Investigations into the Physical and Chemical Properties of Baltic Sea Ice

Mats Granskog

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Original papers
This thesis is based on the following papers, which are referred to by their Roman numerals:


V. Granskog, M. A., K. Virkkunen, D. N. Thomas, J. Ehn, H. Kola, and T. Martma, Chemical properties of brackish water ice in the Bothnian Bay, the Baltic Sea, accepted to *Journal of Glaciology*

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The author’s contribution to each publication mentioned above is shown in Table 1, classified into three categories; idea, practical work (includes sample collection, preparation and analytical work), and writing (includes data analysis and writing of the paper).

Table 1: Author’s own contribution to each publication in % as follows; 1 <20%, 2 20–70%, and 3 >70%.

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Investigations into the physical and chemical properties of Baltic Sea ice

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Abstract

Sea ice is a key component of polar and sub-polar seas, including the Baltic Sea. It not only affects climate, from global to local scales, but also strongly modifies the conditions in the marine environment through freezing and eventual melt in several ways. The role of snow in sea ice growth is presumed to be high in the Baltic Sea, although very little quantitative information is available on the contribution of precipitation to ice growth in the Baltic Sea. Even less is known about the chemistry of sea ice and its role as a moderator of (bio)geochemical cycling and budgets of elements in the Baltic Sea. The aim of this Thesis is to shed new light on these matters.

The importance of snow and precipitation on the growth of Baltic Sea ice is vital. For the first time, the stable oxygen isotopic composition of ice, snow and water were used to quantify the amount of snow and precipitation incorporated into the sea ice cover. Results show that meteoric ice (precipitation transformed to ice) constitute up to 35% of the total sea ice mass, much higher than reported elsewhere. Furthermore, the formation of superimposed ice (refrozen snow melt or rain) seem to be important as well, presumably due to the mild ice climate conditions in the region.

The atmospheric load is also important in the chemical budgets of several elements, in particular nitrogen and lead, in the sea ice cover. The sea ice cover acts as a buffer for accumulated substances until its inevitable melt. However, the accumulated nutrients are transported through the ice at times when the ice becomes permeable. This, in turn, makes the accumulated nutrients available in the lower ice layers as well as in under-ice water, potentially affecting algal growth. The chemical budgets and the seasonal cycling of elements with selective rejection/retention during freezing of seawater are potentially affected, especially in the shallow regions of the Bothnian Bay.

Key words: sea ice, snow-ice, superimposed ice, meteoric ice, chemistry, nutrients, trace elements, Baltic Sea
1 Introduction

Sea ice is a typical feature in the polar oceans and covers about 7% of the world ocean (e.g. Leppäranta, 1998; Wadhams, 2000). Sea ice also forms at lower latitudes, in such seas as in the Baltic, the Caspian and the Okhotsk Sea. However, there are significant differences in the regions with perennial, seasonal and/or coastal (landfast) ice. The seasonal sea ice cover is a prominent feature of the Baltic Sea, with a long-term average annual maximum coverage of about 45% of the surface area (Seinä and Palosuo, 1996), and sea ice has both socio-economic and environmental impacts. However, because the Baltic Sea stretches for a considerable distance in the north-south direction, ice conditions within the sea vary considerably. In the northernmost basin, the Bothnian Bay, ice occurs every winter and the ice covered period may be longer than the ice-free season (Leppäranta et al., 1988). In the southern parts, ice is formed depending on the severity of the winter and usually persists only for some weeks, or even less.

Even though sea ice on a global scale is a thin, fragile, dynamic and solid layer, it serves as a boundary between two much larger fluids - the ocean and the atmosphere. Having important consequences for the climate system on Earth, because this solid film regulates the loss of solar energy, gained at the equatorial latitudes, which has been transported by the ocean towards polar oceans which are ice covered. Hence sea ice exerts an important influence on the exchanges of heat, energy and materia between the larger fluids. Thus, sea ice has an important role in modifying ocean circulation, weather, and therefore the climate of ice-covered oceans and nearby areas. It limits the exchange of gases and particulates between the ocean and atmosphere, and potentially collects accumulation from the atmosphere during its lifespan (Pfirman et al., 1995; Rahm et al., 1995). Due to its dynamic characteristics, sea ice can transport freshwater and heat for long distances, and also carries along material collected during ageing from the atmosphere, the seawater, and the seafloor (Pfirman et al., 1995). Sea ice also hosts a variety of life-forms; on the surface, in snow slush layers, within brine pockets and channels within the sea ice sheet, on the underside of, and in ice platelet layers beneath sea ice (e.g. Brierley and Thomas, 2002). Sea ice comprises therefore a complex system where physical, chemical and biological processes interact. These processes interplay on a vast range of spatial and temporal scales to produce what we finally sample and observe, usually on small scale, but usually take for granted that is representative of sea ice on larger scale.

2 Background, motivation, and goals of this work

This study concerns the physical and biogeochemical properties of sea ice in the Baltic Sea, and their relationships. Detailed studies on the structural, physical and biogeochemical properties of sea ice in the Baltic Sea were carried out in the fashion discussed by Lange (1988). That is, with concurrent detailed structural, stable oxygen isotopic and biogeochemical analyses of the samples. Although similar observations have been conducted earlier, however, without concurrent investigations into the structural properties of the sea ice (e.g. Norrman and Andersson, 1994; Rahm et al., 1995; Kaartokallio, 2001).
For the first time, results from measurements of major ions and trace elements in Baltic Sea ice are reported, to give an insight into the potential importance of sea ice in geochemical cycles and budgets in the Baltic Sea (Gulfs of Bothnia and Finland). The results presented here are based on sea ice, snow, and water samples collected in the ice covered parts of the northern Baltic Sea. Samples have been prepared and analyzed in cold rooms and (clean) room laboratories. Experiments during natural conditions were also carried out to investigate processes affecting sea ice biogeochemical properties during initial sea ice growth in brackish waters.

The primary objective of this study was to relate the observed biogeochemical properties of sea ice with the physical and structural properties, and thereof to growth conditions, if any relationships exist. Some attempts have been made to relate ice structure with nutrients and major ions in the Arctic Ocean (Meese, 1989). The use of detailed observations of ice structure and stable oxygen isotopic properties can be used to determine the origin of the ice, and then to elucidate the influence of different growth processes on sea ice (bio)geochemical properties (papers I, III, V).

The second objective was to study the behavior of trace substances during ice formation. The fractionation of major ions and nutrients during sea ice formation in the Arctic Ocean has been studied by Meese (1989). Similar studies have not, to the knowledge of the author, been performed in brackish waters such as the Baltic Sea and very seldom for natural sea ice anywhere else for that matter (paper V).

The third objective was to study the potential effect of sea ice as a transportation agent for chemical substances (e.g. nutrients and trace elements). Recently the effect of the sea ice cover as an important medium for trace elements has been postulated (Measures, 1999; Sedwick and DiTullio, 1997), but no direct evidence, in the form of observations of sea ice, has been published. The aim was to use the chemical properties of sea ice to judge how it influences geochemical budgets and cycling of nutrients, major ions and trace elements in the Baltic Sea (papers I, III, V).

Perhaps as an offshoot to the main objectives listed in the above paragraphs, the development and composition of Baltic Sea ice became an important part of this work. Even though detailed studies of ice structure have been performed prior to this work (e.g. Fransson et al., 1990; Kosloff, 1993; Omstedt, 1985; Palosuo, 1963), the use of stable oxygen isotopes aided in improving the knowledge about growth processes, and especially the role of snow-ice and superimposed ice formation in the Baltic Sea. In this sense, these results make a fundamental contribution to this thesis (papers II and IV). This may sound trivial, as the snow fraction of the sea ice in the Baltic Sea is often presumed to be high, yet the only prior study which looked at this in some detail is the one by Palosuo (1963). Some modelling studies have also shown the importance of the snow cover as well (Leppäranta, 1983; Saloranta, 2000; Cheng, 2002).

During the time span of this work, both the methods used and the knowledge about the problems associated with the work improved step-wise. Finally, by the last stages of this work, the methods were developed to the level they should have been throughout the whole project. However, despite the obvious methodological artifacts in the beginning of the work, this work gives a basic overview of the relation-
ships of structural and biogeochemical properties of sea ice in the Baltic Sea, and hopefully initiates further and more in depth studies on the subjects covered in this thesis.

In addition to papers I–V some other publications relates to this thesis. Granskog (1999) investigated the composition of sediment inclusions in Baltic Sea ice. In Kawamura et al. (2001a), the first results of concurrent structural and stable oxygen isotopic observations of Baltic Sea ice were reported, data which is re-analysed in paper IV. In Meiners et al. (2002), the study focussed on the physical, chemical and biological characteristics of the ice cover in different parts of the Baltic Sea. Finally, in a forthcoming paper by Granskog and Kaartokallio (2004) an attempt is made to assess the importance of the seasonal sea ice cover to the cycling and budgets of nutrients and heavy metals in the northern Baltic Sea.

3 Sea ice characteristics in the Baltic Sea

Studies related to sea ice have been performed for several decades in the Baltic Sea, first motivated by the development of winter navigation (see Leppäranta et al., 2001). Finland and Estonia are the only nations in the world where all harbours freeze every winter, which partly explains the keen interest in sea ice studies. Therefore, in the 1950s geophysical studies of sea ice properties and climatology were commenced (e.g. Palosuo, 1961, 1963), and during the following decades studies have mainly focused on large scale problems, such as sea ice climatology and dynamics (e.g. Leppärenta, 1981; Haapala and Leppärenta, 1996, 1997). However, during the last two decades environmental questions have become increasingly important, and ecological sea ice studies have been introduced into the field of sea ice research in the Baltic Sea (e.g. Huttunen and Niemi, 1986; Ikävälinko, 1997). Studies on the role of sea ice in cycling of chemical species, especially those accumulated from the atmosphere, have also received some attention (e.g. Rahm et al., 1995). In this section, a brief introduction to the present knowledge about Baltic Sea ice is given with an emphasis on those aspects that are regarded relevant for this thesis.

3.1 Classification of sea ice

Sea ice, according to the WMO (World Meteorological Organization) sea-ice nomenclature (WMO, 1970), consists of all forms of ice found at sea which have originated from the freezing of seawater. The solid form of water (H₂O) is ice, which is less dense than its melt due to hydrogen bonding between water molecules. By ice, we refer here to ordinary ice (ice I) encountered at the conditions on the surface of the earth (Weeks and Ackley, 1982). Ice floats in its melt (water), a property that among the elements appears to be shared only with bismuth at the conditions prevailing at the surface of the Earth (Weeks, 1998). This exceptional property of ice has been crucial for life on earth; if ice would sink, life on earth would look quite different for obvious reasons.

Sea ice can be broadly described as new ice, young ice, first-year ice, and multi-year ice. These categories broadly reflect the age of the ice and include different forms and thicknesses of ice at various stages of
development. In the Baltic Sea, the ice can usually be categorized into new ice, young ice or first-year ice (see SMHI, 1981).

At smaller scales, sea ice can be classified according to its structural properties. The most comprehensive classification according to textural properties has been presented by Eicken and Lange (1989). They distinguished five distinct texture classes in their study in the Weddell Sea (Table 2). Eicken and Lange (1989) also linked oceanographic and meteorological aspects of ice growth and recognized three genetic ice classes, namely frazil, tranquil congelation, and disturbed congelation (see Eicken and Lange, 1989; Table 2).

Table 2: Textural classification of sea ice samples from the Weddell Sea according to Eicken and Lange (1989).

<table>
<thead>
<tr>
<th>Textural Class</th>
<th>Grain size (cm)</th>
<th>Grain shape</th>
<th>Brine inclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granular</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polygonal granular</td>
<td>&lt;1</td>
<td>isometric, planar boundaries</td>
<td>spherical droplets at grain junctions</td>
</tr>
<tr>
<td>Orbicular granular</td>
<td>&lt;1</td>
<td>isometric, convex, rounded grain boundaries</td>
<td>irregular pockets, droplets between grains</td>
</tr>
<tr>
<td>Columnar</td>
<td>1–10</td>
<td>elongated</td>
<td>parallel layers within grains</td>
</tr>
<tr>
<td>Intermediate columnar/granular</td>
<td>1–10</td>
<td>slightly elongated; grains</td>
<td>oblong; string of isolated pockets</td>
</tr>
<tr>
<td>Mixed columnar/granular</td>
<td>&lt;1–10</td>
<td>domains of granular and columnar</td>
<td>pockets and layers within and between</td>
</tr>
<tr>
<td>Platelet</td>
<td>&lt;1–10</td>
<td>inclusion free, platy crystals in</td>
<td>grains</td>
</tr>
<tr>
<td></td>
<td></td>
<td>matrix of granular, mixed, or</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>intermediate c/g</td>
<td></td>
</tr>
</tbody>
</table>

While the texture classes describe the structural properties of the ice matrix, the genetic classification describes the meteorological and oceanographic conditions that cause the growth of the ice (Eicken and Lange, 1989). However, these can not be unambiguously determined. In addition to the three genetic classes (frazil, tranquil and disturbed congelation) recognized by Eicken and Lange (1989), one could add sea ice with a meteoric ice contribution (snow-ice and superimposed ice) as the fourth genetic ice class, since its formation mechanisms differ considerably from those of the other three classes.

Frazil ice is formed after a surface accumulation of ice crystals that have been formed in the upper part of the water column (dynamic conditions). Congelation ice (tranquil and disturbed) is formed by the freezing of seawater at the ice-water interface (static conditions). Snow-ice and superimposed ice are
formed by freezing of seawater and/or snow (i.e. precipitation) at the ice-snow interface, i.e. on top of an existing sea ice sheet (Haas et al., 2001).

3.2 General sea ice conditions in the Baltic Sea

The Baltic Sea belongs to the seasonal sea ice zone, and freezes over to some extent every winter. The low salinity water and the shallowness assist in the freezing process. The time series of the maximum annual ice extent in the Baltic Sea (MIB), reconstructed from historical records from the early 18th century to early 20th century and based on observations since the turn of the last century, is one of the world’s longest time-series describing ice conditions (see e.g. Seinä and Palosuo, 1996).

In the Baltic Sea ice climatology research, the MIB has received much attention. The dominating feature of the MIB is a very large interannual variability that ranges from 10 to 100% of the total Baltic Sea area (Haapala and Leppäranta, 1997). Several studies have investigated the relationship between large-scale atmospheric conditions and ice conditions in the Baltic Sea (e.g. Tinz, 1995; Jevrejeva, 2001; Jevrejeva and Moore, 2001). Considerable evidence suggests that large-scale atmospheric circulation patterns are significantly correlated with the ice conditions in the Baltic Sea (Jevrejeva, 2001). During average and mild winters, warm air masses associated with westerly moving cyclones from the Atlantic dominate the Baltic climate, while in severe winters blocking anticyclonic patterns dominate (Jevrejeva and Moore, 2001).

Ice formation starts in mid-November in the northernmost coastal areas and extends southward, first along skerries and outward from the coasts as the winter progresses. Ice forms first in shallow inner skerries where the water is fresher and shallower, thus has a lower heat content, and where the ice cover can be anchored to islands and shoals. This prevents the break up of even a thin ice cover by winds or waves (Palosuo, 1963). The landfast ice cover usually extends to the outer skerries, where the water depth is typically between 5 to 15 meters. Further off-shore the ice cover is highly dynamic (Leppäranta, 1981). During an average winter the ice covers the entire Bothnian Bay by mid-January, and at the time of the maximum ice extent, at the turn of February and March, the ice covers the Gulfs of Bothnia, Finland, and Riga. Some coastal regions further south also freeze over. At this time, the ice covers about 190 000 km$^2$. As an example, Figure 1 shows the maximum ice extent during winters 1999 to 2002, when the field studies presented in this thesis were performed. Winter 1999 was classified as normal and the maximum ice extent of 157 000 km$^2$ was reached in early February. Winters 2000, 2001, and 2002 were all mild ice winters, the ice extent was at maximum 95 000 km$^2$, 128 000 km$^2$, and 102 000 km$^2$, respectively.

In summary, the large-scale ice conditions in the Baltic Sea are well known, and they show that there is a large natural variability in the freezing date, thickness, extent, and break-up date (Haapala and Leppäranta, 1997). Perhaps surprisingly, little is known about the small-scale properties of the ice, the processes during initial ice formation, and the temporal development of the ice properties in the Baltic
Sea. One reason for the gaps in knowledge is perhaps the need for large logistical efforts that are required in order to study processes in harsh field conditions, which are both time consuming and expensive.

3.3 Physical characteristics of Baltic Sea ice

3.3.1 Textural properties

Detailed observations of initial ice formation in brackish waters are sparse. The formation of sea ice in oceanic waters, with a salinity of around 34 PSU, has been thoroughly reviewed in e.g. Weeks and
Ackley (1982), Weeks and Ackley (1986), Weeks (1998) and Wadhams (2000) and will not be given in detail here. Sea ice formation in any brackish water (salinity less than 24.7 PSU), such as the Baltic Sea, resembles more the ice formation in freshwater lakes than that which takes place in the oceans during the cooling phase of the water column and during initial freeze-up. Because the temperature of maximum density of seawater is reached prior to its temperature of freezing (see e.g. Weeks and Ackley, 1982). Even though the northern Baltic Sea has low surface water salinity, the ice formed resembles that of sea ice (with preferred horizontal c-axis, jagged grain boundaries, and a substructure within the grains associated with brine layers) (Palosuo, 1961; Kawamura et al., 2001a). At parent water salinities higher than about 0.6 PSU, the ice formed has these sea ice characteristics, and only in proximity of river estuaries the ice is basically freshwater ice (Palosuo, 1961). In essence, the study of sea ice is that of the solidification of solutions of water with some salts added.

Earlier studies have given us basic knowledge about the textural characteristics of Baltic Sea ice (Omstedt, 1985; Fransson et al., 1990; Weeks et al., 1990; Kosloff, 1993; Kawamura et al., 2001a). These studies show large variability in ice structure and the contribution from different ice types to the total ice thickness. Studies in the Gulf of Bothnia pack ice imply that dynamic thickness growth, i.e. ridging and rafting, play an important role (Omstedt, 1985). For level ice that was possibly rafted, Weeks et al. (1990) reported that up to 80% of the ice cover was composed of granular ice. Fransson et al. (1990) also reported very variable structural properties of pack ice. However, there are very few, if any, detailed observations on the initial formation and temporal evolution of the ice in pack ice areas of the Baltic Sea. The above observations in pack ice indicate that dynamic growth conditions may prevail, and the thickness growth and development of sea ice in the open areas of the Baltic Sea may resemble that of the Antarctic waters, where the pancake cycle has been suggested to be important (Lange et al., 1989). Virtually nothing is known about the role of snow (snow-ice and superimposed ice) in the growth of pack ice in the Baltic Sea.

As expected, the landfast ice that usually extends to the 5–15 m isobath (Leppäranta, 1981) grows more statically than the ice in the open areas. Dynamic thickness growth is less important, except in areas where pack ice is grown into the expanding landfast ice cover when the season progresses. Thermodynamic growth is therefore the only contributor to ice thickness growth. Structurally, the level landfast ice cover can roughly be divided into a two layer medium, with a granular upper layer and a columnar ice bottom layer (Kawamura et al., 2001a). The upper layer is partly composed of snow-ice or superimposed ice (e.g. Kawamura et al., 2001a) and the remaining is frazil-ice, ice formed during turbulent conditions in supercooled water. Often, however, a third ice type is present, namely transition ice (or intermediate granular columnar) (e.g. Weeks et al., 1990). Transition ice shows very irregular horizontal banding, with crystals exhibiting a slight elongation in the vertical (growth) direction (Weeks et al., 1990). In the Antarctic, transition ice has been associated with nearby leads, ice deformation and a rough hydrodynamic regime (Eicken and Lange, 1989). According to Weeks et al. (1990) a similar explanation may also apply for the Baltic Sea. Omstedt (1985) and Fransson et al. (1990) have also found considerable
amounts of transition ice layers in the pack ice of the Bothnian Bay.

The contribution of snow-ice and/or superimposed ice to the thickness growth of landfast sea ice in the Baltic Sea is at best substantial, and is larger than in the high Arctic (Kawamura et al., 2001b). Palosuo (1963), for example, studied the contribution of white ice using a special gauge-stick, on which zero-level mark was installed on the upper surface of the ice in the very beginning of the ice season. He found that almost half of the ice cover could be composed of white ice, or more exactly from upward growth of the ice sheet (Figure 2). There was, however, a large interannual variability in the amount of white ice. Indeed, his results showed the importance of snow (or precipitation), but the observations do not allow for differentiation between snow-ice and superimposed ice growth. Recently, stable oxygen isotopes have been used to study the amount of snow (precipitation) included in sea ice (e.g. Lange et al., 1990; Jeffries et al., 1994). Several studies have shown that snow contributes significantly to the thickness growth of sea ice in Antarctic waters (Lange et al., 1990; Eicken et al., 1994; Jeffries et al., 1994, 1997, 1998; Kawamura et al., 1997). The reported maximum snow fraction in Antarctic sea ice is 14-16% of the total sea ice mass (Jeffries et al., 1997). In the seasonally ice covered Sea of Okhotsk, the snow fraction was estimated to be about 8% (Ukita et al., 2000). In the high Arctic the contribution of snow-ice seems negligible (Kawamura et al., 2001b). In the study of the mass-balance of landfast sea ice at one site in the Gulf of Finland, Kawamura et al. (2001a) observed that the snow (meteoric ice) fraction in the sea ice varied between 2 to 26% within the ice season. A significant part of the meteoric ice was thought to be superimposed ice. Cheng (2002) also noted (through observations and modelling) that surface and subsurface snow melt contributed to ice growth at the ice surface in the Gulf of Bothnia. Despite the limited data from the Baltic Sea, they indicate a significant contribution from snow to the development of sea ice as compared to other ice covered seas, especially in years when the snow accumulation is high (Palosuo, 1963; Kawamura et al., 2001a). The relatively thin ice sheet in the Baltic Sea readily supports snow-ice formation. A relatively small amount of snow deposited onto the ice cover can result in flooding of the ice cover with seawater which potentially results in snow-ice formation. The mild conditions again seem to be favourable for the formation of superimposed ice layers (Kawamura et al., 2001a; Cheng, 2002).

3.3.2 Salinity

Bulk salinity is a fundamental and routinely measured sea ice property. The brine trapped into the sea ice lattice is important for several reasons. The volume of the brine, which depends on the bulk salinity and temperature, governs the permeability of the ice cover, and is important for the geophysics, biology and remote sensing of sea ice covers (e.g. Golden et al., 1998). The thermal conductivity, mechanical, electrical, optical, and acoustical properties are in many cases a function of the sea ice porosity, i.e. brine volume. This in turn is associated with the amount and distribution of brine in the sea ice (e.g. Cottier et al., 1999). Several processes have been considered to govern the salinity of sea ice at a given time, including; initial brine entrainment and desalination processes such as brine pocket migration, brine expulsion, gravity drainage and flushing. Desalination processes can be classified into two types, those
Figure 2: Measured upward growth and sea ice salinity in Saggö (north of Åland island) in winter 1957/58 according to Palosuo (1963). The part of the ice above the zero-level is white-ice, as measured by a gauge stick, and the ice below is black-ice. The topmost graph shows the air temperature in Maarianhamina (Åland). At the bottom bulk ice salinity ($\sum S_i$) and seawater salinity ($S_w$) is shown. (Reproduced with the permission of FIMR)

in cold ice during the growth period and those in warm ice (see Eicken, 2003). Detailed accounts on desalination processes for sea ice formed at oceanic salinities have been summarised in e.g. Weeks and Ackley (1982, 1986), Weeks (1998) and Eicken (2003).

Whenever seawater freezes, most impurities are rejected from the ice lattice, resulting in plates of pure ice. The plates originate as dendrites with tips protruding into the seawater. It is between these tips that brine is trapped. The plate width can vary from a few tenths of a millimeter to 1 millimeter and is dependent on the growth rate. With increased warming, disconnected brine inclusions coalesce into vertical channels that can lead to redistribution, drainage and desalination of the ice (e.g. Meese, 1989; Weeks, 1998; Eicken, 2003).

Initial brine (salt) entrapment at the salinities of ocean waters has been studied in detail by Cox and Weeks (1975, 1988) and Nakawo and Sinha (1981). Experiments and observations have shown that
initial brine entrapment is related to the growth rate $\nu$ and is directly proportional to the seawater salinity $S_w$. According to Weeks and Ackley (1986), the salinity of a new ice layer $S_i$ can be described as a function of the effective segregation coefficient $k_{eff}$ (sometimes also called partition coefficient or solute distribution coefficient) and the seawater salinity far away from the ice-water interface as follows (Eicken, 2003):

$$S_i = k_{eff} S_w$$  \hspace{1cm} (1)

For static ice growth the segregation coefficient depends on the growth rate, and is accordingly to the experiments of Cox and Weeks (1988) and field observations of Nakawo and Sinha (1981) as follows:

$$k_{eff} = \frac{0.26}{0.26 + 0.74 \exp(-7243\nu)}, \quad \nu > 3.6 \times 10^{-5} \text{ cm s}^{-1}$$ \hspace{1cm} (2)

$$k_{eff} = 0.8925 + 0.0568 \ln \nu, \quad 3.6 \times 10^{-5} \geq \nu \leq 2.0 \times 10^{-6} \text{ cm s}^{-1}$$ \hspace{1cm} (3)

$$k_{eff} = 0.12, \quad \nu < 2.0 \times 10^{-6} \text{ cm s}^{-1}$$ \hspace{1cm} (4)

Figure 3 shows the initial salinity of ice layers based on the above growth rate and segregation relations, at seawater salinities representative for Baltic Sea conditions.

Figure 3: Initial ice salinity $S_i$ at different seawater salinities ($S_w$ (PSU)) representative for Baltic Sea conditions as a function of growth rate $\nu$ according to equations 1–4.

What should be noted is that the above relationships (equations 1–4) have been derived for seawater with salinities around 34. The segregation coefficient is also concentration dependent, especially for very low impurity solutions (see e.g. Gross et al., 1977), which should be considered at the Baltic Sea conditions.
However, detailed studies on the relation of growth rate and segregation have not been conducted at salinities representative for the Baltic Sea, and without this information we have to assume that the relationships derived for seawater at higher salinities are valid for Baltic Sea ice as well (Figure 3).

Deviations of observed salinity profiles from that forecasted by the growth rate and segregation model (equations 1–4) are due to desalination processes during consolidation and ageing. In general the desalination processes (or the most efficient ones) are dependent on the porosity of the ice, and the porosity of the Baltic Sea ice expectedly differ from that of more saline ice (see below). However, quantitative information on desalination processes in Baltic Sea ice is virtually non-existent. The reader is directed to the summary of e.g. Weeks and Ackley (1986) for descriptions of and quantitative estimates for desalination processes (in more saline ice).

Due to its fundamental importance (often as an explanatory variable), the salinity of Baltic Sea ice has also been measured numerous, during geophysical as well as ecological sea ice investigations. However, this information is very sporadic both in time and space. Baltic Sea ice reflects the low water salinities. The bulk salinities in the northern Baltic Sea are generally less than 2 PSU (Figure 3), and even lower depending on the ambient water salinity, growth conditions and thermal history of the ice (e.g. Fransson et al., 1990; Palosuo, 1963; Kawamura et al., 2001a). The most systematic study on ice salinity and its development in the Baltic Sea is that by Palosuo (1963), even though the vertical resolution was rather coarse. The ice salinity was monitored on a weekly basis at seven sites along the Finnish coast, with ambient salinities ranging from almost freshwater to 5-6 PSU. Figure 2 shows an example of the evolution of ice salinity and white-ice (upward growth) and black-ice (of seawater origin) at one of the sites reported in Palosuo (1963).

Salinity profiles of Baltic Sea ice have also been reported by e.g. Fransson et al. (1990), Weeks et al. (1990) and Kawamura et al. (2001a). Often the salinity profiles have a C-shaped appearance with highest salinities in the uppermost parts of the ice cover, presumably because of rapid growth, flooding and snow-ice formation. Figure 4a shows an example of the average sea ice salinity in the southern Bothnian Bay during the BEPERS-88 experiment, when a large number of ice cores were collected from an area of 1 x 2 km. The water salinity was about 4 PSU (Fransson et al., 1990).

The low ice salinity is also reflected by relatively low brine volumes, despite quite high ice temperatures (Figures 4b and 5), which may have affect the habitability of sea ice by organisms in the Baltic Sea (Krembs et al., 2001, and references therein). The permeability of the ice is affected, and according to the law of fives (Golden et al., 1998) at a temperature of -5°C and salinity of 5 PSU sea ice has a brine volume of 5%, which makes it permeable because brine pockets and inclusions are then assumed to be interconnected. However, in the Baltic Sea the law of fives does not obviously hold true, since the sea ice salinity very seldom reaches 5 PSU, except in the southerrnmost parts (Mock et al., 1997). Using the formulations of Leppäranta and Manninen (1988), one can obtain that for ice with a bulk salinity of 1 PSU temperatures as high as -1 °C are needed for brine volumes large enough for Baltic Sea ice to become permeable (Figure 5). That is, if the relation between ice permeability and porosity holds
Figure 4: Mean a) sea ice salinity (±s.d.) and b) brine volume (±s.d.) profiles in the southern Bothnian Bay (water salinity 4 PSU) according to observations during the BEPERS-88 experiment (redrawn from Fransson et al. (1990)).

true for the low saline Baltic Sea ice as it does for more saline sea ice. Low brine volumes obviously affect transfer across the ice-water interface, which is important for e.g. nutrient replenishment for ice associated algae and for convective heat transport through the sea ice (Lytle and Ackley, 1996), as well as for desalination processes of Baltic Sea ice.

3.4 Biogeochemistry of Baltic Sea ice

Chemical processes that occur during sea ice formation and ageing are less well understood than the physical processes. The initial entrapment of other dissolved inorganic constituents present in seawater should follow that of salts. For example, the initial incorporation of dissolved inorganic nutrients should obviously follow that of the major salts. Changes that occur in major ion ratios, for example in sulfate to chloride ratios, during sea ice formation are probably important in understanding the geochemistry and chemical budgets in polar regions (Anderson and Jones, 1985). The structural and physical processes are, to a large extent, expected to govern the chemical (and biological) properties of sea ice (Lange, 1988). However, what complicates the matter further is the complex interplay between physical, chemical and biological processes within the sea ice matrix (Thomas and Dieckmann, 2002). The physicochemical environment of sea ice is highly variable, both in space and time, which is largely governed by the pre-
Figure 5: Brine volume (%) of sea ice at different salinities (S (PSU)) representative for Baltic Sea conditions as a function of temperature. Brine volumes were computed according to Leppäranta and Manninen (1988). The 5% brine volume value is indicated by the solid horizontal line.

Vailing air temperature. Superimposed on the abiotic factors is the influence of the organisms thriving in the ice itself, both on the chemistry and even the physical nature of the sea ice (Thomas and Dieckmann, 2002).

Tsurikov and Tsurikova (1977) were among the first to note the possible implications of sea ice chemistry, and they suggested that further studies on trace elements and radioactive isotopes are needed to understand the role of sea ice as a carrier of various pollutants in the oceans. Surprisingly, the situation has not changed much since the late 1970s, perhaps with the exception of numerous studies on radionuclides in Arctic sea ice (e.g. Meese et al., 1997; Pavlov and Stanovoy, 2001). There are still rather sparse observations on the influence of sea ice on surface water chemistry in the oceans, even though the potential of sea ice on ocean chemistry, and especially pollutant transport, has been acknowledged recently (e.g. Pfriman et al., 1995; Lange and Pfriman, 1998). Studies indicate that sea ice plays a role in the level of iron in surface waters both in the Arctic (Melnikov, 1991; Measures, 1999) and the Antarctic (Sedwick and DiTullio, 1997), and thus can potentially affect ocean productivity. Frache et al. (1997) discussed the effect of melting pack ice on the surface water concentrations of Cd, Cu, Fe and Ni in the Ross Sea, Antarctica. In the Arctic Ocean, results show that sea ice influences the concentrations of organochlorine pollutants in ice-associated organisms (Borgå et al., 2002). Sea ice also potentially affects the levels of pesticides in seawater, pesticide concentrations being higher close to the ice edge (Chernyak et al., 1995). However, what is important to note is that all this evidence is based on indirect observations, i.e. observations of seawater, and no direct evidence of sea ice properties exist to support
their assumptions on the influence of (melting) sea ice. 

Meese (1989) made the most detailed prior study on the major ion and inorganic nutrient chemistry of natural sea ice, and she also took in consideration the structural properties of the ice when she interpreted her observations. Selective fractionation (segregation) of ions during freezing, which is diffusion controlled, results in changed ion ratios during initial ice formation (Malo and Baker, 1968). However, with consolidation and ageing temperature gradients provide a means of selectively immobilizing specific cryohydrates, such as CaCO$_3$·6H$_2$O and Na$_2$SO$_4$·10H$_2$O, which leads to fractionation and variation in major ion ratios (Weeks and Ackley, 1982). Which has been evident for example in that sulfate to chloride ratios are different in sea ice than in the parent seawater (e.g. Reeburgh and Springer-Young, 1983), and other ions which form cryohydrates at (relatively) high temperatures are immobilized in sea ice (e.g. Meese, 1989). However, in general, the ratio of major ions in sea ice remains fairly close to that in seawater (e.g. Addison, 1977; Meese, 1989), indicating that sea ice formation does not have a major effect on the ion ratios either in the ice or in the brine rejected from the ice. Although changes in ion ratios would occur, these would be reversed during ice melt. Thus, sea ice has no significant effect on Arctic Ocean (major ion) chemistry over long periods of time (Meese, 1989; Reeburgh and Springer-Young, 1983). The major ion chemistry of Baltic Sea ice has not received any attention, at least not to the knowledge of the author. Therefore, there are no estimates on the potential of ice formation/melt in the budgets of major elements in the area.

Since the 1980s, some researchers have investigated the ecology of sea ice in the Baltic Sea (e.g. Huttunen and Niemi, 1986). In seasonally ice covered seas, the sea ice cover plays a major role in ecosystem functioning (Thomas and Dieckmann, 2002). However, the sea ice ecosystem in the Baltic Sea has not yet been satisfactorily described (Kaartokallio, 2001), and hence the same accounts the biogeochemistry. Up to date studies of the biogeochemistry of sea ice in the Baltic Sea have been mainly restrained to landfast sea ice in the Quark area in the Gulf of Bothnia (Norman and Andersson, 1994; Haecky et al., 1998; Kaartokallio, 2001) and the Kiel Bight (Mock et al., 1997). Some studies have been made in the pack ice of the Gulf of Bothnia as well (e.g. Meiners et al., 2002; Ikävalko, 1997). Biogeochemical properties of sea ice, e.g. inorganic nutrients and chlorophyll-$a$, have been reported along with sea ice community structure in the above mentioned studies. However, the influence of physical properties (other than salinity) and thereby growth processes on the observed biogeochemical status of the sea ice has not got the attention, except by Meiners et al. (2002), that it clearly deserves. The general lack in sea ice chemical studies is even more pronounced in the ice formed in the Baltic Sea than it is in Antarctic sea ice (e.g. Clarke and Ackley, 1984; Garrison et al., 1990; Dieckmann et al., 1991). There seems to be a need for more detailed studies in both spatial and temporal variability, and the interactions between physicochemical and biological processes in the Baltic Sea ice environment. Several aspects of sea ice biogeochemistry, which can be regarded as important in many regards, such as the major ion, dissolved gas (e.g. DMS and halogens) and dissolved organic matter (DOM), have not received any attention in Baltic Sea ice studies. Although the conditions in many regards might differ considerably from those in
other sea ice regions. Recently Meiners et al. (2002) argued that a combination of abiotic factors, most of all the low porosity and therefore poor nutrient availability, would control the accumulation of biomass within Baltic Sea ice. Therefore, one could assume that the biogeochemistry of Baltic Sea ice would, to a large extent, be controlled by abiotic factors. One aspect that could be mentioned in this context is the influence of the large amount of snow accumulated on the sea ice, resulting in a high snow-ice portion (e.g. Palosuo, 1963; Kawamura et al., 2001a). It has an impact on the nutrient dynamics of the Baltic Sea ice (e.g. Rahm et al., 1995; Meiners et al., 2002), to a degree that is much more important if compared to the polar regions. Another aspect is the above mentioned low brine volume of Baltic Sea ice (e.g. Fransson et al., 1990; Meiners et al., 2002), perhaps with the exception of the southernmost Baltic Sea (Mock et al., 1997).

The influence of a sea ice cover in the Baltic Sea can also be seen in that the pelagic phytoplankton community differ in composition during ice-free and ice-covered winters (Hajdu et al., 1996). Some species are probably introduced into the water column from the sea ice, whereas others are adapted to low light conditions in the under-ice waters (Haecky et al., 1998).

Some interest has also been given to the role of sea ice as a trap of atmospheric deposition and in the cycling of nutrients and POPs (persistent organic pollutants) on a basin wide scale. Rahm et al. (1995) estimated that atmospheric deposition of nutrients onto the sea ice in the Bothnian Bay accounted for a significant portion of the annual load into the basin; 9–25% for nitrogen and 3–8% for phosphorus. The source of this atmospheric deposition to the Baltic Sea is atmospheric transport, for example Germany, Denmark, Poland, Sweden and United Kingdom contribute about half of the total atmospheric load of nitrogen (HELCOM, 1997). The ice cover can be regarded as a temporary buffer which accumulates substances from the atmosphere during the winter season, and the accumulated substances are released during a relatively short time during ice melt (Granskog, 1999). In seasonally ice covered lakes the ice cover is likely to have a significant impact on the seasonal variation in pollutant input (Piliposian and Appleby, 2003), and the same could be argued for the ice cover in the Baltic Sea although direct evidence does not exist. Melnikov (1991) argues that the ice melt period coincides with a period of a burst in biological activity, and harmful substances released from the ice cover can have an effect. In this manner, nutritive substances released from sea ice could also potentially affect the biological productivity in the under-ice water column, as well as within the ice. However, there are no studies that show the fate of substances released from the ice cover. Indirect evidence for increased levels of some substances due to sea ice melt has been presented in the Arctic (e.g. Melnikov, 1991; Measures, 1999) but remain undiscovered in the Baltic Sea. Bioaccumulation of organochlorine pollutants in ice-associated organisms has been observed in the Arctic (Borgå et al., 2002).

In summary, the biogeochemistry of Baltic Sea ice remain a clearly inadequately studied subject. Relatively sparse and sporadic observations exist, compared to the number of studies on seawater in the Baltic or sea ice in the Antarctic waters. Even though sea ice comprises a rather small part of the total volume of the oceans, it is an important feature in the polar and sub-polar seasonally ice covered oceans.
and seas. Sea ice is a key factor in global and local climate and ecosystem functioning in ice covered seas. As an transportation agent of solid materials, it provides a way for pollutants to be transported (e.g. Pfriman et al., 1995), which otherwise would not be transported as far away from their source, and are then potentially introduced to the food web during melt (e.g. Borgå et al., 2002). Sea ice also provides a platform for accumulation and redistribution of atmospheric pollutants (Pfriman et al., 1995). However, observations on the above mentioned processes are very sparse in the Baltic Sea and the importance of sea ice in biogeochemical cycles remains to be explored.

4 Field data, experiments and methods

In this section the gathered data and applied methods are briefly described. For more details, the reader is referred to the papers.

4.1 Field data and experiments

For this work, sea ice samples were collected during the winter seasons 1999 to 2002 in various parts of the Gulfs of Bothnia and Finland. The samples gathered for the work presented in the papers are summarized in Table 3. Ice cores were collected using an ice corer. In addition, snow and under-ice water samples were collected whenever required. Sampling along the northern Baltic Sea coast was carried out to get an overview of the conditions in the whole study area. Studies on the temporal evolution of the ice cover were set to the Gulf of Finland, to an easily accessible site nearby the facilities provided by the Tvärminne Zoological Station (papers I-IV). For paper V, the work was made in the vicinity of the Bothnian Bay Research Station (experiment) and on-board Swedish icebreakers in the western Bothnian Bay pack ice.

4.2 Methods

For all analyses, the ice samples were divided into sections according to the ice structure, with the exception of paper I and partly paper III. The purpose was to be able to distinguish between the properties of ice of different origin, e.g. columnar ice from granular ice.

Depending on the study, a variety of analyses were performed on the collected ice, snow and water samples. Most notably these included ice structure, salinity and stable oxygen isotopic composition ($\delta^{18}$O) in all studies, with the exception of no $\delta^{18}$O analysis in paper I. In addition, the measurements included particle content, chlorophyll-α, nutrient, major ion and trace element determinations depending on the investigation. Table 4 summarises the measurements carried out in each study.

Ice structure was recorded when thin sections prepared from the ice cores were illuminated between crossed polarizers that revealed the crystal structure of the samples. This information was used to di-
Table 3: Summary of samples collected for the papers.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Time</th>
<th>Study area</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Jan–Apr 1999</td>
<td>Finnish coasts of Gulf of Finland and Gulf of Bothnia and Swedish coast of Bothnian Bay</td>
<td>23 sites on landfast sea</td>
</tr>
<tr>
<td>II</td>
<td>Mar–Apr 2000</td>
<td>Finnish coast</td>
<td>15 sites on landfast sea ice</td>
</tr>
<tr>
<td>III</td>
<td>Jan–Apr 2000</td>
<td>Gulf of Finland (time-series)</td>
<td>Weekly sampling through ice season</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mar–Apr 2000</td>
<td>15 sites on landfast sea ice</td>
</tr>
<tr>
<td>IV</td>
<td>Jan–Mar 1999–2001 (time-series)</td>
<td>Gulf of Finland (one site)</td>
<td>Weekly sampling through three ice seasons</td>
</tr>
<tr>
<td>V</td>
<td>Feb 2002</td>
<td>Bothnian Bay (one site)</td>
<td>Experiment conducted in landfast sea ice</td>
</tr>
<tr>
<td></td>
<td>Feb–Apr 2002</td>
<td>Bothnian Bay</td>
<td>9 sites in pack-ice</td>
</tr>
</tbody>
</table>

Table 4: Summary of the main analyses done in each study, \( i, s \) and \( sw \) denote that measurements were undertaken for ice, snow, and under-ice water, respectively.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Ice Structure</th>
<th>Salinity</th>
<th>( \delta^{18}O )</th>
<th>Nutrients</th>
<th>Trace elements</th>
<th>Major ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>( i )</td>
<td>( i, sw )</td>
<td>–</td>
<td>( i, sw )</td>
<td>( i, sw )</td>
<td>–</td>
</tr>
<tr>
<td>II</td>
<td>( i )</td>
<td>( i, sw )</td>
<td>( i, sw, s )</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>III</td>
<td>( i )</td>
<td>( i, sw )</td>
<td>( i, sw, s )</td>
<td>( i, sw, s )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>IV</td>
<td>( i )</td>
<td>( i, sw )</td>
<td>( i, sw, s )</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>V</td>
<td>( i )</td>
<td>( i, sw )</td>
<td>( i, sw, s )</td>
<td>–</td>
<td>( i, sw, s )</td>
<td>( i, sw )</td>
</tr>
</tbody>
</table>

vide the samples into structural units for further analysis (with the exception mentioned above). Salinity (practical salinity units) of the samples was determined from melted samples using a conductivity meter (Radiometer CDM 83 or Schott handylab LF 1) and UNESCO (1983) algorithms or a handheld laboratory salinometer (WTW LF 196).

The \( \delta^{18}O \) was determined using standard methods with a mass spectrometer (Finnigan MAT Delta-E). Reproducibility of replicate analyses is generally better than 0.1‰. In papers II–V, the oxygen isotopic
data (together with structural data) of snow, ice and under-ice water were used to discriminate snow-ice and superimposed ice layers from other granular ice layers and/or to estimate the meteoric ice fraction, namely the fraction of ice of atmospheric origin (snow and rain) in the ice cover (e.g. Lange et al., 1990; Jeffries et al., 1994; Kawamura et al., 2001a). The isotopic mass balance equations of Jeffries et al. (1994) were used to estimate the fraction $f$ of sea water ($sw$) and meteoric ice ($s$) as follows:

\[ f_s + f_{sw} = 1 \]
\[ f_s \delta_s + f_{sw} \delta_{sw} = \delta \]

which can be solved for $f_s$ as follows:

\[ f_s = \frac{(\delta - \delta_{sw})}{(\delta_s - \delta_{sw})} \]

in the above equations $\delta_s$, $\delta_{sw}$, and $\delta$ are the $\delta^{18}$O values for snow (precipitation), sea ice, and the sample, respectively. For the $\delta_{sw}$ a range of values were used to account for the isotopic fractionation during freezing that ranges from zero (no fractionation) to a value observed during columnar ice growth (fractionation about 2‰). These values are applied because the exact fractionation during snow-ice formation can not be determined unambiguously. Hereby, several $f_s$ values are attained, from a minimum (no fractionation at freezing) to a maximum (maximum fractionation at freezing) estimate, which give a plausible estimate for the meteoric ice fraction in the sea ice. Another fact that needs to be considered is the variation in $\delta^{18}$O composition of snow, rain, and seawater in the Baltic Sea basin (Punning et al., 1991; Fröhlich et al., 1988). In temporal observations these changes can be taken into account (paper IV), but in point sampling this variation can not be accounted for (paper II) and it induces some uncertainty in the $f_s$ estimates.

Nutrients were determined with an autoanalyser or manually with a spectrophotometer using standard seawater procedures (Grasshoff, 1983). The accuracy and precision of these methods have been controlled by use of certified reference materials. Algae biomass was estimated with chl-a. 50–200 mL of the melted ice sample was filtered onto a Whatman GF/F glass fiber filter (25 mm). The filters were placed in 10 mL of 96% ethanol and chl-a was extracted in the dark for 24 hours. The extract was filtered through a GF/F filter, and fluorescence was measured using a Perkin-Elmer LS 2B fluorometer calibrated against pure chl-a (Sigma). Chl-a concentrations were calculated according to HELCOM (1988).

For trace element and major ion determinations, care was taken to avoid contamination of the samples. However, contamination can not be avoided in the sampling process (e.g. metal parts in the corer) so the samples have to be decontaminated prior to analysis (see Candelone et al., 1994). Therefore the (potentially contaminated) outer surfaces of the sampled ice cores are removed before melting the samples for
analysis. Trace elements were determined using graphic furnace atomic absorption spectrometry (Varian GTA 96) or inductively coupled plasma mass spectrometry (Thermo Elemental X7 ICP-MS). Major ions were determined by ion chromatography (Dionex Dx-120) using methods developed for glacial ice (Kekonen et al., 2002).

5 Summary of papers

The structural, physical and biogeochemical properties of Baltic Sea ice have been studied in a comprehensive manner to gain understanding about the relationships between physics, chemistry, and biology of Baltic Sea ice. The objectives and main results from papers I–V are summarized in the following sections.

5.1 Paper I

The title of paper I is Observations of sea ice and surface water geochemistry – implications for importance of sea ice in geochemical cycles in the northern Baltic Sea. In the paper, the structure and geochemical properties of landfast sea ice along the northern Baltic Sea coast were investigated. The objective was to relate the salinity, structure, and particle content to the geochemical properties of sea ice.

For the first time, trace element levels in Baltic Sea ice were presented. Both nutrients and trace elements were independent of salinity. The particle content and atmospheric deposition (and subsequent snow-ice formation) were judged as important in controlling the geochemistry of Baltic Sea ice. Sea ice is a potential source of lead (Pb) to surface waters during ice melt, probably due to atmospheric deposition. More detailed investigations into the geochemical status of sea ice in the Baltic Sea were proposed.

5.2 Paper II

The title of paper II is Development, structure and composition of landfast sea ice in the northern Baltic Sea. In the paper, the structural and stable oxygen isotopic composition ($\delta^{18}O$) of landfast sea ice on 15 sites along the Finnish coast was studied. The main objectives was to look at the structural characteristics and the snow contribution to sea ice growth.

The results showed that snow (precipitation) contributes significantly to ice growth in the landfast sea ice region of the Baltic Sea. Averaged over all the sites, 18–21% of the total sea ice mass was composed of snow (or precipitation), significant when compared to other ice covered seas. It was proposed that future studies should focus on the pack ice region, since it composes the most of the sea ice cover (both in mass and extent) in the Baltic Sea.
5.3 Paper III

The title of paper III is **Nutrient status of Baltic Sea ice – evidence for control by snow-ice formation, ice permeability and ice algae**. In this paper, the temporal evolution of sea ice physical and biogeochemical properties were mapped throughout the ice season at one site in the Gulf of Finland. In addition, spatial variability was examined from samples along the whole length of the Finnish coast (same sites as in paper II). The main objective was to study the processes governing the nutrient status of Baltic Sea ice in detail.

This work was the first combined effort to study the interplay between physical, chemical and biological properties of Baltic Sea ice. The results showed that there are a number of important factors affecting the nutrient status of Baltic Sea ice, among those regarded as most important were atmospheric deposition and snow-ice formation (nitrogen), ice permeability (transport of atmospheric nutrients downwards in the ice), and uptake by ice algae (phosphorus). Nutrients deposited onto the ice surface can be transported downwards in the ice, during periods of increased permeability, potentially affecting the biological productivity in the ice and under-ice water. The build-up of ice algae communities is strongly controlled by abiotic factors, especially that of the ambient water salinity.

5.4 Paper IV

The title of paper IV is **Seasonal development of the properties and composition of landfast sea ice in the Gulf of Finland, the Baltic Sea**. In this paper, the seasonal development of ice structure, salinity and stable oxygen isotopic composition were investigated during three consecutive winters. The objective of this paper was to study the interannual variability in ice structure and composition, and especially the contribution of snow to ice growth.

The results showed large seasonal and interannual variability in sea ice composition. In texture the ice cover is composed of an upper granular layer and a basal columnar layer, the former contributing on average about one third of the total ice thickness. Superimposed ice is a recurring process at these latitudes, especially late in spring with episodic occurrence of superimposed ice layers, which is due to freezing of snow-melt and liquid precipitation. Formation of snow-ice and superimposed ice formation are important for the mass balance of sea ice in the area, with a meteoric ice fraction from 0 to 35% (by mass) depending on season and year. The formation of intermediate granular columnar ice layers seem to be connected to turbulent conditions.

5.5 Paper V

The title of paper V is **Chemical properties of brackish water ice in the Bothnian Bay, the Baltic Sea**. In this paper, the behavior of major ions, stable oxygen isotopes (δ18O), dissolved organic carbon (DOC), and selected trace metals (aluminum, iron, zinc) were studied during the initial freezing of low
saline water (3 PSU) in a freezing experiment. Samples were also collected from young and first-year sea ice with an unknown thermal and growth history to study the chemical properties of naturally grown sea ice in the Bothnian Bay.

The objective was to study the fractionation of a range of different chemical classes during initial ice formation processes at low salinities. One purpose of this work was to shed more light on the chemical properties of sea ice in the Baltic Sea, which to date were virtually unknown.

The results show that major ion chemistry is strictly related to salinity, while trace metals are not. The exact reason for this is unclear, but it seems that secondary processes, such as atmospheric deposition and biological activity, may more strongly govern the trace element chemistry of sea ice than salinity alone. For example, iron and aluminum were in excess in the ice in relation to salinity, as was dissolved organic matter. Selective retention/rejection of some chemical species during ice formation may have an effect on the chemical budgets during the ice season, especially in shallow areas of the Bothnian Bay. However, further studies in winter are required to quantify the effect of ice growth on chemical budgets in the area.

The observations of level ice in the pack ice region indicated that snow also plays an important role in the development of the ice cover. The meteoric ice fractions to the total ice thickness ranged from 6 to 23%.

5.6 Synthesis of the results

The main results from the work presented in the above-mentioned papers can be concluded as follows;

Snow, or more exactly precipitation, is vital for the development of Baltic Sea ice. Precipitation is important especially in two cases; 1) a significant contributor to the mass of sea ice and 2) for the chemistry. The use of structural properties and isotopic composition clearly support the observations of Palosuo (1963) that snow-ice formation is important. However, what could not be shown by Palosuo (1963) was that superimposed ice, formed of refrozen snow melt or frozen rain, contributes significantly to ice growth at these latitudes as well. Re-interpretation of the data collected by Palosuo (1963) indicate that superimposed ice formation is not unusual in the Baltic Sea area. The observations and modelling work of Cheng (2002) support this as well, however, the role of rain was ignored. Compared to other sea ice regions the contribution of precipitation (meteoric ice) to sea ice growth is high in the Baltic Sea. One should in particular note the high superimposed ice contribution (e.g. Jeffries et al., 1997; Kawamura et al., 1997; Haas et al., 2001). Interannual variability in the contribution of precipitation to sea ice growth was almost as large as that reported by Palosuo (1963). Preliminary results from the pack ice region implies that also there the contribution of snow is significant. The observed meteoric ice fraction being from 6 to 23% (average 15%).

Abiotic factors seem to be important both for the chemistry and the biology of the Baltic Sea ice. Salinity seems to control the habitability of the ice (see also Krembs et al., 2001; Meiners et al., 2002). This
compares well to observations along salinity gradients in the Hudson Bay (Canada) (e.g. Legendre et al., 1992). However, one should note that the salinity is not the single factor in the build-up of algal biomass within the ice. Other factors such as snow depth (light availability), nutrient availability and ice growth processes are also important. Nutrient status of sea ice is, however, strongly affected by atmospheric loading, and the subsequent incorporation of snow and rain into the sea ice cover by snow-ice and superimposed ice formation (see also Rahm et al. (1995)). For example, the nitrogen levels are about twice as high in snow-ice layers than in the rest of the sea ice cover. In this aspect, the Baltic Sea ice evidently differs from sea ice in any other region. In the Antarctic, there is evidence that flooded seawater on heavily snow-laden sea ice introduce nutrients to the upper parts of the ice cover (Fritsen et al., 1994). This resembles the nutrient replenishment in the Baltic Sea ice, but the mechanisms are somewhat different with the atmosphere as a key nutrient source in the Baltic Sea. However, the importance of the atmosphere on the nutrient budget of Baltic Sea ice decreases towards north, as one can assume from deposition estimates in the Baltic Sea area (Granat, 2001). Apparently the role of atmospheric deposition of nutrients is less significant for the nutrient status of Arctic than Baltic sea ice.

Temporal changes in sea ice properties, in particular temperature which affects the porosity of the ice, seem to strongly affect the transport of accumulated nutrients from the ice surface to the under-ice water column. It could be shown that an apparent increase in ice porosity led to a flushing of nutrients through the ice cover, which in turn increased the nutrient levels in the lower parts of the ice cover. This potentially affected the growth of ice algae. The mild ice climate conditions in the Baltic Sea are not only responsible for the superimposed ice formation described earlier (which require snow melt or liquid precipitation during the ice growth period) but also for the rapid changes in ice properties, such as the temperature and the salinity, and thereby in porosity. The thin ice cover responds quickly to changes in atmospheric conditions, whether it is changes in air temperature or snow accumulation. This results in quite uniform ice salinity profiles and hence similar salinities for different ice types when averaged over longer periods (two weeks or longer).

As well as affecting the nutrient status of sea ice, the atmosphere is a source of trace elements. This work reports results of investigations on trace metal levels in sea ice in Baltic Sea for the first time. Lead (Pb) is accumulated during winter in such amounts that the sea ice and snow cover is potentially an important source of Pb during melt. Evidently trace metals are not related to the salinity as strongly as major ions (seawater salts), presumably because active secondary processes, such as atmospheric deposition and biological processes control their concentrations more effectively. During initial ice formation, some elements such as iron and aluminum, are found in excess in sea ice relative to salinity. The reason for this remains, however, open.

It can not be stressed enough that especially studies looking at the temporal evolution of the sea ice environment need to have a holistic approach in order to understand the observed changes, since they are caused by an interplay between physicochemical and biological processes. In this sense, the present work should give a baseline, as to which factors should be taken into account in forthcoming studies.
5.7 Suggestions for future sea ice studies in the Baltic Sea

Suggestions for future studies include;

- The growth and composition of pack-ice in the Baltic Sea is not well known. Even though sporadic observations exist, systematic investigations should be performed. Such basic questions as sea ice and snow thickness distribution, textural and $\delta^{18}O$ composition need to be addressed along with chemical and biological investigations.

- The presence of a snow cover on sea ice, as well as its seasonal development, especially during spring melt-freeze cycles, deserves more attention. Further data are relevant both for the observation of superimposed ice formation, as well as development and validation of thermodynamic sea ice models with the formation of snow-ice and superimposed ice layers included (see also Cheng, 2002). The inclusion of rain in the models seem also relevant at the Baltic Sea conditions.

- The low porosity of Baltic Sea ice will evidently affect its hydraulic properties, therefore in situ studies of the permeability of Baltic Sea ice at different salinities and temperatures should be performed. This is important for e.g. the infiltration of seawater to the ice-snow interface (snow-ice formation) as well as exchange processes of sea ice with the snow pack and under-ice water. Transport of surface meltwaters through the ice is important for the nutrient dynamics, but should also be taken into account in thermodynamic models with snow-ice and superimposed ice formation, because this transport provides a sink of surface melt that is not used for surface ice growth.

- To examine the exact role of sea ice in geochemical cycling and budgets there is a need for concurrent snow, sea ice cover, and under-ice water column hydrochemical studies throughout the ice season. Especially important is the spring melt season, and the transition from ice coverage to open water. This applies to both landfast and pack ice areas in the Baltic Sea.

- Studies on the microstructure, i.e. the distribution and the sizes of brine pockets and channels on Baltic Sea ice would be needed.

- Detailed studies on the in situ composition and properties of sea ice brine in the Baltic Sea ice should be undertaken. This could be accomplished by sampling brine using e.g. refrigerated centrifuges. Measurements could include physical properties of the brine, such as viscosity and density, and detailed analysis of its chemical composition.

- Virtually no studies have been undertaken where detailed hydrochemical observations have been performed during the period of snow and sea ice melt, when substances accumulated onto and possibly (photo)chemically transformed, are released to the underlying waters. There is clearly a need for such studies, as well as investigations looking at uptake and bioaccumulation of pollutants in ice-associated organisms as observed in the Arctic (Borgå et al., 2002)
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