PRIMARY MARINE AEROSOL PRODUCTION: STUDIES USING BUBBLE-BURSTING EXPERIMENTS

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List of papers

This thesis is based upon the following papers, referred to in the following text by their Roman numerals.


Statement

I, Kim A. H. Hultin, made the following contributions to the papers presented here:

**Paper I**
I was responsible for the laboratory aerosol measurements, analysis of the aerosol data and was the main contributor to the writing. Bubble spectra measurements were made by Leo Cohen, TNO, and ambient aerosol measurements by Mikael Ehn, FMI, both analyzed by Douglas Nilsson.

**Paper II**
I conducted most of the aerosol measurements, analyzed the aerosol data and took the lead role in authoring the paper. Biological sampling was made by Laura Gomez-Consarnau and Jarone Pinhassi.

**Paper III**
I analyzed the data and had the leading role in authoring the paper. The measurements were made by Julia Zábori and Radovan Krejci.

**Paper IV**
Douglas Nilsson performed and analyzed the eddy covariance data, while I made the laboratory aerosol measurements and analyses and performed the aerosol back trajectories. I contributed to writing the paper, although Douglas Nilsson had the leading role.
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1 Introduction

This thesis is devoted to the atmospheric constituents known as aerosol, more specifically to marine aerosol. Aerosol is defined as liquid or solid particles suspended in a gas, such as air. Atmospheric aerosol can be of both natural (e.g., from volcanic eruptions, wind-blown soil dust or sea spray from the world’s oceans) and anthropogenic (e.g., from combustion of fossil fuels or biomass, or from agriculture) origins, and spans sizes from a few nanometers to tenths of micrometers. The size of these particles strongly influences both their atmospheric lifetime and their optical properties (Brasseur et al., 2003; Seinfeld and Pandis, 2006).

Aerosol particles are defined as primary or secondary particles depending on how they are produced. While primary aerosol particles are emitted directly into the atmosphere (such as in the case of sea spray or wind-blown dust), secondary aerosols are formed in the atmosphere via gas-to-particle processes known as nucleation and new particle formation (Kulmala et al., 2004). Atmospheric aerosols are also transformed during their atmospheric lifetime by microphysical processes such as condensation, coagulation and cloud processes, and removed from the atmosphere via dry- or wet deposition mechanisms. For example dry deposition by turbulent eddies or wet deposition by precipitation (Seinfeld and Pandis, 2006).

The summary of the thesis is meant to give a background to the subject of marine aerosol and their effect on the Earth’s climate. In addition, the summary serves the purpose of giving an overview on how marine aerosol can be studied. The main findings of the four papers included in the thesis, and some thoughts regarding improvements in future investigations of this natural source of atmospheric aerosol are also briefly presented.
2 Aerosol and climate

In Figure 1, a summary of the present state of knowledge regarding the factors underlying the radiative forcing of the Earth’s climate is presented. According to the IPCC report from 2007 the scientific consensus is that the observed global warming, with a high degree of probability, is anthropogenically forced (IPCC, 2007).

Greenhouse gases warm the lower atmosphere since they are nearly transparent to incoming solar radiation but absorb and re-emit

![Figure 1. Global average radiative forcing (RF) estimates and ranges in 2005 for anthropogenic carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O) and other important agents and mechanisms, together with the typical geographical extent (spatial scale) of the forcing and the assessed level of scientific understanding (LOSU). The net anthropogenic radiative forcing and its range are also shown. These require summing asymmetric uncertainty estimates from the component terms, and cannot be obtained by simple addition. Additional forcing factors not included here are considered to have a very low LOSU. Volcanic aerosols contribute an additional natural forcing but are not included in this figure due to their episodic nature. The range for linear contrails does not include other possible effects of aviation on cloudiness (adopted from the fourth assessment report of the IPCC, Summary form policymakers 2007).](image-url)
outgoing long wave radiation. The anthropogenic aerosol on the other hand, has a net cooling effect of almost the same magnitude as anthropogenic carbon dioxide, hence counteracting the warming induced by the greenhouse gases. Atmospheric aerosols therefore have the ability to mask part of the global warming signal. The effect is however limited; the longest lifetime of aerosol particles in the atmosphere is on the order of weeks, while the effective lifetime of carbon dioxide is on a century time scale (Seinfeld and Pandis, 2006). Aerosol affects the climate system through radiative forcing in many ways, often categorized into direct and indirect effects.

2.1 Direct and semi-direct aerosol effects

Depending on their optical properties, aerosol can either directly scatter or absorb solar radiation, and thereby alter the radiative balance. The aerosol direct effect is most efficient for particles with diameters between 0.2 and 2 µm, which correspond to the power peak in the solar spectrum (Lewis & Schwartz, 2004).

Absorption of solar radiation by aerosol particles heats the air mass, reduces relative humidity and increases the static stability relative to the surface. When absorbing aerosol is part of a cloud, their presence may cause evaporation of cloud droplets and a reduced cloud cover, an effect called the semi-direct effect. This leads to a positive forcing, amplifying the warming influence of absorbing aerosol. Conversely, if a layer of absorbing aerosol particles is present above a cloud, the increased static stability may lead to a lower entrainment rate and a shallower and moister boundary layer. Absorbing aerosol above clouds may thus lead to a negative forcing instead (Ackerman et al., 2000; Johnson et al., 2004).

2.2 Indirect aerosol effects

The aerosol indirect effect regards the mechanisms by which aerosols modify the microphysical properties of clouds, hence the amount, lifetime and radiative effects of clouds.

Aerosol particles have the potential to serve as cloud condensation nuclei (CCN). The brightness of a cloud is determined by available CCN, an effect known as the Twomey effect (Twomey, 1977). An increase in CCN causes an increase in the droplet number concentra-
tion and a decrease of mean droplet size in a cloud of nearly constant liquid water content. More droplets lead to an increased reflection of solar radiation from the formed cloud, and thus lead to a climate cooling.

Assuming that the amount of water in the cloud is not altered by the increase of CCN, the decrease in mean radius of the cloud droplets and the more narrow cloud droplet size distribution results in lower precipitation efficiency (Rosenfeld, 2006; Freud et al., 2008). Not only does this lead to suppression of precipitation in affected clouds, it can also lead to an increased lifetime of the clouds (called the Albrecht effect, Albrecht (1989)) – and an increase in cloudiness. This further increases the reflection of solar radiation back to space.

Aerosol particles can also act as ice nuclei. The glaciation effect refers to an increase in ice nuclei resulting in rapid glaciation of a supercooled water cloud due to the difference in vapor pressure over ice an water. The ice crystals quickly reaches precipitation size with the potential of turning a non-precipitation cloud into a precipitation cloud, decreasing the cloud lifetime which lead to a positive forcing (Lohmann and Feichter, 2005).

Also included as aerosol indirect effects are the thermodynamic effect, the riming indirect effect and the surface energy budget effect (see Lohmann and Feichter (2005) for a review on the subject). The first one refers to that the smaller cloud droplets induced by increased aerosol concentration can delay the onset of freezing, the second that the smaller cloud droplets can decrease the riming efficiency, while the surface energy budget effect deals with the overall effect that an increased amount of aerosol and increased cloud optical thickness decreases the net surface solar radiation.

How efficiently aerosol particles form cloud droplets depend on their size, chemical composition and on cloud dynamics, in particular the water vapor super saturation in the cloud. Approximately the same particle sizes of aerosol are important both for the direct and indirect effects (Raes et al., 2000; McFiggans et al., 2006).
3 Primary marine aerosol

About 70% of the Earth’s surface is covered by oceans, and marine aerosol represents a significant fraction of aerosols found in the atmosphere. In clean marine conditions, the marine aerosol number concentration is about 100-400 particles cm$^{-3}$. This is a low value compared to for example rural sites (concentrations about 2000-10000 cm$^{-3}$), or polluted urban sites (up to $4\times10^6$ cm$^{-3}$, Seinfeld and Pandis (2006)). Still, when considering aerosol mass, the flux of sea salt particles is the largest natural aerosol source, with an estimated global mass flux of around $1\times10^{16}$ g yr$^{-1}$ (Gong et al., 1997; Grini et al., 2002).

Not only are sea salt particles the single most important factor controlling the scattering of solar radiation near the surface over open ocean (Haywood et al., 1999). Sea salt particles play a significant role in cloud microphysics and chemistry, especially in marine stratocumulus clouds (O’Dowd et al., 1999), and can also provide a substantial sink for atmospheric trace gases, both natural and man-made (O’Dowd et al., 2000). However, primary marine aerosol does not exclusively consist of sea salt. To refer to primary marine aerosol without specifying its composition the term sea spray can also be used.

3.1 Production mechanism

Primary marine aerosol particles mainly reach the atmosphere when bubbles burst as a result of waves breaking at the ocean surface. Minor contributions can come from the impact of rain- or snowfall on a water surface (Blanchard, 1983) or by supersaturation of oxygen through extensive photosynthesis by marine algae (Wania et al., 1998). The bubble-bursting process is in general assumed to result in three different kinds of droplets. Film droplets are considered to be fragments of the disintegrated film caps of the bursting bubble. Jet droplets reaches the atmosphere from the collapsing bubble cavity after the rupture of the bubble film (Blanchard, 1963), as illustrated in
When the wind stress is sufficiently great, droplets called spume droplets are torn directly from the wave crest (Monahan et al., 1983). These droplets are projected nearly horizontally, and are thought to be larger than most jet- and film droplets.

**Figure 2.** The bubble-bursting mechanism. a) An air bubble at an air-water interface. b) The production of jet and film droplets from a bursting bubble. From Blanchard (1983).

Primary film droplets are produced when the bubble film shatters, and are ejected in all directions. Secondary film droplets appear to be produced from impaction of the larger, downward moving primary film droplets (Spiel, 1998). Compared to film droplets, the number of the vertically rising jet droplets is small and their size generally larger. While aerosol from jet droplets is mainly found in the supermicrometer size range, the submicrometer aerosol is considered to be mainly composed of film droplets (Cipriano and Blanchard, 1981; Afeti and Resch, 1990; Reineke et al., 2001). The bubbles producing the majority of the film droplets are expected to be rather large in this context; larger than 2-2.5 mm in diameter (Blanchard and Syzdek, 1988; Resch and Afeti, 1992). What is described above is the commonly accepted picture, although it may not be the complete picture. For example, Bird et al. (2010) found evidence that 5 mm-bubbles also can also create numerous smaller daughter bubbles as the curved film of the ruptured bubble can fold and entrap air as it retreats, which result in jet droplets.

All droplets quickly undergo evaporation in the atmosphere as the relative humidity is lower at higher altitudes than directly over seawater (the relative humidity is on average about 80% in the atmosphere, compared to about 97% directly over seawater (O’Dowd and de Leeuw, 2007)). As a rule of thumb for oceanic conditions, the aerosol radius at formation approximately equals two times the radius at
RH=80%, and 4 times the dry radius, which is what commonly is measured during aerosol sampling: \( r_0 \approx 2r_{80} \approx 4r_{\text{dry}} \) (Lewis and Schwartz, 2004).

As bubbles rise to the surface, surface active material in the bulk water aggregates to the walls of the bubbles (Scott, 1975; Hejkal et al., 1980). The organic chemicals are formed within the water body or from materials carried to the water surface by winds, air currents and precipitation (Wotton and Preston, 2005). The bubble upwelling region causes an outflow of water and can result in the removal of the surface microlayer above the rising bubble plume (Blanchard, 1983). At rupture, the collected material from both the bulk water and the surface microlayer is ejected into the air to form primary marine aerosol particles (Blanchard and Syzdek, 1982; Smith et al., 1993; Clarke et al., 2003; Cavalli et al., 2004). The result is a wind driven source of aerosol particles consisting largely of sea salt and organic compounds (Monahan et al., 1983; O’Dowd et al., 1997; Nilsson et al., 2001).

The different chemical compounds in the aerosol can either be internally mixed with sea salt (i.e. in the same particle), or externally mixed (as separate particles).

### 3.2 Source functions

A source function attempts to describe the surface flux of sea spray aerosol; the number, size and composition of particles produced per unit surface area and time. It is a key component required for modeling of the marine aerosol. Available source functions have been determined using different methods and physical principles. Most of them are derived using indirect methods to infer the rate of production as a function of wind speed, for example the whitecap method used by Mårtensson et al. (2003). The surface manifestation of a bubble plume is a whitecap, which can be parameterized as a function of environmental parameters such as wind speed, atmospheric thermal stability and water temperature (Monahan and O’Muircheartaigh, 1986). In the whitecap method, parameterizations of the fraction whitecap cover from field experimental data are combined with laboratory measurements of sea spray production rates per whitecap area.

In recent years attempts have been made to improve the sea spray source functions by direct flux measurements using the eddy covariance method (see section 5.2). This includes both size resolved aerosol fluxes and bulk divisions between non-volatile (presumably main-
ly sea salt) and volatile compounds by heating the aerosol (Nilsson et al., 2001, 2007; Geever et al., 2005; Norris et al., 2008, Paper IV). The advantage of using a direct method is that all particles within the detectable size range can be measured, and hence there are no limitations resulting from bubble-mediated production (O’Dowd and de Leeuw, 2007). Some of the available submicrometer aerosol source functions are displayed in Figure 3. The results from these modern source functions are now approaching each other in the range 0.1-1 μm, in good agreement compared to the variations of up to 8 orders of magnitude seen in the comparison of Andreas (1998).

Figure 3. Aerosol number emission flux size distributions for sea salt applied to a wind speed of 9.8 ms⁻¹. From Nilsson et al. (2007).

3.3 Primary marine aerosol number size distribution

Aerosol particles in the marine boundary layer are usually grouped by the diameters of the particles, and are characterized by four modes: nucleation mode ($D_p < 0.02 \, \mu m$), Aitken mode ($D_p = 0.02 - 0.1 \, \mu m$), accumulation mode ($D_p = 0.1 - 0.6 \, \mu m$), and coarse mode ($D_p > 0.6 \, \mu m$, Seinfeld and Pandis (2006)). While the coarse mode particles typically represent up to 95% of the total mass of the aerosol particles, it may only represent about 5-10% of the particle number. These names are not commonly used regarding laboratory produced sea
spray, as they originate from ambient observations (accumulation mode refers for example to those particle sizes that have the longest lifetime in the atmosphere), and results partly from airborne processing and aging of the aerosol.

Until a decade ago, primary marine aerosol studies were mainly focused on supermicrometer aerosol particles due to their effect on atmospheric transmission and the sea-air transfer of heat, mass and water vapor (e.g., Andreas, 1998), for which aerosol mass is a key parameter. With the realization of the role aerosols play in the climate of the Earth (see section 2), focus shifted to studies of sea spray submicrometer particles over the size range from roughly 0.01 μm to 1 μm.

Several studies on laboratory-generated sea spray aerosol have been conducted over the last few years (e.g., Mårtensson et al., 2003; Sellegri et al., 2006; Keene et al., 2007; Tyree et al., 2007; Fuentes et al., 2010; Papers I-IV), a few of which are presented in Figure 4. In general, they point to a dominant mode around 0.1-0.2 μm, a size range that is climatically important because it means sea spray aerosol can potentially account for a significant fraction of CCN, particularly under high wind conditions (Figure 4).

**Figure 4.** Aerosol number size distribution generated from artificial bubbles: northeastern Atlantic (circles on thick line, Paper I), Bermuda Institute for Ocean Sciences (thin line, Keene et al. (2007)), filtered seawater from Scripps Institute of Oceanography Pier (dashed curve, Tyree et al. (2007)), artificial seawater (dashed/dotted line, Mårtensson et al. (2003)), and artificial seawater from Sellegri et al. (2006) (from the equation and parameters included in Table 1 in Sellegri et al. (2006) and scaled by 10^5 for comparative purposes, dotted line). From Paper I.
Discrepancies between studies can relate to the use of different methods, different waters, and measurement artifacts. For example, diffusion losses in the sampling systems for the smallest particles (Paper I).

3.4 Composition

3.4.1 Sea salt

By definition, salinity is a dimensionless number based on water conductivity. A typical value for the majority of the world oceans is 35 psu (practical salinity units), making sea salt a natural part of the primary marine aerosol. Most of the dissolved material in seawater consists only of a few ionic species together forming sea salt: Cl\(^{-}\), Na\(^{+}\), Mg\(^{2+}\), SO\(_{4}\)\(^{2-}\), Ca\(^{2+}\), K\(^{+}\) and HCO\(_{3}\)\(^{-}\). The ratios of these species are quite constant throughout the oceans (Lewis and Schwartz, 2004; Seinfeld and Pandis, 2006).

Marine aerosol in the Aitken, accumulation and coarse modes has been observed to consist in part of sea salt (e.g., O’Dowd and Smith, 1993; Murphy et al., 1998; Clarke et al., 2003), with the supermicrometer marine aerosols consisting almost exclusively of sea salt (Cavalli et al., 2004; O’Dowd et al., 2004; Facchini et al., 2008).

3.4.2 Organic compounds

A large part of the oxygen in the atmosphere is produced by marine organisms, mostly phytoplankton. All living organisms are made of carbon and all cells are enclosed by thin plasma membranes. These biological membranes are exceedingly complex structures composed of a mixture of lipids, proteins, and carbohydrates. Both the lipids and the proteins are amphipathic, they consist of a hydrophilic and a hydrophobic end. The lipid molecules spontaneously aggregate to bury their hydrophobic tails in the interior and expose their hydrophilic heads as bimolecular sheets, bi-layers. As cells die, they decompose and the hydrophobic cellular constituents rise toward the ocean’s surface where they accumulate (Karp, 1999; Alberts et al., 2002). Organic molecules that contain a polar group (in the case of lipids, the hydrophilic head) generally reduce the surface tension of water and are commonly called “surface active” or “surfactants” (Gill et al., 1983).
Most of the organic matter in seawater originates from phytoplankton production (Biddanda and Benner, 1997). The concentrations of dissolved and particulate organic matter, DOM and POM, vary greatly with location, time and depth (Millero, 2005).

It is currently accepted that sea spray produced from biologically active water not only include organics, the organic fraction can dominate over sea salt mainly toward smaller submicrometer particles. Previous studies have shown that the organic mass fraction increases with decreasing sizes, both in ambient measurements (Cavalli et al., 2004; O’Dowd et al., 2004) and from laboratory investigations (Facchini et al., 2008). The fraction of organic material has been shown to vary between seasons and locations. In highly productive north Atlantic waters, Facchini et al. (2008) found up to 77% of the total carbon by mass in individual submicrometer diameter size fractions to be organic carbon, while Modini et al. (2010) found only about 4% by mass in submicrometer aerosol coastal water east of Australia.

As many marine-derived organic compounds suppress surface tension, their incorporation into marine aerosols may reduce the super saturation required to activate particles into cloud droplets (e.g., Facchini et al., 2000; Decesari et al., 2005).

3.4.3 Bacteria

Marine bacteria play a vital role in marine surface waters. It has for example been recognized that they consume up to 50% of the photosynthetically produced organic matter in the ocean (Azam et al., 1983; Azam, 1998). The abundance of bacteria in surface waters ranges from about $10^5$ to $10^7$ cm$^{-3}$, and is significantly positively correlated with chlorophyll concentrations, and thus with phytoplankton biomass (Azam et al., 1983; Linley et al., 1983).

A recent study by Ceburnius et al. (2008) concluded that water insoluble organic carbon in submicrometer marine aerosol had a primary source at the sea surface, while water soluble organic carbon pointed to a production via secondary processes. Bacteria in the marine atmosphere contribute to this insoluble organic aerosol component, and several studies support the conclusion that their main means of conveyance to the atmosphere is via the bubble-bursting process (e.g., Blanchard and Syzdek, 1970; Marks et al., 2001; Aller et al., 2005; Paper II).

Some marine bacterial species have been found to be efficient ice nuclei (e.g. Maki et al., 1974; Schnell, 1977). At sub-zero tempera-
tures warmer than -40 °C, aerosol particles in clouds initiates freezing through the heterogeneous nucleation of ice directly from water. The most active naturally occurring ice nuclei (IN) are of biological origin and have the capacity to catalyze freezing at temperatures as high as -2 °C (Maki et al., 1974). This capacity and the formation of ice crystals in clouds can influence precipitation formation (e.g., Christner et al., 2008; Pratt et al., 2009). Thus, these processes couple together marine-derived organic material, cloud microphysics, and climate into a complex feedback system.
4 Aims of the thesis

4.1 General aims
As seen in Figure 1, the level of scientific understanding regarding the total effect aerosol have on climate is for the most part considered low, and the uncertainty regarding the magnitude of the aerosol effect is high. In order to acknowledge and understand the anthropogenic impact on climate, we have to understand the underlying natural processes and describe them as accurately as possible. Because of the large extent of the world’s oceans, marine aerosol is one of the most important components of the climate system. Although sea salt is an important part of marine aerosol with respect to mass, there is increasing evidence of a large organic fraction of the submicrometer marine aerosol. This is likely to have significant impact on marine aerosol optical properties and marine cloud formation. Climate models so far include only sea salt, however typically not the entire submicrometer size range. The general aims of this thesis were to characterize the emission of primary marine aerosol particles down to about 0.02 μm, and to quantify the organic fraction.

4.2 Specific aims
To test if laboratory made bubble-bursting produces a realistic bubble spectrum, and thus a realistic aerosol spectrum (Paper I).

To see if there are additional parameters affecting the aerosol production apart from wind speed (Papers I and II).

To investigate the link between surface water chlorophyll concentration and aerosol number concentration (Paper I).

To determine how effectively marine bacteria use the bubble-bursting mechanism (Paper II).
To examine the possibility of a diurnal cycle in aerosol production (Papers II and IV).

To investigate whether sea salt is externally or internally mixed with organic material (Papers I, III and IV).

To combine laboratory- and flux measurements in order to improve the sea spray source function down to submicrometer aerosol size ranges (Paper IV).
5 Methods

Figure 5. The sites used to sample surface seawater in this thesis. A: northeastern Atlantic, cruise with R/V Celtic Explorer (2006). B: Askö (2005), C: Garpen (2005), and D: Kongsfjorden, Svalbard (2010). From Google Earth.

Although wind speed is the single dominating factor controlling the production of sea spray aerosols, other variables such as water temperature, oxygen saturation or the presence of surfactants may also be important, however their roles are poorly understood. In order to understand what affects the primary marine aerosol production, laboratory experiments are necessary since generated fresh primary aerosols can be analyzed without interference due to modification processes and without secondary aerosol in the atmosphere involved. In addition, during laboratory experiments the “wind speed” (bubble production rate) can be held constant, a process that easily otherwise can obscure the effects of other parameters. In an experimental container, the effects of the above mentioned parameters and the aerosol mixing state were the subjects of interest during these studies.

In contrast to laboratory-made aerosol, the eddy covariance technique offers a direct way to measure the magnitude of aerosol net exchange between the surface and atmosphere. However, this method is limited to size resolved fluxes above about 0.1 μm due to slow re-
response times of the available instruments. Connecting the eddy covariance results to laboratory-made aerosol, which was here measured down to 0.02 μm, could allow a sea spray source function from 0.02-2 μm to be determined.

Surface water from four different locations was investigated (Figure 5). While one site represents open ocean (A, Paper I), the two Baltic and the Arctic sites are coastal (B and C, Paper II, C, Paper IV, and D, Paper III). Below follow short descriptions of the principal methods used in this thesis, in addition to continuous measurements of water properties such as salinity, temperature and dissolved oxygen.

5.1 Laboratory-made aerosol

Previous studies have investigated the primary marine aerosol by using wave tanks (Monahan et al., 1982; Bowyer et al., 1990) atomizers (e.g., Taketani et al., 2009), aeration through glass frits or diffusers (Mårtensson et al., 2003; Keene et al., 2007; Tyree et al., 2007), or water jets (Cipriano and Blanchard, 1981; Facchini et al., 2008). Some investigators have compared more than one method (Sellegri et al., 2006; Russell and Singh, 2006; Fuentes et al., 2010). The advantage of using an impinging jet of water as compared to atomizers or aeration through frits or diffusers is primarily that the air bubble size spectrum is not monodisperse. Compared to the use of a wave tank, the water jet apparatus can be of smaller size and still produce a high number of particles due to large water flows, resulting in high bubble densities. Here, this technique has successfully been used in a carefully sealed 50 L aquarium bowl or a 20 L polyethylene bottle, producing only primary marine aerosol.

5.1.1 Aerosol size distributions

To obtain the aerosol size distribution a Differential Mobility Particle Sizer (DMPS) system together with an Optical Particle Counter (OPC, GRIMM GmbH 7.309) was used. Combining both instruments results in a number size distribution of dry diameter $D_p = 0.02 - 2.2 \mu m$. The DMPS system consisted of a Differential Mobility Analyzer (DMA, Stockholm University) and a Condensation Particle Counter (CPC, TSI 3010) (Papers I-IV).
5.1.2 Volatility properties and mixing state

In order to obtain information about the mixing state of the particles, a Volatility-Tandem Differential Mobility Analyzer (V-TDMA) was used. Firstly, a DMA (Stockholm University) selected particles of a specific size range. The particles were then heated in a thermodenuder (Stockholm University), and the number size distribution of the remaining particles were measured using a second DMA (a copy of the first one) in combination with a CPC (TSI 3010) with a cut-off of 0.006 \( \mu m \) (Paper III).

5.1.3 Bacterial enumeration

Bacterial sampling took place both in seawater (total bacterial numbers and colony-forming bacteria) and in aerosol phase of the laboratory-made aerosol (colony-forming bacteria). While total bacterial numbers include all bacteria (live or dead) present in the water, colony-forming units (CFU) is a measure of only living bacteria and those that forms colonies growing on an agar plate. Compared to total bacterial numbers, the viable count is typically less than 0.1% for open ocean (Kogure et al., 1979) (Paper II).

5.1.3.1 Total bacterial numbers

Seawater samples were fixed with 0.2 \( \mu m \) pore-sized filtered formaldehyde (final concentration 4%), stained with Acridine Orange, filtered onto 0.2 \( \mu m \) pore-size polycarbonate filters (Poretics, Osmonics Inc.), and counted by epifluorescence microscopy within 48 hours.

5.1.3.2 Colony-forming units

For seawater samples, 100 ml of 10x and 100x diluted seawater samples on duplicate ZoBell agar plates made with Baltic seawater. CFUs from the aerosol phase were obtained after filtering 1, 0.75 and 0.5 m\(^3\) air from the laboratory tank onto gelatin filters (Sartorius). These filters were transferred onto ZoBell agar plates, which were incubated at room temperature until colonies were visible (5-10 days). Gelatine filter controls were made from the tank after each experiment with the water jet turned off and thus no aerosol production.

5.1.4 Bubble measurements

Subsurface bubble spectra in the size range from 30 to 1000 \( \mu m \) were measured using an optical bubble measurement system (a mini-BMS
developed at TNO, the Netherlands, described in Leifer et al. (2003)). The sensor heads of the system was placed about 4 cm below the water surface, and as the bubbles entered the sample volume by natural advection, they were imaged by a video camera. After image processing, the bubble size distribution was calculated (Paper I).

5.2 Ambient aerosol fluxes – eddy covariance

The most direct way of determining the in-situ aerosol flux is the eddy covariance method, where a net upward flux indicates that particle emissions dominates over (dry deposition) sinks (Nilsson et al., 2001). This method includes high-frequency measurements of vertical wind speed and concentration of aerosol particles, and the calculation of turbulent fluxes from these parameters (Paper IV).

To obtain size resolved aerosol concentrations, two OPCs were used (prototypes corresponding to GRIMM model SVC-EDM 265) sampling with 1 Hz time resolution, where one was heated to 300 °C in order to separate sea salt from the more volatile species of the aerosol. The three-dimensional wind speed was measured using a Gill Ultrasonic anemometer R3, sampling with 20 Hz time resolution.
6 Summary of papers in the thesis

6.1 Paper I: northeastern Atlantic Ocean

This study was made during a cruise over the highly biologically active waters of the northeastern Atlantic in the summer of 2006. The major scientific goal was to investigate, and possibly parameterize, the effect of phytoplankton on sea spray production. Chlorophyll $\alpha$ was used as a proxy for this. No direct relation between the produced aerosol number concentration and the level of chlorophyll $\alpha$ in the surface water was observed on the short time scales investigated during the cruise (10 min averages). The aerosol number production was negatively correlated with dissolved oxygen in the water ($r < -0.6$ for particles of dry diameter $D_p > 0.2 \, \mu m$). An increased surfactant concentration as a result of biological activity affecting the oxygen saturation is thought to diminish the particle production.

The enhanced upward mixing of deeper ocean water as a result of higher wind speed appears to affect the aerosol particle production, indicating that wind speed influences aerosol production in more complex ways than simply by increasing the amount of whitecaps. The different properties of the deeper water masses reaching the surface at high wind speeds may also have the possibility to alter the aerosol production and composition.

The bubble spectra produced by the jet of seawater was representative of breaking waves at open sea, and the particle number production was positively correlated with increasing bubble number concentration with a peak production of 40-50 particles per bubble.

6.2 Paper II: Baltic Sea

Two coastal sites in the Baltic Sea were used to investigate aerosol and bacterial emissions from the bubble-bursting process. The aerosol size distribution spectra from the two sites were similar and conservative in shape where the modes were centered at about 0.2 $\mu m$ dry diameter. A 0.6 $\mu m$ mode was also found, most clearly pronounced at
Garpen. This could be a coastal influence as the water at Garpen was not only sampled near the coast, but also very close to the sea floor.

We found a distinct decrease in aerosol production with increasing water temperature. A clear diurnal cycle in sea spray aerosol production was found as well, anti-correlated both with water temperature and dissolved oxygen, which to our knowledge has never been shown before. A link between decreasing aerosol production in daytime and phytoplankton activity is likely to be an important factor for these results.

Colony-forming bacteria were efficiently transferred to the atmosphere via the bubble-bursting process, with a linear relationship to their seawater concentration.

6.3 Paper III: Arctic Ocean

Water from Kongsfjorden, Svalbard sampled during late winter was used to obtain the volatile properties and mixing state of primary marine aerosol by the V-TDMA method. In addition, the effect of water temperature on the aerosol concentration was investigated. The V-TDMA was originally built for airborne measurements, and was for the first time used to investigate sea spray aerosol.

Foremost external mixtures of non-volatile aerosol, presumably sea salt and volatile organic aerosol were observed for all particle sizes investigated, ranging between 0.025-0.158 μm. As much as 73% by number of the aerosol up to $D_p=0.100$ μm evaporated after heating to 300 °C, which corresponds to the organic fraction of the aerosol. The smallest organic aerosol number fraction was observed for the largest particle size ($D_p=0.158$ μm).

All aerosol sizes were sensitive to changes in water temperature with an inverse relationship to increasing water temperature. Water temperature did however not influence the aerosol mixing state or organic fraction, and should foremost be regarded as an important controlling factor of the number concentration of primary marine aerosol production.

The organic fraction was possibly underestimated due to already evaporated material nucleating in the cooling section of the thermodenuder, and the use of an active carbon trap in the cooling section of the thermodenuder to adsorb evaporated material is suggested to improve the results.
6.4 Paper IV: Baltic Sea, eddy covariance method

Size resolved sea spray fluxes derived using the eddy covariance method from one of the coastal sites in the Baltic Sea used in Paper II were here compared to simultaneous laboratory-made sea spray. The eddy covariance technique demands instruments with high frequency sampling, which can be difficult for sizes below about 0.1 µm. As the laboratory-made aerosol was detected down to 0.02 µm, combining the two methods could yield a wider sea spray flux spectrum. In order to examine only the non-volatile part of the sea spray, it was heated to 300 °C. The results presented are to our knowledge the first near coastal sea spray fluxes with limited fetch.

The non-volatile aerosol flux correlated better with wind speed than did the volatile aerosol flux (r=0.74 vs. r=0.23, respectively). Anthropogenic influences from central and eastern Europe, according to back trajectory analysis, frequently contaminated the aerosol fluxes, and the downward mixing of these aerosol particles is thought as a contributing factor to the lower wind speed correlation of the unheated sea spray.

There was a clear diurnal cycle in sea spray flux per whitecap, where both tank and in-situ data agreed on a midday minimum. This supports the possible existence of a biologically driven diurnal cycle in sea spray production as suggested in Paper II.

Aerosol flux size distributions and organic number fractions from the wind sector with the longest fetch corresponded well with previous studies at open ocean conditions, while it appeared to be less organic sea spray produced from more fetch-limited wind directions. This may be an artifact due to larger deposition fluxes of anthropogenic particles embedded in the upward net flux as a result of the closeness to the coast.

For the data most resembling open ocean conditions, tank- and ambient aerosol fluxes were combined and compared to the Mårtensson et al. (2003) model for sea salt, and to the Ellison et al. (1999) model for organic surfactants. The combined tank- and ambient fluxes most resembled a simple organic surfactant model or displayed larger fluxes than that model, which could suggest that there were more organic material present in the original droplets than what one monolayer accounts for. Another explanation is that water or water soluble organic material still remained within the droplets/particles.
7 Concluding remarks and outlook

This study has focused on primary marine aerosol particles, and processes controlling their production. Four sites in three different waters have been investigated, and all showed similar spectral features: aerosol number size distributions were stably centered close to 0.2 μm $D_p$ with little variation apart from magnitude (Papers I-III). The average organic number fractions of the aerosol encountered by heating the aerosol to 300 °C though displayed larger variations. The organic fractions originating from northeastern Atlantic Ocean ranged between 5 and 33% with a peak at 140 nm $D_p$ (Paper I). The Arctic water ditto was 25-65%, with a peak at 63 nm $D_p$ (Paper III). Estimations from eddy covariance fluxes from the Baltic Sea put the average organic mass flux fraction in the range of 35-80%, peaking at the lowest size measured, close to 300 nm $D_p$ (Paper IV). Other key findings are:

- Laboratory made bubble-bursting in the small experimental tanks used here produced a realistic bubble spectrum well in agreement with previous studies from both wind tanks and real oceanic measurements (Paper I).

- An elevated salinity increased the aerosol production (Paper II), while water temperature exhibited an inverse relationship with aerosol production (Papers II and III).

- No scientifically significant correlation between aerosol production and chlorophyll $\alpha$ was found (Paper I).

- The primary marine aerosol concentrations were observed to decrease at times of increased phytoplankton activity; from one week to another at Askö, and on a diurnal basis at Garpen (Paper II).
• There was a high tendency for colony-forming bacteria to be efficiently transported to the atmosphere by bubble-bursting (Paper II).

• A clear diurnal variation in aerosol production with a daytime minimum was observed at the Baltic Sea, both for laboratory made aerosol (Paper II), and for ambient sea spray flux normalized to the whitecap area (Paper IV). The observed minimum coincided with the peak in dissolved oxygen in the water, suggesting a biologically driven diurnal cycle.

• Foremost external mixtures of sea salt and marine organics have been observed (Papers I and III).

• The combination of laboratory made sea spray with ambient flux data into a continuous size spectrum from $D_p=0.02-2 \, \mu m$ unfortunately did not yield a conclusive result (Paper IV).

No single parameter was identified as being the controlling factor of primary marine aerosol production during laboratory conditions. Salinity, water temperature, dissolved oxygen as well as biological activity co-vary and their individual influences were difficult to separate under the natural conditions chosen here. In order to distinguish the dominant parameter, or rather find the cut-off point where one parameter takes the lead over another, more extensive data sets in space and time are necessary. Thus, a full year is suggested to obtain a complete seasonal cycle.

Many results in this study points out phytoplankton activity as a key player affecting the aerosol production negatively. Our results showed no correlation between aerosol production and chlorophyll $\alpha$, which commonly is used as a proxy for biomass. The data presented here are though ten-minute averages, and perhaps a correlation could have been found studying a longer time frame. The composition of phytoplankton-derived organic matter and the time lag between increased phytoplankton activity as measured by chlorophyll $\alpha$ and the production of these exudates is highly relevant, and could possibly be found using continuous measurements of larger periods of time. The question arises, is the time lag between phytoplankton activity and an altered aerosol production of hours or days?
Additional measurements of the surface water chemical composition should be prioritized as the transfer of organic material to the aerosol phase most likely is controlled by the solubility and surface tension properties of marine organic matter (Facchini et al., 2008). This need is also emphasized by the wide range of results obtained from laboratory-made investigations regarding the submicrometer organic mass fraction (Papers I, III and IV).

The foremost external mixtures of sea salt and organics observed here contradict many observations of ambient marine aerosol. As primary marine aerosol can interact with anthropogenic aerosol emissions and aerosol precursor gases at ambient conditions, our result does not rule out the possibility of an external mixture at formation. The mixing states of primary marine aerosol originating from water of high and low phytoplankton activity could teach us more about the role saturation of surfactants has. Do external mixtures of sea salt and organic compounds mainly occur at times when bursting bubbles are not completely covered by organics?

An important goal for this study was to connect the knowledge gained from laboratory investigations to real sea spray production as a first step to transfer our results from the small experimental scale to the real world. Even though the method used here is acknowledged to produce realistic bubble spectra, possibly the bubble production in the experimental tank, our “wave”, occasionally is too small. To test if a larger experimental tank with a higher water flow resulting in a deeper water plume and longer bubble life as suggested by Fuentes et al. (2010) connects better to the ambient fluxes, would answer that question.

The bubbles yielding the submicrometer marine aerosol particles are traditionally considered to be large, over about 2 mm diameter (e.g., Blanchard and Syzdek, 1982; Resch and Afeti, 1992). Although the bubble size distribution was investigated in Paper I, the upper instrumental limit was only 1 mm and there was no strong correlation between submicrometer aerosol and bubbles of that size or smaller. With the recently updated information about smaller daughter bubbles resulting in numerous jet droplets also from large bubbles (Bird et al., 2010), even bubbles smaller than our lower instrumental limit of 30 μm should also be investigated further. In addition, the bubble spectra and the bubble’s lifetime on the sea surface respond to changes in parameters such as salinity, water temperature as well as the concentration and composition of organics (e.g., Weber et al., 1983; Slavenwhite and Johnson, 1999; Leifer et al., 2000; Tyree et al., 2007). To
fully understand the impact of different environmental parameters on the marine aerosol load and composition, and in turn their effect on climate, one needs to focus on the bubbles producing the aerosol. Thus, only with thorough investigations of bubbles and their response to environmental changes, can the knowledge on submicrometer primary marine aerosol improve.
8 Acknowledgements

During the work of this thesis, I have spent several weeks either on a research ship or on small islands, in one case without stable electricity. I have spent endless hours in front of my computer trying to make sense of the data I have collected. In the world of research it is easy to despair, and quite impossible to reach the end of an education like this without support. Many people have crossed my path and affected this work in numerous ways, to which I owe my thanks. I would like to extend special thanks to:

My supervisor Douglas Nilsson who made particles as small as 0.02 µm so interesting, so vivid, so important and so clear that I felt I almost could touch them individually. Thanks for letting me try my own way – and for pushing me back to focus when needed. A large thank you also goes to my co-supervisor Radek Krejci. Not only have you taught me how to fix a broken CPC (did I tell you I dropped the lens once? I probably didn’t…), you have always found time to read, and improve, my manuscripts no matter the hour of day. Ian Cousins is thanked for his support, and Åke Hagström for very nice lab equipment solutions, great food and good laughs.

Johan Ström for teaching me about aerosol measurement techniques when I first arrived at ITM, only two weeks before my first field campaign when these newly learned skills quickly was put to their test.

I would like to thank my co-authors for your time, ideas and for giving me necessary and constructive criticism. Especially I wish to thank Monica Mårtensson for always having time for my questions no matter how small, Jarone Pinhassi for giving me a crash-course over the phone on how to write a scientific paper (and for sharing an anecdote starring a lifeboat, which I won’t forget easily), and Gerrit de Leeuw for his encouragement and support during the MAP-06 cruise.

All technicians who helped me in numerous ways during data sampling: Kai Rosman, Juri Wahler and Leif Bäcklin.

I would like to thank HC Hansson for having a door open for me, and Anki Andersson for solving endless administrate inquires and
making “fika” the best part of the day. I’m also most obliged to Hamish Struthers for making sure my English was understandable.

All past and present PhD students. I sincerely thank you for lunches, coffees, therapy, good laughs, chats and the occasional kick in the butt when needed. Especially I wish to thank Anna (there is never a wrong time for a ‘latte’ or a vampire discussion), Patricia (…or for banana bread), Gustavo (…or to relax and listen to some good music), Emma (…or for laugh or for a discussion on feminism), Sanna (…or to focus on the fun parts of life), and Camilla (the best office-mate in the world!). I am of course grateful to all you others at ml. But please, fix the heating and make the automatically controlled ceiling lamps be turned on during daytime instead of during nighttime.

Thanks also to my friends and believers outside work, whom I have forsaken lately when my head has been filled with thesis. Especially I wish to thank Sonja Löfmark for your support, relaxed attitude and good taste in coffee. I will miss our morning walks!

Finally, I wish to thank my loving and supporting family; my sharp and creative mother Lotta, my insightful and humorous father Ingemar, my unusually sane and unusually smart wife Hanna and my prankish and very sweet son Micha. This thesis would not have seen the light of day without your support.

Thank you.
9 References


