1.0 ppt of  $I_2$  in the Arctic atmosphere during spring time. Although there is a clear indication of iodine chemistry in the polar atmosphere, the source of inorganic iodine has not been clarified yet. Also, there is a significant difference in iodine emission between Antarctic and Arctic sea ice. This is probably associated with the fact that Antarctic ice is thinner, while in the Arctic multiyear thick ice is still more abundant. Thick ice prevents solar radiation to penetrate underneath the ice, and disables phytoplankton to bloom and produce significant amounts of iodine compounds (Nicolaus et al. 2012). Besides losing its areal coverage, Arctic sea ice is also thinning fast and losing multiyear ice, iodine emission rates therefore may increase in the future (Cuevas et al. 2018).

It is widely known that inorganic iodine can be produced by photochemical reactions of biogenic iodocarbons emitted from the ocean and ozone deposition to the open sea surface (Vogt et al. 1999, O'Dowd et al. 2002, Carpenter et al. 2012; MacDonald et al. 2014). Recent studies have highlighted the relationship between inorganic iodine compounds and polar sea ice as well as snow/ice covered regions in Antarctica (Spolaor et al. 2013; Granfors et al. 2014; Vallelonga et al. 2017), which may occur also in the Arctic. It was suggested that iodine emissions are attributed to the production of iodide ( $I^-$ ) and hypoiodous acid (HOI) by microalgae (e.g. pennate diatoms, dinoflagellates, flagellates) growing underneath or within the sea ice, and then being emitted to the atmosphere by permeation through the porous ice or fractures in the thin sea ice pack or due to melting of sea ice during the summer (Atkinson et al. 2012; Saiz-Lopez et al. 2015).

The snowpack can be another source of iodine emissions. High concentrations of iodine were found to be confined within the snowpack during wintertime and being released to the atmosphere through the photochemistry-induced re-mobilisation of iodine from the snowpack in the summer in Antarctica (Frieß et al. 2010; Spolaor et al. 2014). The emission mechanism is currently unclear, but could be potentially due to the accelerated (photo-)oxidation of iodide in ice/snow (Kim et al. 2016; Watanabe et al. 2019) and/or the photolysis of iodate in frozen salt (Gálvez et al. 2016). In the Arctic, whether the iodine compounds are primarily emitted from the open ocean (Mahajan et al. 2010) or from ice/snow covered regions still remains an open question, although a recent field observation by Raso et al. (2017) points out that the snowpack can be a source of  $I_2$  to the Arctic boundary layer.

Despite many open questions related to the sources and the exact chemical nature of iodine emissions, iodine is likely becoming more and more important in atmospheric chemistry and especially for understanding aerosol formation. Measurements from the RECAP ice-

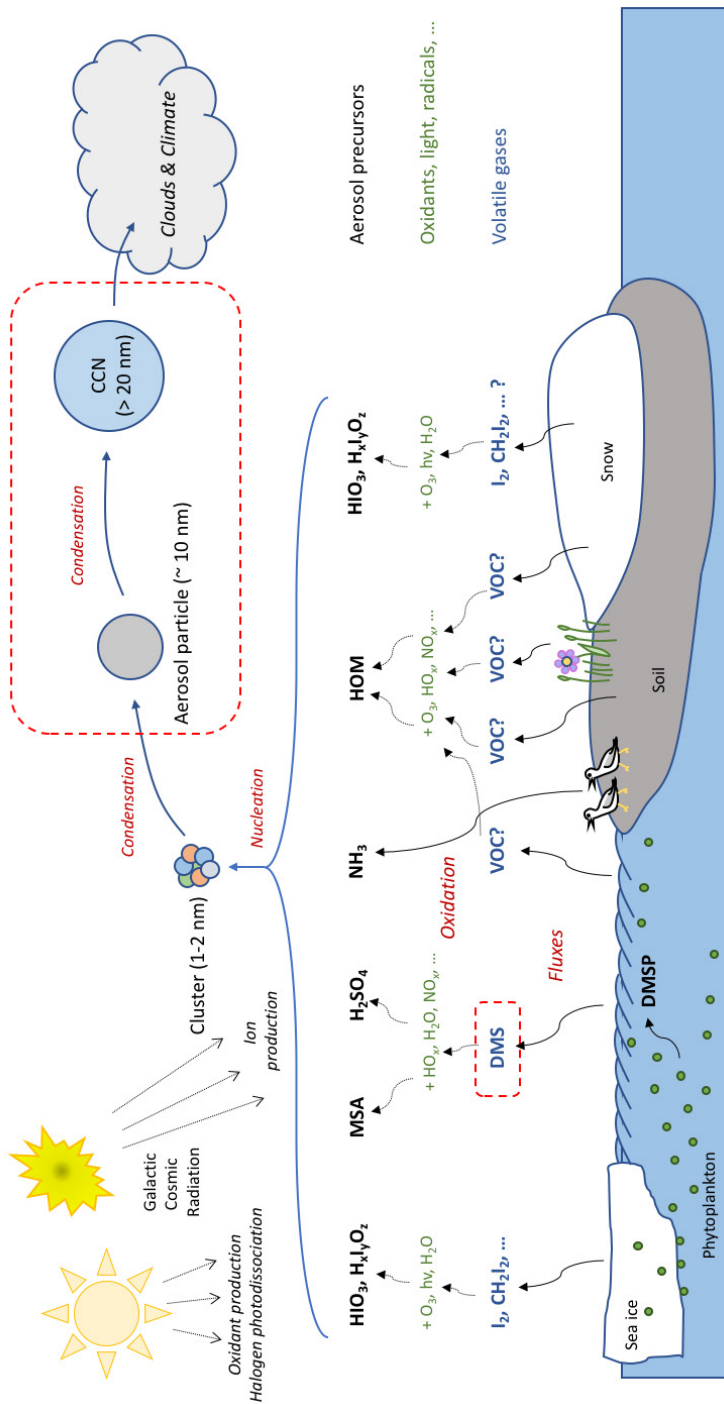
core (East Greenland) show that concentrations of atmospheric iodine have tripled (!) in the northern hemisphere within the past decades (Cuevas et al. 2018). They suggest that this increase is driven by anthropogenic ozone pollution and the thinning of Arctic sea ice, the latter resulting in enhanced phytoplankton productivity underneath the ice. Systematic measurements of gas phase iodine species would be required to resolve this question.

### 1.3.4 What is the role of volatile organic compounds (VOC) in Arctic aerosol formation?

As stated earlier, highly oxidized organic molecules (HOM, e.g. Ehn et al. 2014) from natural or anthropogenic VOC sources are highly important constituents and drivers of NPF and globally main constituents of secondary aerosol (Jimenez et al. 2009). In certain conditions and concentrations, HOM may even nucleate without  $\text{H}_2\text{SO}_4$  or other inorganic species (Kirkby et al. 2016). Whether that is the case in Svalbard, or Arctic in general, is not known. At a coastal Antarctic site, more than a thousand kilometres away from the nearest macroscopic land vegetation, peat lands or thawing permafrost (i.e. Sandwich islands), no indication of HOM was obtained (Jokinen et al. 2018). However, Arctic tundra flourishes in summertime, vegetation forms peat, and soils are in places rich in organic matter. Arctic tundra has been thus recognized as a source of VOC (Lindwall et al. 2016). Further, field measurements in Greenland indicates that thawing permafrost releases VOCs (Kramshøj et al. 2018).

The sea surface microlayer has also been recognized as source of Arctic VOC (Mungal et al. 2017). Another, surprising source of (oxidized) VOC is the photochemically active snowpack. OVOCs like acetaldehyde and acetone have been measured in the snowpack of Alert, Nunavut, Canada (Guimbaud et al. 2002; Houdier et al. 2002). Styrene fluxes have also been measured in the snow pack in Alert, indicating it to be a potential contributor of VOCs (Kos et al. 2014). Formic and acetic acid fluxes have also been measured in the snowpack of Greenland and the South Pole (Dibb and Arseneault 2002). These VOC, may or may not be converted to HOM in the gas phase oxidation reactions with potential consequences to Arctic NPF and especially to growth to CCN. Experimental evidence is, however, largely lacking, though studies have also been extended from the mere quantification of VOCs to the measurement of the oxidation products of biogenic volatile organic compounds (isoprene, monoterpenes, and sesquiterpene) in the Canadian High Arctic (Fu et al. 2009).

Figure 1 summarizes the known and speculated sources of volatile species, their oxidation processes, resulting aerosol precursors, the conversion of these precursors to small clusters by nucleation, and further growth to climatically relevant CCN sizes by condensation.



**Figure 1:** Simplified scheme of potential processes leading to secondary aerosol formation in Svalbard. Almost none of the relevant quantities and compounds – including all condensable aerosol precursor vapours – are systematically measured today.

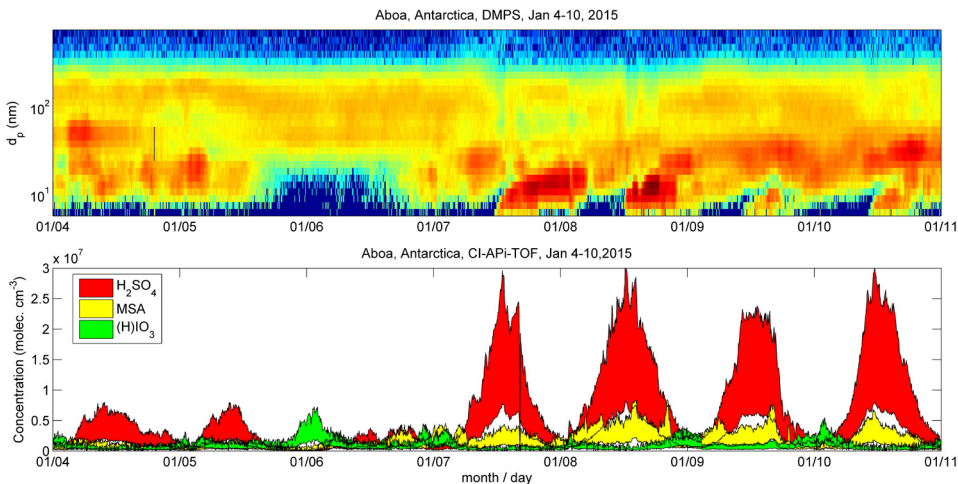
## **1.4 Novel technology that allows resolving and monitoring NPF processes**

### **1.4.1 Atmospheric monitoring of vapours and small particles**

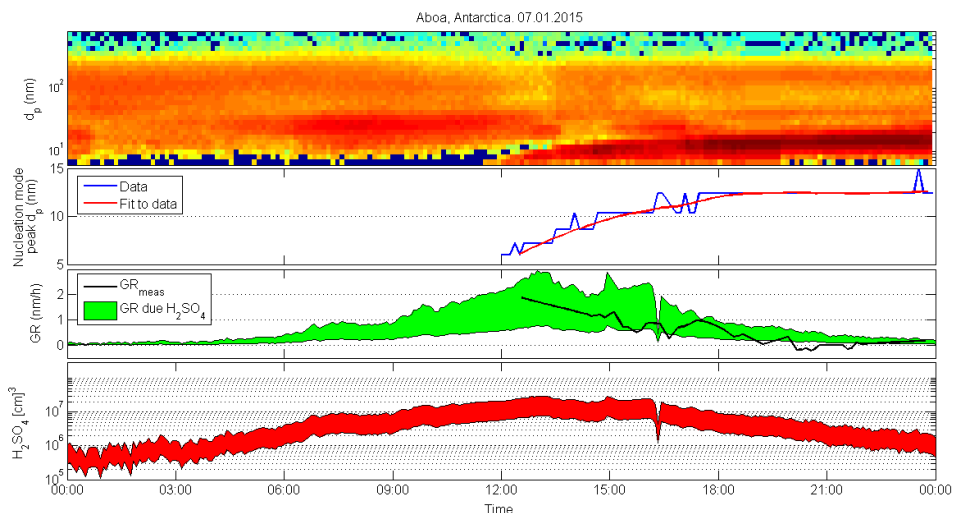
In this chapter, we discuss a novel measurement technology with which a deep insight in aerosol formation in Svalbard and elsewhere in the Arctic could be obtained and with which a systematic long-term monitoring programme, necessary for observing the changes in highly sensitive processes associated with NPF, could be carried out. This type of technology and methods are also suggested among others in chapter 4 “Recommendations” to be promoted for long-term monitoring in Svalbard.

Since there are no data available from Svalbard that we could use in this report for enlightening the potential of these methods, we discuss the technology in light of exemplary data collected from the other side of the planet, the Finnish Antarctic Research Station Aboa, Queen Maud Land, eastern Antarctica. Out of all sites where freely available data exist, Aboa is climatically the most similar to Svalbard. Like Svalbard, the Aboa station is in the vicinity of a plankton-rich ocean, as well as sea ice and coastal bird colonies (in this case primarily penguins). Result from this site therefore may, to some extent, reflect also the atmospheric processes in the Svalbard region. The main difference between Aboa and Svalbard is that there is no macroscopic vegetation nearby Aboa, and that the flora is only represented by some cyanobacteria and other unicellular species in the summertime meltwater ponds. Climate at Aboa is colder, even though Aboa is located further away from the pole at 73°03'S while Svalbard (Ny-Ålesund) lays at 78°55'N. In general, the surroundings of Svalbard are becoming more and more marine, while the same is not true for the Aboa region. Summertime UV-radiation at Aboa is also much stronger due to the ozone hole and ubiquitous reflecting glaciers. Despite the differences, Aboa is still climatically the closest point of comparison where data exist and the processes observed there may provide indications on processes taking place in Svalbard. Data were collected in 2014-2015 summer season and are partly published by Jokinen et al. (2018).

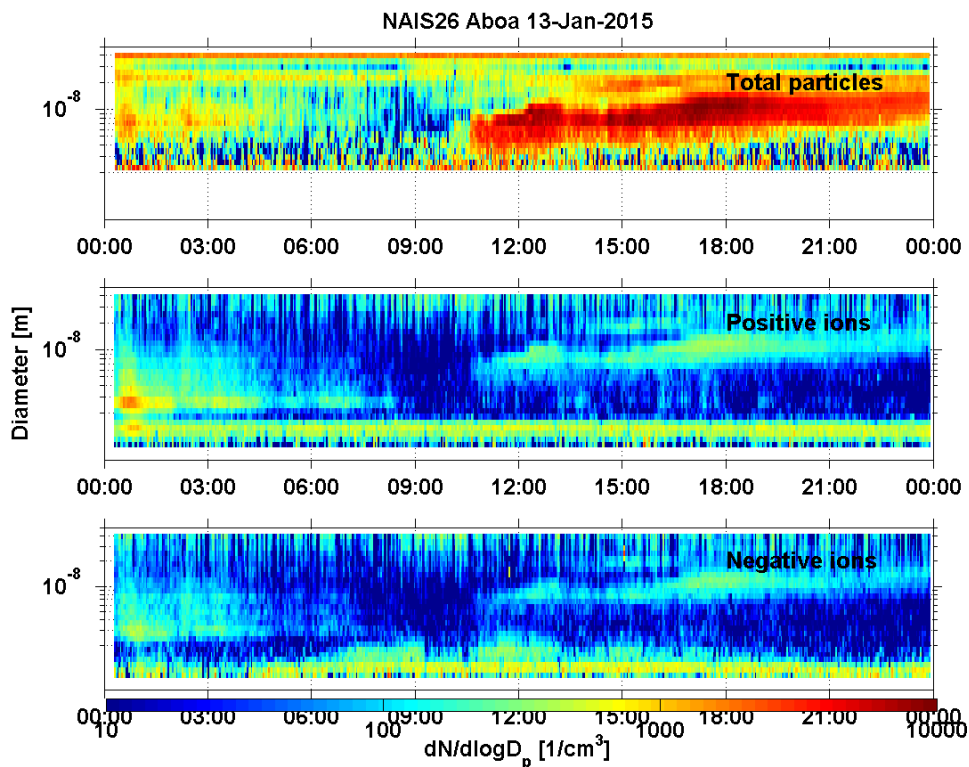
The core of the measurement setup comprised a Differential Mobility Particle Sizer (DMPS) – which is essentially the same instrument as a Scanning Mobility Particle Sizer (SMPS) currently operated at the Gruevabadet laboratory and Zeppelin Observatory in Svalbard, a Neutral cluster and Air Ion Spectrometer (NAIS, manufactured by Airel Ltd, Asmi et al. 2009), a Particle Size Magnifier (PSM, manufactured by Airmodus Oy/Ltd, Finland, Vanhanen et al. 2011), an Atmospheric Pressure interface - Time-of-Flight mass spectrometer (API-TOF, manufactured by ToFwerk A.G. Switzerland, Junninen et al. 2010) and a nitrate ion Chemical Ionization API-TOF (CI-API-TOF, Jokinen et al. 2012). The DMPS was used to measure aerosol size distribution between 7 nm and 800 nm. The NAIS was used for recording the size distribution of naturally charged ion clusters and particles in the size range of 0.8 to



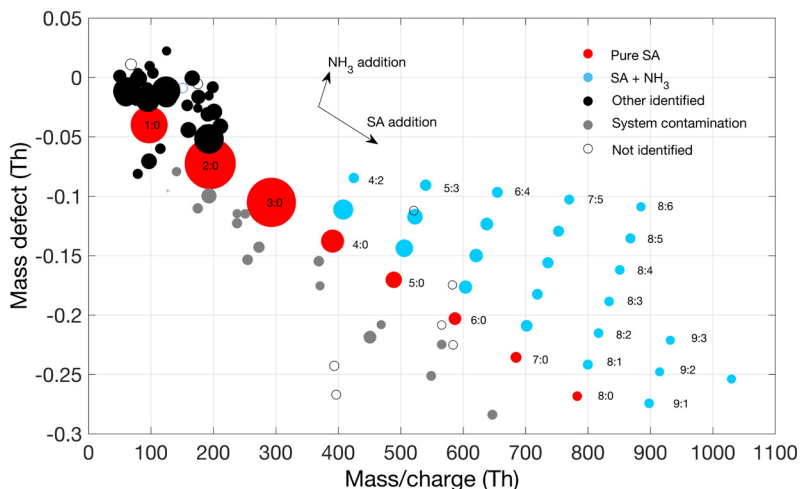
**Figure 2:** The upper panel shows a 1-week time series of aerosol size distribution data collected by a differential mobility particle sizer at the Finnish Antarctic Research Station Aboa. Aerosol formation in this case coincides with very high sulphuric acid ( $\text{H}_2\text{SO}_4$ ) concentrations. Also, MSA concentrations are elevated in comparison to non-event time periods. Iodic acid ( $\text{HI(O}_3\text{)}$ ), which is an important aerosol precursor at least in northern Greenland, next to sea ice, shows no correlation with particle formation at Aboa. Simultaneous measurements of aerosol size distributions and particle precursor vapours are the first step towards understanding the formation mechanisms of new particles.



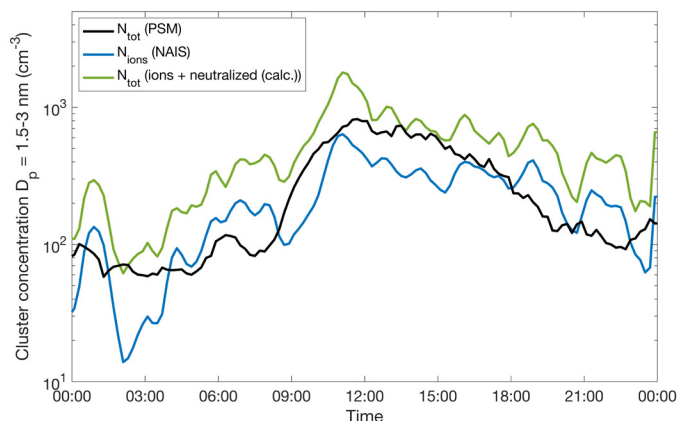
**Figure 3:** Measurements of condensable precursor vapours and aerosol growth rate enables conceptually resolving the aerosol growth mechanism. Here, the peak of nucleation mode is measured from the DMPS data (2<sup>nd</sup> panel) and from the time evolution of the peak, the growth rate is derived (3<sup>rd</sup> panel). Condensation due to sulphuric acid can be calculated (Nieminen et al. 2010) from measured sulphuric acid concentrations (4<sup>th</sup> panel) assuming irreversible condensation (typically a well justified assumption in case of sulphuric acid (Kirkby et al. 2011)). In this case, measured and calculated growth rates agree well (3<sup>rd</sup> panel) suggesting that sulphuric acid is the primary condensing species.



**Figure 4:** More insight in the initial steps of new particle formation, the nucleation process, can be obtained by measurements of negative and positive ion size distributions, together with the total aerosol size distribution by means of the Neutral cluster and Air Ion Spectrometer (NAIS). It should be noted that NAIS is capable of detecting neutral (total) particles reliably only above diameters of approx. 2-3, while ion detection can be extended down to molecular  $\sim 1$  nm sizes. The figure illustrates that in the morning with increasing radiation, small negative omnipresent cluster ions start to grow. This is seen as an increased signal in the size range of 1.5 – 2.5 nm. Positive cluster ions do not grow, suggesting that, in this case, particles form by negative ion – induced nucleation (Kirkby et al. 2011).



**Figure 5:** If initial clusters form by ion-induced nucleation, their chemical composition can be determined using an Atmospheric Pressure interface – Time-Of-Flight mass spectrometer (Api-TOF). This example has been recorded during intensive particle formation and depicts an observed mass spectrum. The mass defect is the difference between the measured (exact) mass and the integer mass defined by the sum of protons and neutrons in the atomic nuclei of molecules in the cluster and it's used together with the isotopic distribution for an accurate identification of the atomic composition. Here, both pure sulphuric acid (SA) clusters (red) and sulphuric acid – ammonia (SA-NH<sub>3</sub>) clusters (blue) are dominating the mass spectrum during the event, together with above discussed data, suggesting that aerosol nucleation takes place via ternary sulphuric acid – ammonia – water negative ion-induced nucleation. Water is lost from the clusters in the sampling process, but laboratory experiments suggest that water contributes to cluster formation (Kirkby et al. 2011).



**Figure 6:** Simultaneous measurements of ion (blue, NAIS) and total cluster concentrations (black, PSM) suggest that, in this case, particle formation is dominated by ion induced nucleation. From the measured ion cluster concentrations, the fraction of ion clusters that are neutralized during the cluster growth by collisions with the ions of opposite polarity can be accounted for by assuming the resulting neutral clusters are stable. In environments where neutral nucleation mechanism dominates (e.g. Kulmala et al. 2013; Sipilä et al. 2016), total concentration is typically clearly higher.

40 nm and neutral particles from approx. 3 to 40 nm. The PSM was used for measuring the total concentration of clusters/particles between 1.5 and 3 nm in diameter. The API-TOF recorded the mass spectrum of naturally charged ion clusters (negative/positive) in the mass range of 50 to 1200 Th while the CI-API-TOF was deployed to measure concentrations of potential particle precursor vapours, including  $\text{H}_2\text{SO}_4$ , MSA,  $\text{HIO}_3$  and a variety of extremely low vapour pressure HOM. Out of potential aerosol precursors, concentrations of bases (ammonia, amines) were not measured, because sensitive enough technology for measuring predicted low concentrations of relevant bases does not exist.  $\text{H}_2\text{SO}_4$ , MSA,  $\text{HIO}_3$  and HOM can be measured by CI-API-TOF with high sensitivity, with lowest limit of detection (LOD) below  $10^5$  molecules  $\text{cm}^{-3}$  (1 part per quadrillion, 0.001 ppt, Jokinen et al. 2012). Typical methods for e.g. ammonia detection can hardly reach 100 ppt, which is not sufficient in pristine clean environments. However, the presence of ammonia can be confirmed from ion cluster chemical composition measurements by API-TOF and concentration can be indirectly estimated e.g. by comparison of measured cluster distribution to cluster distributions obtained from laboratory experiments (e.g. Kirkby et al. 2011).

Data collected from Aboa are summarized in Figures 2-6. Figure 2 depicts a 1-week time series of aerosol size distribution data. Aerosol formation in this case coincides with very high  $\text{H}_2\text{SO}_4$  concentrations. Also, MSA concentration is elevated in comparison to non-event time periods.  $\text{HIO}_3$ , which is an important aerosol precursor at least in northern Greenland, next to sea ice, shows no correlation with particle formation at Aboa. Simultaneous measurements of the aerosol size distribution and particle precursor vapours are the first step toward understanding the formation mechanisms of new particles. Measurements of condensable precursor vapours and aerosol growth rate enable conceptually resolving the growth mechanism of aerosols as shown in Figure 3. Here, the peak of nucleation mode is measured from the DMPS data (2<sup>nd</sup> panel), and the growth rate is derived from the time evolution of the peak (3<sup>rd</sup> panel). Condensation due  $\text{H}_2\text{SO}_4$  can be calculated (3<sup>rd</sup> panel) (Nieminen et al. 2010) from measured  $\text{H}_2\text{SO}_4$  concentrations (4<sup>th</sup> panel) assuming irreversible condensation (typically a well justified assumption in case of  $\text{H}_2\text{SO}_4$  (Kirkby et al. 2011)). In this case, measured and calculated growth rates agree well (3<sup>rd</sup> panel) suggesting that  $\text{H}_2\text{SO}_4$  is the primary condensing species.

More insight in the initial steps of NPF, i.e. the nucleation process, can be obtained by measuring negative and positive ion size distributions, together with the total aerosol size distribution by NAIS (Figure 4). It should be noted that NAIS is capable of detecting neutral (total) particles reliably only above approx. 2-3 nm in diameter, while ion detection can be extended down to molecular  $\sim 1$  nm sizes. The figure illustrates that in the morning with increasing radiation, small negative omnipresent cluster ions start to grow. This is seen as an increased signal in the size range of 1.5 – 2.5 nm. Positive cluster ions do not grow, suggesting that, in this case, particles form by negative ion – induced nucleation (Kirkby et al. 2011). If initial clusters form by ion-induced nucleation, their chemical composition



can be determined using an API-TOF. The example shown in Figure 5 was recorded during intensive particle formation and depicts an observed mass spectrum. The mass defect is the difference between the measured (exact) mass and the integer mass defined by the sum of protons and neutrons in atomic nuclei of molecules in the cluster, which are used together with the isotopic distribution for accurate identification of atomic composition. Here, both pure  $\text{H}_2\text{SO}_4$  (SA) clusters (red) and  $\text{H}_2\text{SO}_4$ - ammonia ( $\text{SA-NH}_3$ ) clusters are dominating the mass spectrum during the event, together with above discussed data suggesting that aerosol nucleation takes place via ternary  $\text{H}_2\text{SO}_4$  - ammonia - water negative ion-induced nucleation. Water is lost from the clusters in the sampling process, but laboratory experiments suggest that water contributes to the cluster formation (Kirkby et al. 2011).

To draw conclusions on whether the ion-induced pathway dominates the new particle formation, simultaneous measurement of the concentrations of ion (blue, NAIS) and total clusters (black, PSM) are needed. The result of such measurements is shown in Figure 6, suggesting that in this case particle formation is dominated by ion induced nucleation since the total cluster concentration does not significantly exceed ion cluster concentrations. From the measured ion cluster concentration, the fraction of ion clusters that are neutralized during the cluster growth by collisions with the ions of opposite polarity can be accounted for by assuming the resulting neutral clusters are stable (green). In environments where the neutral nucleation mechanism dominates (e.g. Kulmala et al. 2013; Sipilä et al. 2016), the total concentration is typically much higher.

The above discussed measurements are needed also in Svalbard in order to resolve and monitor the mechanisms of NPF in the Arctic.

### 1.4.2 Monitoring of phytoplankton

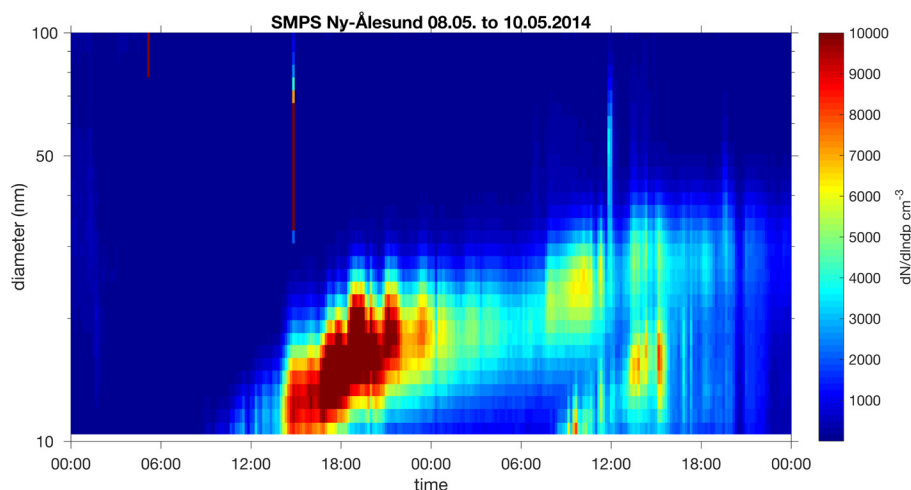
However, despite the capacity to resolve and monitor the concentrations of aerosol precursor vapours and detailed molecular steps of new particle formation, atmospheric measurements alone are insufficient for an holistic understanding of the associated biosphere - atmosphere interactions. In order to increase our understanding on the controls of microalgal composition and productivity, we depend on observational long-term monitoring projects such as the moorings deployed in Kongsfjorden (Cottier et al. 2018) in combination with a mechanistic understanding of certain key processes that can only be investigated by carefully designed campaigns and experimental approaches (e.g. Hoppe et al. 2018). In the future, optimized algorithms for Arctic coastal retrieval of remote sensing-based ocean colour may provide a powerful tool to increase our understanding of temporal and spatial dynamics in aerosol production by Arctic microalgae.

Furthermore, investigations on emissions of biogenic vapours from terrestrial ecosystems - soil and tundra vegetation - would be required to understand the role of volatile organic

compounds in the processes leading to new particle and, in general, secondary aerosol formation.

## 2. Overview of existing research and knowledge in Svalbard

Only few key measurements relevant for understanding NPF and monitoring quantities connected with secondary aerosol formation are systematically recorded in Svalbard. Aerosol size distribution and new,  $>10$  nm, particle formation is currently measured on a long-term basis by SMPS systems at the Gruvebadet laboratory and Zeppelin Observatory



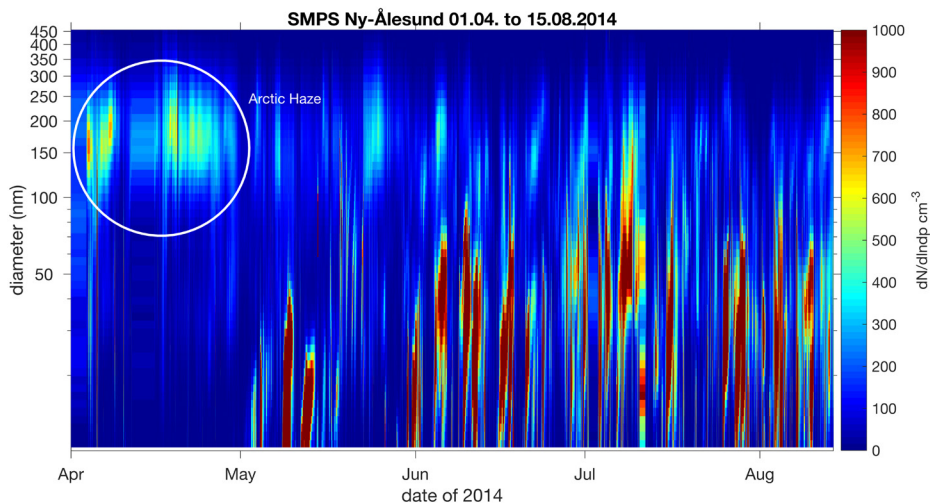
**Figure 7:** Typical aerosol formation event as measured by SMPS system in Gruvebadet, Ny-Ålesund during the phytoplankton bloom period in May.

in Ny-Ålesund. Simplified, SMPS is an instrument that charges sampled aerosol particles and classifies them according to their electrical mobility (which can be converted to particle diameter) and counts the classified particles one by one by means of a condensation particle counter (CPC). In a CPC, particles are exposed to supersaturated (usually) butanol vapour. Vapour condenses on particles growing them to optically detectable sizes after which they are counted based on the signals from scattered light of a laser beam.

Figure 7 shows an example of aerosol size distribution data collected in Gruvebadet laboratory during the phytoplankton bloom period. In this case, the measurements are performed from 10 nm up to 450 nm. Aerosol formation starts from molecular sizes of approx. 1 nm, therefore the SMPS system is blind to the initial steps of particle production

and weaker formation events, when particles do not reach the 10 nm detection threshold, are not recorded. At the Zeppelin observatory, aerosol measurements start from 3 nm sizes, but no long-term measurements on <3 nm particles, that would be critical for understanding the initial steps of new particle formation, are carried out in a systematic manner. Figure 2 depicts data from a longer period (1<sup>st</sup> April to 15<sup>th</sup> August 2014). Here, anthropogenic air pollution, Arctic haze, is seen as an abundance of 100-300 nm particles during April. Intense NPF starts in the beginning of May and continues at least until the end of the measurement period. Earlier reports that focus on NPF in Svalbard utilizing data collected in Zeppelin and Gruebadet include those by Ström et al. (2003), Ström et al. (2009), Tunved et al. (2013), Giardi et al. (2016), Lupi et al. (2016), Dall'Osto et al. (2017) and Dall'Osto et al. (2019), discussed above.

Out of the atmospheric vapours and gases responsible for the production of aerosol or aerosol precursor vapours, DMS is monitored on a semi-continuous manner in Zeppelin observatory by The Korea Polar Research Institute (KOPRI) and ozone is monitored by NILU. Neither DMS nor ozone is measured at Gruebadet. None of the potential aerosol precursor vapours –  $H_2SO_4$ , MSA,  $HIO_3$ , HOMs (hundreds of compounds) and ammonia ( $NH_3$ ) – has



**Figure 8:** Aerosol formation continues intensely until the end of the measurement period in mid-August suggesting that besides phytoplankton activity, other sources of particle precursor vapours exist. Only measurement of gas phase vapours would reveal the nature of condensing species and give hints regarding the potential source of these vapours.

been monitored anywhere in Svalbard before recent proof-of-concept experiments at Gruevbadet laboratory, conducted in collaboration with the University of Helsinki and CNR, Italy in March – August 2017. The study deployed API-TOF,  $\text{NO}_3^-$ -CI-API-TOF, NAIS, PSM and SMPS sensors. The study has continued with a limited setup since April 2018. Those experiments are also the first deploying instrumentation for sub-3 nm particles in Svalbard. Data from these studies are not yet available though, and cannot be analysed or discussed here. Nevertheless, these are campaign type measurements and will not serve as a long-term monitoring program unless continued.

It is notable that, while the high phytoplankton biomass from the spring bloom in the Arctic ocean and North Atlantic usually starts to decay in May or June (Hegseth et al. 2019), particle formation events continue occurring at least until mid-August (Figure 8). This observation may suggest that phytoplankton activity and DMS emission rates may still be high, even though biomass build-up is balanced by grazing pressure from higher trophic levels as usually occurring in stratified post-bloom situations (Behrenfeld and Boss 2018). Alternatively, there could also be another source of aerosol precursor vapours in the area. The identity of relevant aerosol precursors, their sources and temporal variability remain unknown without gas phase measurements of the most relevant possible precursor. Measurements of particle precursor vapours and <10 nm particles are, however, necessary to get more insight in the formation process. Long-term data are required to see trends associated with the warming of the Arctic as well as changes in the extent and properties of sea ice.

### 3. Unanswered questions

Figure 1 shows a simplified scheme on the potential sources of primary volatile compounds, and their conversion to aerosol precursors. As already discussed above, currently systematic long-term observations are performed only for aerosol particles above approx. 10 nm in diameter (Gruevbadet/CNR, Zeppelin/SU), CCN properties (Zeppelin/SU) and solar radiation (Zeppelin / NPI and Ny-Ålesund / AWI). Cosmic radiation, the primary source of ions which are potentially highly important for aerosol formation, is monitored, though aerosol formation is not sensitive to small variations in cosmic radiation intensity. Some studies have been performed on phytoplankton and related marine DMSP measurements (Kongsfjorden; Hoppe unpublished data) as well as gas phase DMS (Zeppelin/KOPRI). For other quantities, including VOC emissions and concentrations, measurements of all aerosol precursors except ammonia, 1-3 nm molecular clusters and cluster growth to and above 10 nm have only been performed in a preliminary field campaign (UH+CNR). Important oxidant, hydroxyl radical (OH), is not recorded in Ny-Ålesund at all. This indicates that there is a massive gap in systematic, long-term high-quality measurements of almost all of the quantities relevant for secondary aerosol formation, which needs to be filled. In the next section, we discuss some of the technology that would help in filling the gaps.

## 4. Recommendations for the future

We suggest following instrument upgrades on permanent atmospheric measurements in Svalbard:

Mass spectrometer systems capable of measuring aerosol precursors vapours ( $\text{H}_2\text{SO}_4$ , MSA, all low volatile HOM-species,  $\text{HIO}_3$ ,  $\text{H}_x\text{I}_y\text{O}_z$ ), primary volatile compounds (VOCs, iodine-species, DMS) and naturally charged ion clusters. This can be achieved by nitrate- or bromide-ion CI-API-TOF, API-TOF and PTR-TOF/VOCUS instruments. A system capable of switching between ionization methods would enable the detection of wider range of required compounds with a single instrument (Manufacturers providing the necessary technology include at least ToFwerk A.G Switzerland; Karsa Oy/Ltd, Finland; Aerodyne Research Inc USA and Ionicon Analytic GmbH, Austria).

An instrument for recording size distribution of naturally charged ion-clusters and aerosol particles (commercially available instruments are NAIS and Balanced Scanning Mobility Analyzer, BSMA, both delivered by Airel Ltd Estonia).

An instrument for recording neutral 1-3 nm clusters (commercially available instruments are PSM, manufactured and delivered by Airmodus Oy, Finland and the Diethylene Glycol – Condensation Particle Counter, DEG-CPC, manufactured by TSI Inc. USA).

These instruments should be located in Gruebadet or Zeppelin station in Ny-Ålesund, preferably in both. Since Kongsfjorden and the ocean nearby Ny-Ålesund experiences mostly absent sea ice, measurements should ideally be performed also along the coasts surrounded by ice. However, as this is not likely to be feasible in Svalbard, a logistically more meaningful location would be e.g. the Villum research station in Greenland. This suggestion calls for deep collaboration with other Arctic sites. To get a comprehensive picture of the consequences of sea ice decline and thinning, measurements in both environments – ice free and ice covered – are strongly needed. Data series from the above detection instrumentation would preferably have a time resolution of approximately one minute.

If long-term measurements of VOCs are not feasible, due to the current lack of sensitive enough instrumentation within the scientific community working in Svalbard, we suggest a 6-month measurement campaign in spring-summer season utilizing a VOCUS to resolve the concentrations and chemical nature of VOCs and long-term monitoring of VOC concentrations using offline analysis methods, such as Tenax tubes and off-line gas chromatography. Offline VOC flux measurements from the ocean, soil and snow would help in pointing out the primary sources of VOCs in the area.

It would be desirable to establish a systematic long-term monitoring program of

phytoplankton populations and associated DMSP production in Kongsfjorden, which would also support gas phase measurements performed in Ny-Ålesund. While spring-bloom monitoring has been conducted regularly since 2014 (Hoppe et al. unpublished data) and a pilot study on year-round sampling has been initiated this year (Hop and Assmy, unpublished data), there are currently no capacities for sophisticated biochemical measurements (e.g. for DMS and DMSP).

A problematic, but important issue, for which we currently do not have a feasible solution, are the gas phase ammonia measurements. As discussed above, there is currently no technology for reliable ammonia quantification in presumably very low ammonia concentrations (maybe <100 ppt) around Svalbard. If such measurement could be performed, such activity should be strongly promoted.

Besides these above suggested amendments, it is absolutely imperative to guarantee the continuation of existing DMS and aerosol measurements – located in Gruebadet and Zeppelin stations – in Svalbard.

Future collaboration between the institutes and stations working on the topics discussed in this report should be promoted. To our knowledge, phytoplankton studies in Kongsfjorden are currently primarily performed (occasionally) by AWI and NPI, aerosol measurements are carried out by CNR-Italy and Stockholm University, gas phase measurements of precursor vapours and clusters are (occasionally) conducted by University of Helsinki and DMS measurements by KOPRI. These institutes have already established collaboration over the past years. Other institutes working with a connection to topics discussed here, should be encouraged to join efforts with existing collaborations.

## 5. Data availability

Data collected from Svalbard, Ny-Ålesund and presented in Figure 7-8 are owned by CNR-Italy and available on request from [mikko.sipila@helsinki.fi](mailto:mikko.sipila@helsinki.fi).

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