SUBMICROMETRE AEROSOL EMISSIONS FROM SEA SPRAY AND ROAD TRAFFIC

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List of Papers

I  Laboratory simulations and parameterization of the primary marine aerosol production.  

II  Eddy covariance measurements and parameterisation of traffic related particle emissions in an urban environment.  

III  Primary marine aerosol emissions: size resolved eddy covariance measurements with estimates of the sea salt and organic carbon fractions.  

IV  Are submicrometre sea salt emission parameterisations consistent with observed remote marine aerosol distributions?  

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The first ideas belong to: Paper I, Douglas Nilsson and H-C Hansson; Paper II, Douglas Nilsson and Christer Johansson; Paper III, Douglas Nilsson; Paper IV, Monica Mårtensson. I have done most of the measurements and the major part of the data analysis in Paper I and II. The major part of the data analysis and the manuscript in Paper III are done by Douglas Nilsson. I have modified the model for the marine conditions and done the model runs and the evaluation of the results in Paper IV. I have written the most parts of Paper I, II and IV.
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1 Introduction

The direct and indirect aerosol climate effects are potentially as large as that of greenhouse gases, although with much larger uncertainties (IPCC, 2001, 2007). Aerosols are suspensions of fine liquid and/or solid particles in the air and their variability in both time and space is largely in contrast to greenhouse gases, which are relatively uniformly distributed in the atmosphere. The net effect of aerosols is a cooling of the Earth. Another aspect of the aerosols is that some of them cause serious health effects, as asthma, cardiovascular issues, lung cancer and premature death (WHO, 2003, 2005).

The knowledge about the aerosol’s chemical and physical processes and their radiative effects has been enhanced during the last decades. However, still an incomplete understanding remain about sources, magnitudes and distribution, transformation and sink processes for the aerosols, and the aerosol-cloud interaction, including the formation of cloud condensation nuclei (CCN). One way to reduce the uncertainties in the new generation of coupled climate models is to find source parameterisations for the natural and anthropogenic emissions. Especially the submicrometre aerosol particles have to be better quantified. For health effect assessment modelling, it is important to have knowledge about the emissions in urban areas, in order for policy makers to know the impact of future emission regulations.

The oceans cover 70% of the Earth surface. The flux of sea salt particles from the oceans is the largest aerosol source and influences the properties of the atmosphere and the climate over the Oceans and a large part of the continental landmasses. If a climate change with a global warming occurs, the natural emissions of aerosol particles are expected to increase due to higher wind speed and temperature, resulting in an increased cooling effect (IPCC, 2001). The anthropogenic aerosols emissions, on the other hand are smaller than the natural emissions. However, estimates show that their influence on climate has the same magnitude as the natural, which make them as important to quantify. A large fraction of these particles come from the road traffic. A problem with the traffic related aerosol emissions is the health effects caused by particles. The importance of this is emphasized by the estimate that world population will rise by 50% in the next 50 years largely by growth of urban areas in less developed countries (U.S. Bureau of Concensus, 2000). Aerosol emissions are expected to increase by a factor of 2 during the next 40 years mainly in the growing urban areas (Wolf and Hidy, 2000) with far reaching impact on the regional and global air quality (WMO, 1997).
To understand the climate effects from the anthropogenic aerosols, it is important first to understand how the natural aerosols affect the climate on Earth, and then to study how the natural and anthropogenic aerosols interact with each other. The current observed global average temperature increase since the beginning of the industrial revolution is 0.8°C. How large would it have been without the cooling effect of aerosols? How large will the cooling from the aerosols be in the future?

1.1 Aerosols

Primary aerosols are emitted directly as particles to the atmosphere and secondary aerosols are formed in the atmosphere by gas-to- particle processes. Aerosol particles sizes span over four magnitudes, from a few nanometres to tenths of micrometres, with different lifetimes, radiative properties and CCN potentials. Microphysical processes occurring in the atmosphere, like condensation and/or coagulation as well as cloud processes transform the aerosol. The chemical compounds in the aerosol can be internally mixed, in the same particle, or externally mixed, in different particles. Both types can be present at the same time. The chemical composition of the smallest particles is difficult to measure, as their mass concentrations are small. The lifetime depends on both the size and the chemical composition as the particles are removed through dry and wet deposition, (Seinfeld and Pandis, 1998).

![Figure 1. The number size distribution for the remote marine aerosol from Bates et al. (2000) and the urban aerosol from Hussein et al. (2004).](image-url)
Number size distributions for marine and urban aerosols can be seen in Figure 1. The figure shows the number concentration of particles ($N$) per cm$^3$ from 3 to 600 nm $D_p$ for the marine and from 8 to 400 nm $D_p$ for the urban aerosol. The averaged marine aerosol is without anthropogenic sources from a field campaign in the Atlantic Ocean (Bates et al., 2000), $N$ is $\sim$400 cm$^3$. This aerosol has been transformed by the processes in the atmosphere. The urban aerosol is from Hussein et al (2004), it is an average from measurements during six years in Helsinki, $N$ is $\sim 14400$ cm$^3$.

The original aerosols emitted from the ocean and in the city centre may have other size distributions and compositions than in Figure 1. We are interested to measure the emissions, ($F$), the number of particles per m$^2$ and second, before any processes have transformed them. This is what the modellers need to include these aerosol sources in their models.

1.1.1 Marine aerosols

Primary marine aerosols are emitted from the water surface into the atmosphere directly as droplets with the composition of seawater enriched with some chemical compounds (organic carbon), bacteria, viruses, or debris of these, which originate from the upper water column and from the film that may cover the water surface. The major source of the primary marine aerosol is the bursting of air bubbles produced by breaking waves (e.g. Blanchard and Woodcock, 1957).

The first methods to count sea salt particles did not provide size resolved distributions. However, already Aitken (1881) discovered that small sea salt and sulphate particles are easily activated as CCN. Among the first attempts to obtain particle size distributions are field measurements by Owens (1926), and laboratory experiments by e.g. Köhler (1941), both of which investigated the hygroscopicity of sea salt particles of different sizes. The work continued, (by e.g. Woodcock, 1949, Twomey, 1955, and Woodcock and Blanchard, 1957), with collection and sizing of particles, studies on the transformation of sea salt particles to cloud droplets, measurements of the horizontal and vertical distribution, the relation between number concentrations and wind speed and with laboratory experiments producing particles through bubble bursting.

The method of heating CCN was used, in both the Northern and Southern Hemisphere, by Twomey (1971), who found a large volatile fraction in the marine CCN. This method was further developed and the heating system was applied on aerosols (e.g Hoppel et al., 1990 and O'Dowd and Smith, 1993), resulting in data showing particles consisting of sea salt in the size range from 12 nm to 200 $\mu$m $D_p$. O'Dowd and Smith (1993) measured the non-volatile fraction with an Optical Particle Counter (OPC), during a cruise on the North Atlantic in 1989. The data were classified depending on air mass, and a large variation of the sea-salt and sulphate fractions was found.
Originally, the scientific community favoured primary sea spray particles as the source for the marine CCN, but concluded that the super micrometre sea salt particles were insufficient to explain the observed CCN concentration. Then it was hypothesised that sulphate aerosols derived from dimethylsulphide (DMS) released by ocean algae dominated the marine CCN, (Charlson et al. 1987). When this source appeared to be insufficient, (Raes, 1995) introduced input of aerosols entrained from aloft. However, new particle formation (nucleation) and subsequent growth to CCN size required to confirm the Charlson et al. (1987), hypothesis are only very rarely observed in the marine boundary, and entrainment in sufficient amount are not always available, and dependent on sufficient aerosol concentrations above the boundary layer.

Meanwhile, the old research field of sea spray had come alive. Evidences for submicrometre sea salt particles accumulated (e.g. O’Dowd and Smith, 1993; Murphy et al., 1998). Direct flux measurements of the emission of aerosol particles from the ocean using eddy covariance showed a much larger emission fluxes of submicrometre particles than previously predicted, (Nilsson et al., 2001; Geever et al., 2005; Paper III). A large fraction of the submicrometre marine aerosol has been found to consist of organics, (e.g. Middlebrook et al 1999, Cavalli et al., 2004; Paper III), the primary marine organics will be further discussed in Paper III.

1.1.2 Road traffic related aerosols

Road traffic is a large source for aerosols. The number concentration is often as high as $10^5$ cm$^{-3}$ in the city centres, Paper II, and as high as $10^6$ cm$^{-3}$ along roads (e.g. Kittelsson, 1998). The majority of the particles are smaller than $D_p$ 0.1 µm, see Figure 1. The total number of particles emitted is larger for diesel vehicles than for gasoline vehicles and the aerosol contain more soot particles. The mean size is around 90 nm for the diesel and around 60 nm $D_p$ for the gasoline exhaust (e.g. Harris and Mariq, 2001). The emission from the gasoline vehicles is more sensitive for the cruising speed, at higher speeds more particles are emitted and older cars emit more particles than newer. The particles from the exhaust consist mostly of carbon, unburned fuel and oil and ash (e.g. Kittelsson, 1998). If the diesel cars are equipped with particle traps, the soot particles with a mode around 90 nm are reduced. However, the number of smaller volatile particles instead increases (Burtscher, 2005). Particles are also emitted due to the wear of brake linings, tyres and road pavement with high PM10 (the mass of all particles large than $D_p$ 10 µm) levels (Johansson et al., 2007) as a consequence. In some countries, studded tyres are commonly used increasing road wear drastically (Norman and Johansson, 2006). The amount of smaller particles emitted from these sources has to be further investigated.
The most common measurements of the urban aerosols are for PM2.5 and PM10, but the size resolved number concentration is measured in some cities (e.g. Olivares et al., 2007; Hussein et al., 2004 and Ketzel et al., 2003). The road traffic related particles have also been measured in tunnels (e.g. Kristensson et al., 2004). For measurements of the urban emission has the eddy covariance method been used once before paper II by Dorsey et al. (2002).

The total surface area with roads and vehicles is small compared to the oceans. Despite this the magnitude of the total global vehicle emissions is estimated to be of the same order of magnitude as the ocean (number of particles), resulting in large local effects on the air quality. Urban aerosols can affect the climate on a regional scale, with changes in cloudiness and precipitation (Rosenfeld, 2000). The different types of particles emitted from the traffic can either have cooling or warming effects, e.g. soot particles absorb the incoming sunlight resulting in a warming of the atmosphere, in contrast to the majority of aerosols. Many of the particles are hydrophobic, which results in a residence time in the atmosphere as long as 4-8 days. These particles can be transported up to 4000 km.

As it seems that the anthropogenic particles from fossil fuel combustion have serious health effects, stronger regulations will come in the future to reduce these emissions. If fossil fuel emissions are reduced due to regulations and increasing oil price or because oil is replaced by sustainable energy sources without or with less particles emissions, the aerosol concentration in the atmosphere can be expected to decrease. Because the lifetime for aerosols is much shorter than for the GHG, the result can be that, the global warming increases rapidly when the anthropogenic aerosol emissions are reduced. Another scenario is that the fossil fuel is replaced with biomass fuels, and depending on the technology used the result then can be an increase in particle emissions.

The transportation of goods with heavy duty vehicles within the European Union as well as probably worldwide, has increased during the last years and even if regulation for the carbon dioxide and particulate matter will come, we can see a problem for the air quality if this trend will continue. There is also an increase in personal transports by cars, which might be diminished by new transport solutions in the future.

1.2 Health effects of road traffic related particles

The assessment of the health effects from particles from motor vehicles requires knowledge of the emissions. Epidemiological studies show a strong link between PM 2.5 (the mass of all particles smaller than $D_p \leq 2.5\mu m$) and mortality and morbidity. Even though these studies do give a possibility to calculate the total risk for health effects as mortality they can not be used to assess the risk for the contributing sources. In Sweden it is estimated that
5300 deaths per year are caused by particles. However, even if a majority of these aerosols come from long-range transport, the original sources can still be the traffic in Europe. The small aerosol particles, from the traffic see Figure 1, are hydrophobic when emitted which give them a long residence time. During the transport they transform and grow through condensation and oxidation mainly from inorganic compounds as sulphates and nitrates but also organic compound from natural and anthropogenic sources. When reaching Sweden the mass has become larger and they contribute significantly to the mass of PM2.5. The long range mass fraction comprises about 70% of the exposure to the Swedish population (Forsberg et al, 2005).

In the Netherlands a study has shown that living near a major road increased the risk for cardiopulmonary mortality (Hoek et al., 2002). It is possible that the ultra-fine particles and particulate matter from the vehicle exhaust are responsible for these health effects. Different studies have shown that high exposure of transport-related particles is associated with bronchitis and cough in children (WHO, 2005). Other studies show that people with occupational exposure to vehicle exhaust has higher risk for respiratory symptoms or disease. During different controlled studies volunteers have been exposed to particulates, resulting in increased levels of markers for airway inflammations in humans. Animal exposure studies have also been done where airway inflammations where found. Cell-culture studies found changes in the formation of oxygen compounds, changes in the antioxidant defence and increased inflammation. In WHO (2005), the risks are summarized;

- Increased risk of death, particularly from cardiopulmonary causes.
- Increased risk for respiratory symptoms and diseases that are related to allergies.
- Maybe increased risk of developing an allergy.
- Changes in the autonomic nervous system regulation and increased inflammatory response.
- Increased risk for lung cancer.

No threshold has been found; all anthropogenic emission of particles results in health risks (WHO, 2003).

As shown in Figure 1, a majority of particles in the city are smaller than $D_p$ 100 nm. These particles have little mass and before they are aged they do not contribute much to PM2.5. In Figure 2 are the number of particles shown together with the mass of the same particles, and the limits for PM2.5 and PM10. However, the small particles have a large number and surface which can make them even more dangerous. Recent studies show that these small particles can cause serious health effects as they penetrate deep in the lungs into the pulmonary alveoli. Figure 2 shows the penetration for different par-
particles sizes into the respiratory tract. These results are important reasons to start more measurements in the urban areas of submicrometre particle number concentrations and fluxes.

![Regional deposition vs. Particle size](https://via.placeholder.com/150)

**Figure 2.** Deposition of particles depending on size in human, together with particle number and mass size distribution at an inner city and suburban site in Stockholm. PM10, PM2.5 and PM1 are indicated.

The limit value in Europe for particulate matter (PM10) is 40 µg m⁻³ as an annual average, and the daily average 50 µg m⁻³ may not be exceeded more than 35 days in a year. Is this regulation enough, or do we need regulations for the smaller particles that have other sources than PM10, as studies show health effects of both PM2.5 and smaller sizes? Answering these questions requires better understanding of the temporal and spatial variability of the emissions in urban areas. Not only of particle mass emissions but also particle number emissions should be described.

### 1.3 Climate effects

The direct effect, the scattering/absorbing of the incoming solar radiation, is most effective for particles with a diameter \(D_p\) between 0.1 and 2 µm, corresponding to the power peak in the solar spectrum. The indirect effect, changes of the cloud properties, depends on the activation of particles to CCN. The smallest aerosol diameter activated in a cloud depends on the chemical composition and the super saturation of water vapour in the cloud,
following the Köhler theory. The activation starts at $D_p$ around 70 nm, in the extreme case from 50 nm at high super saturation in convective clouds, but smaller particles than this can still be of interest as they can grow to larger sizes. The best known radiative mechanisms associated with the indirect effect are:

- **The cloud albedo effect**, (Twomey, 1977); when the number of aerosol particles raise, the size of the cloud droplets decreases. The number of cloud droplets in the clouds then increase, resulting in brighter clouds that reflect more of the incoming solar radiation.
- **The cloud lifetime effect**; as the smaller cloud droplets less efficiently cause raindrops, the cloud lifetime increases compared to clouds with larger droplets, (Albrecht, 1989). Changes in the micro physical properties of the clouds also influence the amount of clouds and the precipitation.

Many emission parameterisations focus on the mass of sea salt, where the super micrometre particles dominate. The source function most commonly used for the number flux is from Monahan et al. (1986). However, this parameterisation is only valid down to $D_p$ (dry) 900 nm. How large is the submicrometre number flux? This is a relevant question from the climate perspective as the sea salt particles are not only important for the direct scattering effect of aerosols, but also important for the indirect effect as they have a potential contribution to the number of CCN. Both these effects depend on the number and sizes of the particles. Sea salt particles are the dominant submicrometre scatterer in ocean regions (e.g. Murphy et al., 1999). The indirect aerosol effect is however much more uncertain, it is believed that the global main contribution comes from marine stratocumulus clouds, due to their large area-coverage and that especially low clouds have a cooling effect.

The General Circulation Models, GCM, have better cloud schemes and aerosol representation compared to earlier versions that only included a bulk aerosol mass, still a lot of work remain to be done with the aerosol processes. The total indirect effect on the Earth range from $-0.3 \ \text{Wm}^{-2}$ to $-1.4 \ \text{Wm}^{-2}$ in an intercomparison between models (Penner et al., 2006). The author’s conclusion is that the largest uncertainty depends on how the aerosol concentration is predicted from a fixed set of sources. It is important to reduce the uncertainty in and between present climate models; the aerosols have to be better represented, both regarding number size distributions and microphysical processes. One way to reduce the uncertainties is to include better parameterisations into the models for the number emissions of the natural and anthropogenic sources.
Figure 3. Global average temperature change simulated by Andreae et al. (2005), with a strong cooling effect, red line, compared with no aerosol cooling effect, blue line and the yellow line in-between represents the values in IPCC-TAR.

It must be understood that the cooling effect of anthropogenic aerosols does not offer a hope to escape the climate change. The observed global average warming so far is a net result of both aerosols and GHG. Due to the much shorter aerosol lifetime compared to GHG, we will face the full consequences of the anthropogenic GHG that are now masked by the anthropogenic aerosol, the day we stop using fossil fuels. If the present day cooling effect of aerosols is underestimated, a doubling of CO$_2$ may cause an 8°C warming in 2100, instead of 4°C, which is the mean value from IPCC see Figure 3 from Andreae et al. (2005).

1.4 The focus of this work

This thesis deal with the emissions of two important primary aerosol sources; one natural, the emission of marine aerosols, and one anthropogenic, the road traffic related aerosols. Both these aerosol sources need better parameterisations. Validating them experimentally and testing them in a process model serve the purpose both to convince other researchers to include them in their models, and to reduce or at least quantify their uncertainty. The use of a process model further allows us to study parts of the problem that we can not measure or have not measured.
The questions we have tried to find the answers to are:

- Can we quantify the submicrometre marine and road traffic related aerosol emissions?
- Are we able to characterise the size resolved aerosol number fluxes?
- What are the fractions of different chemical species?
- Are the aerosols externally or internally mixed?
- Is it possible to identify different sources?
- Which parameters influence the emissions?
- Are we able to parameterize the emissions and use the new parameterizations in a reasonable way in models?

To increase our understanding of the primary aerosol emissions different methods have been used in this thesis:

- Laboratory experiments in Paper I in an effort to find a parameterisation for the primary marine aerosol production.
- Direct flux measurements have been used to quantify the magnitude of road traffic related (Paper II) and the marine (Paper III) aerosol emissions.
- The process model, Paper IV, for simulations of the processes that transform the marine aerosol.

The interactions between model work and experimental work are important in the effort to understand the complexity of the processes in the atmosphere. Both parts are equally important for a better prediction of the influence on climate and understanding of the health effects of the aerosols. In this largely experimental thesis, an important aspect has been to always keep in mind the requirements and limitations of large scale models, with the aim to formulate results in forms that are useful in climate and air quality models. Since the parameterisation from Paper I is already used by large scale modellers, at least we appear to have been successful in this case. In addition, we have introduced an aerosol process model in the thesis work, which have forced us to work with modellers. Hopefully, such collaboration help to improve the understanding of the earth-atmosphere-ocean-biosphere system among scientists, and if we take our responsibility to distribute our research results to the society, among both policy makers and the public, this work can contribute to build a sustainable society in the future.
2 Results

With the opportunity to combine different methods; laboratory experiments, flux measurements and process modelling, I have in this thesis been able to examine the size resolved primary marine aerosol source. Flux measurement together with a database with information about the traffic activity has given knowledge about the source strength of particles from the traffic in Stockholm.

2.1 Laboratory experiments

In 2001 we returned to a research tool that was very popular in the 1950-80’s: Laboratory experiments, where the processes of aerosol formation from the bursting bubbles are investigated during controlled circumstances. Since the 1980’s there has been important development in aerosol instrumentation which allow accurate counting and sizing down to a few nm with the differential or scanning mobility particle sizer (DMPS/SMPS) and down to a ~100 nm with the OPC. With such instrumentations we showed that the production is dominated by a mode typically centred at 100 nm dry diameter. In Paper I an experimentally based parameterisation was derived for the source flux of sea salt particles in the size range 0.020-2.8 µm $D_p$. The number of particles produced per size increments, time unit and whitecap surface is described as a linear function of the water temperature and a polynomial function of $D_p$. This is the first parameterisation to almost cover two full decades of the submicrometre sea salt aerosol production, and also the first to include the effect of water temperature.

2.2 The eddy covariance method

The eddy covariance method, used in paper II and paper III, is the most direct method to quantify turbulent fluxes. The flux measurements presented in Paper II and Paper III are done in the surface layer, the part of the atmosphere closest to the surface where most of life on earth exist and most of the natural and anthropogenic emissions occur. The surface layer is about 10% of the boundary layer and is also called the constant flux layer, as the turbulent fluxes vary less then 10% with height. This implies that fluxes
made within the surface layer can be interpreted as representative for the sinks and/or sources at the surface. If as for the aerosol fluxes in Papers II and III, the aerosol deposition is negligible the eddy covariance measurements can be considered as the aerosol emissions. In the city this method was used to quantify the emissions of particles from the road traffic, Paper II, and by the sea to measure the primary marine aerosol emission, Paper III.

In Paper II the eddy covariance method was used to quantify the urban total aerosol source number flux, for particles with $D_p > 11 \text{ nm}$. Together with a database with traffic activity we have derived one emission factor for a fleet mix and two separately for light duty vehicles and heavy-duty vehicles. The results show that during weekdays ~70-80% of the emissions came from heavy duty vehicles.

In Paper III the size resolved emission of marine aerosol particles was measured with the eddy covariance method. For periods sampled air was heated to 300°C, in order to evaporate semi-volatile organics and isolate the sea salt fraction. The resulting sea salt particle emission validates the parameterisation from Paper I in the 0.1 to 1.1 $\mu$m $D_p$ range at a water temperature of 12°C, for a tropical water temperature (25°C) is Clarke et al. (2006) used to validated the parameterisation.

Paper III also suggests that the particles are internally mixed, i.e. organic carbon, water and sea salt is mixed in the same particles. The total aerosol emission was approximately estimated by a combination of the sea salt parameterisation in Paper I and the model by Ellison et al. (1999), which predicts a surface film of water insoluble organic molecules on the aerosol droplet. This theory about a surface film of fatty acids coating the nascent particles seem too be consistent with the observed sea salt fluxes, the total aerosol fluxes and concurrent data.

2.3 Process modelling

The process model is an excellent tool to investigate how the aerosol changes, depending on the physics (e.g. wind speed, temperature, cloudiness and rain) and chemistry (gas concentrations). The aerosol dynamics model UHMA (University of Helsinki Multicomponent Aerosol model), (Korhonen et al., 2004) has been modified for marine conditions in Paper IV. In the modelling, emissions of sea-salt and DMS have been included together with dynamics, chemistry and clouds representative for the marine boundary layer atmosphere. The modelling starts with sea salt particle emissions based on Paper I and consider how microphysical processes and sources change the composition and size distribution of the aerosol. This influences the aerosol lifetime and how good CCN the particles will become. In Paper IV the resulting transformed aerosol is compared with the number and mass concen-
trations of observed marine aerosol particles (including the concentration parameterisation by O’Dowd et al. 1997).

**Paper IV** demonstrates that despite no new secondary aerosols form, and even when entrainment is turned off, the sea salt source, secondary sulphate, and cloud processing are able to reproduce a typical marine submicrometre aerosol size distribution: an Aitken (particles below 100 nm $D_p$), and an accumulation mode with a so-called Hoppel-minima near the smallest activated CCN size. The sea salt number distribution reproduces the observations by O’Dowd et al. (1997). The CCN number is mainly determined by the sea spray source, only small changes occur due to changes in DMS emission and water temperature. The sea salt forms a spine for the size distribution; although in the end sulphate constitutes 20-80% of the Aitken and accumulation modes. The number of CCN depends mostly on the wind speed; high entrainment fluxes can also have a substantial effect.

Finally, it is worth noticing that we were able to show that the water temperature effect in the **Paper I** parameterisation to some degree cancelled out with our detailed aerosol-cloud scheme, while a simpler approach comparable to that applied by Pierce and Adams (2006) in their GCM (with a fixed CCN size limit of 80 nm) gave a temperature effect that may be false.

### 2.4 The magnitudes of the marine and urban aerosol sources

For a simple first estimation of the order of magnitude of the global sea salt particle emission from the oceans during one year, the parameterisation from **Paper I** is used for $D_p$ 0.020 µm to 1.0 µm together with the one from Monahan et al. (1986) for $D_p > 1$ µm. A global average mean wind speed of 9 ms$^{-1}$, a surface water temperature of 15°C and a boundary layer height of 750 m, have been assumed. Both parameterisations are functions of the wind speed, and the parameterisation from **Paper I** has a temperature dependency. Of course, both the wind speed and water temperature vary a lot globally, but we only aim at a first initial estimate to show the importance of calculating both mass and number.

The global flux of sea salt for $D_p > 1$ µm has been estimated to be between 1000 and 6000 Tg year$^{-1}$ (IPCC, 2001), when the parameterisation from Monahan et al. (1986) is used. As shown in Table 1 our estimate, with the same parameterisation, is $\sim$5500 Tg year$^{-1}$, in good agreement even if our approach is simple. For $0.2 < D_p < 1$ µm IPCC gives a value between 18 and 100 Tg year$^{-1}$. When the parameterisation from **Paper I** is used we arrive at a higher value of 140 Tg year$^{-1}$.

If instead the particle number emission in the size interval $0.2 < D_p < 1$ µm ($121 \times 10^{25}$ year$^{-1}$) using **Paper I** is compared with Monahan et al. (1986)
(87×10^{25} \text{ year}^{-1})$, the latter gives 39\% less particles for these sizes that is important for both the direct and indirect climate effects, see Figure 1, and Paper I for a comparison of the parameterisations. The mass is 39 times larger for $D_p > 1 \mu$m then for $D_p < 1 \mu$m. If we instead look at the number concentration, 52 times more particles are found in the range below $1 \mu$m $D_p$.

Table 1. Estimates of the global emission of sea salt particles for one year with the parameterisation in Paper I, in brackets the values for $0.2 < D_p < 1 \mu$m

<table>
<thead>
<tr>
<th>Diameter $\mu$m</th>
<th>Mass Tg year$^{-1}$</th>
<th>Number $10^{25}$ year$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.01 &lt; D_p &lt; 1$</td>
<td>140 (130)</td>
<td>980 (120)</td>
</tr>
<tr>
<td>$1 &gt; D_p &gt; 17$</td>
<td>5460</td>
<td>20</td>
</tr>
</tbody>
</table>

The emission from the traffic in Stockholm is $\sim 300\times10^6 \text{ m}^{-2} \text{ s}^{-1}$, for $D_p > 0.01 \mu$m. From the ocean is the average emission $1\times10^6 \text{ m}^{-2} \text{ s}^{-1}$ for $D_p > 0.02 \mu$m (with the global average $10 \text{ m}$ wind speed = $9 \text{ m s}^{-1}$ and surface water temperature = $15^\circ\text{C}$). On the order of 1\% of the continents are covered with urban areas with a similar emission of particles as in Stockholm. Then the total source strength of particles from the cities (from $D_p 0.01 \mu$m) has the same magnitude as from the Oceans (from $D_p 0.02 \mu$m). However, the particles, as shown in Figure 1, are small and hence they have shorter lifetime than much of the primary marine aerosol. On the other hand they are much more hydrophobic, which might increase their lifetime substantially. We have to consider that the anthropogenic sources from road traffic have the same magnitude as the natural and how that can affect the climate and air quality. The conclusion that our traffic aerosol emissions in magnitude globally can challenge the aerosol source usually regarded as the strongest natural aerosol source, the sea spray clearly points out the enormous impact of the current transportation habits of the human society. The fact that the primary anthropogenic aerosol is totally different compared to the sea spray in terms of size, chemistry and morphology may not reduce its importance for the climate.
3 Implementation in models

As mentioned before, this research has had the ambition to become useful for other researchers, more specifically for model predictions of air quality and climate, and through their work in the long run for the society. So far, the sea salt aerosol source parameterisation from Paper I has been used in the several models, which we will specify below. The emission factors obtained in Paper II can be considered as representative for a large vehicle fleet and may be used as a validation of emission estimates based on a bottom-up approach, i.e. using emission factors of individual vehicle types and their activity data. Validation of the emissions is usually the most crucial part of urban air quality modelling. Hopefully the validation of the sea salt source in Paper III and the tests in Paper IV will encourage more researchers to include this parameterisation in their models as the much needed sub-micrometre sea salt source.

The parameterisation has been successfully applied in 1-D models (Glantz et al., 2004) and regional models (Foltescu et al., 2005; Andersson et al., 2006; Lundgren, 2006). Glantz et al. (2004) simulated the vertical gradient of the sea salt number and mass concentrations during the North Atlantic regional Aerosol Characterization Experiment Second Lagrangian experiment they used a 1-D ensemble-averaged model. Foltescu et al. (2005) used the parameterisation in the MATCH (Multi-scale Atmospheric Transport and Chemistry) model to simulate the regional-scale European sea salt distribution and managed to improve the sea salt mass fields compared to previous work. Andersson et al. (2006) included the sea salt parameterisation in a 3-D Chemistry Transport Model (CTM) in order to help prediction of inter-annual variation and trends in air pollution over Europe due to climate variability during 1958–2001. The sea salt parameterisation was also introduced in a regional atmospheric predicting model LM-ART by Lundgren (2006). In a case study for May 28-29th, 2005, 3-D simulations over an area west of Ireland showed that both number and mass concentrations of sea salt particles were highly dependent on wind speed with maximum concentration of 300 µg sea salt m\(^3\) and number concentration up to 100 cm\(^3\). A significant vertical transport and advection over land was found for the smallest sea salt particles.

For estimates of the contribution of sea salt particles to global CCN, the parameterisation has recently been used and in a GCM, together with a size resolved aerosol microphysical module by Pierce and Adams, 2006. A com-
parison was done with other parameterisations. Especially in the southern ocean and other remote marine areas, where the contribution of anthropogenic SO$_2$ is low, the emission of ultrafine (including Aitkin) and accumulation mode sea salt particles were shown to have a large impact on the CCN concentration. In the Southern Ocean with high wind speeds, the use of the parameterisation resulted in an increase of the CCN concentration as high as 500%, compared to a model run with only sulphate from natural and anthropogenic sources. The same study showed that in the Southern Ocean the CCN concentration increased by 60% when the ultra fine particles were included ($D_p < 100$ nm); of these 60%, 20% is due to the growth through condensation and coagulation of particles smaller than 80 nm up to the activation size. The temperature dependence included in the parameterisation had a large impact on the CCN in this region of the world, as the emission of ultrafine particles increases when the temperature decreases. In the simulations, Pierce and Adams (2006) assumed a super saturation of 0.2% in all clouds, resulting in activation of particles larger than 80 nm. At higher super saturations smaller sizes can activate and hence the influence of the ultrafine particles can be even larger. In a comparison with measurements of the total number concentration in this region, the model run with the Paper I parameterisation, showed the best agreement, in competition with several other parameterisations.
4 Outlook

With the combination of experimental methods and the UHMA model: many of the questions addressed in this thesis have been answered. However, many questions remain unanswered.

- It was during a highly biological active period at the West coast of Ireland when the size resolved emission of primary marine aerosol particles was characterised down to $D_p$ 100 nm. A large marine source of organic carbon in the internally mixed particles was identified. To investigate how temperature and biological activity influence the emission, this type of measurement must be repeated during other seasons and at other Ocean sites.

- New collocated bubble experiments and flux measurements have been done on the Baltic Sea and the North Atlantic and are now evaluated at ITM, with focus on the organic fraction of the emissions. The question considering how large the size resolved emission of aerosol particles with $D_p<100$ nm are, has not been answered with in situ measurements. Currently we are trying to cover this gap with in situ tank experiments. Systems that can cover this range with direct flux measurements exist, but are expensive. We need new founding for this set up.

- For the road traffic related aerosol emissions size resolved flux measurements have started in Stockholm in 2007. An OPC measure the particles with $D_p>100$ nm and the method of heating the aerosol is applied. Measurements of the size resolved emission of urban particles with $D_p<100$ nm has the same technical limitations as for the marine aerosol.

- For both these sources one should give priority to continuous long term measurements, to investigate if/how the emissions vary depending on season. For the urban emissions, in order to say more about the health effects, we would like to separate the particle emissions into soot/organic particle emissions, road wear, brake wear and tire particle emissions, in addition to heavy duty and light duty vehicle separation. A possible way to achieve this is using the eddy accumulation and making chemical analysis of the collected aerosol.
• The model simulations will be further developed;  
  • We will make use of trajectories to prescribe the transport over the ocean and the environmental parameters such as wind speed, temperature, boundary layer depth, cloudiness and precipitation. This will allow Lagrangian model simulations of the marine aerosol with the different competing aerosol sources, sinks and transformation processes. These model results will be validated with data from field measurements at the end point of the trajectory.  
• Clearly the reader will spot a contradiction in this thesis. While paper III claim that there is a substantial organic carbon fraction in the sea spray, the model in paper IV include sea salt and sulphate chemistry, but no organic chemistry. The reason is simply that the knowledge on the organic chemistry in sea spray is so incomplete that very few attempts have been done to model it. While UHMA have detailed chemistry for the continental secondary organic aerosol, it lacks the necessary chemistry for primary marine organic components and reactions. An attempt to include the organic fraction of the primary marine aerosol emission will be done. Different oxidation schemes for the transformation of the primary marine organics have to be tested.  
• A weakness of field campaigns is that there is rarely available simultaneous measurement of the CCN concentration. If we get the opportunity to finance a CCN counter (Model CCN-100 from Droplet Measurement Technologies Inc.) we could measure the CCN concentration both in new laboratory experiments and in the field. This counter is a quantitative link between the physiochemical properties of the aerosol and the cloud microphysics. When this counter is used together with a Differential Mobility Analyser (DMA) the activation of a specific particle size can be investigated. A new set up of laboratory experiments can be done with the bubble chamber used in earlier experiments. Particles emitted from both synthetic sea-salt with added organic surfactants and real seawater can be used. As the CCN-100 will give the spectra for the activated particles, it will not only give the CCN number but also knowledge about how different composition will influence the growth.

As the chemical composition and size distribution of the aerosol depend on the sources and the transformation during transport, it is most likely that measurements in the future also will show very different results depending on where and when they are done, even if it is in remote marine areas without continental and anthropogenic influences. Hopefully the cooperation between modellers and experimentalist will result in an increased knowledge about the aerosols and decreased uncertainties in climate and air quality models.
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References


Lundgren, K. 2006. Numerical simulation of the spatial and temporal distribution of sea salt particles on the regional scale, MSc thesis at Department of Meteorology, Stockholm University, 52 pp.


