Silicon cycling in the Baltic Sea:

Trends and budget of dissolved silica

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List of Papers

This thesis comprises five appended papers. The papers are referred to by the corresponding Roman numbers (I-V):

I Papush, L., Danielsson, Å. 2006. Silicon in the marine environment: Dissolved silica trends in the Baltic Sea. Estuarine, Coastal and Shelf Science 67, 53-66.

II Danielsson, Å., Papush, L., Rahm, L. 2008. Alterations in nutrient limitations - Scenarios of a changing Baltic Sea. Journal of Marine Systems 73, 263-283.

III Conley, D. J., Humborg, C., Smedberg, E., Rahm, L., Papush, L., Danielsson, Å., Clarke, A., Pastuszak, M., Aigars, J., Ciuffa, D., Mörth, C.-M. 2008. Past, present and future state of the biogeochemical Si cycle in the Baltic Sea. Journal of Marine Systems 73, 338-346.

IV Papush, L., Danielsson, Å., Rahm, L. 2009. Dissolved silica budget for the Baltic Sea. Journal of Sea Research 62, 31-41.

V Papush, L., Henningsson, M., Rahm, L., Danielsson, Å. 2011. Optimised water budget of the Gulf of Bothnia (Baltic Sea). *Manuscript*.

Contributions

My contributions to the appended papers are as follows:

− Retrieving and pre-processing the bathymetric, hydrographic and hydrochemical data for the Baltic Sea interior (Papers I, II, IV and V) and gathering data on riverine water and DSi loads (Papers IV and V).

− Statistical analyses, trend assessments of the DSi, DIN, DIP concentrations and the DSi:DIN, DSi:DIP, DIN:DIP ratios, and analyses of the results (Papers I and II).

− Preparation of the data arrays for budget modelling, e.g. calculating the basin volumes and surface areas, volume-weighted basin-wide salinities and DSi concentrations, as well as riverine water and DSi inputs (Papers IV and V).

− Developing water and Si budget models including their program implementations and calculations in the Matlab$^{®}$ and AMPL environments, and analysis of both the results and model performance (Papers IV and V).

− Analyses of DSi trends and contribution with the basin-wide salinities and DSi concentrations for retrospective budget modelling (Paper III).

− Major responsibility for writing Papers I, IV and V. In Paper II, I contributed to the sections on the nutrient ratio trends and compilation of the data on the diatom growth/uptake half-saturation constants for DSi. My contribution to writing of Paper III included the sections on the DSi trends from 1970 to 2001.

Contents

1. Introduction

Many (if not all) environments have been changing as a result of human activities for a long time. Freshwater and marine ecosystems are no exception and have changed considerably over the last century. Notably, human activities have caused problems in many coastal areas across the globe, including eutrophication, in which excess nutrients such as nitrogen and phosphorus play a major role (Rosenberg *et al.,* 1990; Nixon, 1995). Silicon is another nutrient that is essential for primary producers. Silicon availability strongly influences the growth of one of the largest groups of primary producers – the diatoms (Treugér *et al.*, 1995; Ragueneau *et al.,* 2006). Diatoms are important components of aquatic food webs and may account for up to 30 to 50% of the primary production in the oceans (Nelson *et al.*, 1995). The silicon cycle is related to the carbon cycle due to diatoms' contributions to the export of organic matter from the surface waters to the deep oceans, which, in turn, contributes to the regulation of fluxes of carbon dioxide between the atmosphere and the ocean (Dugdale and Wilkerson, 1998; Ragueneau *et al.,* 2000; Litchman *et al.,* 2009). These algae build their outer cell walls using the silicon present in water as dissolved silica (DSi). Therefore, any processes in terrestrial and aquatic environments that influence the DSi pool will potentially affect diatom production and consequently aquatic food webs.

Decreasing DSi concentrations have been observed in numerous fresh and marine water bodies. Some of these changes are caused by eutrophication, when intensified diatom blooms and subsequent sedimentation of biogenic silica (BSi) exhaust the DSi pool in the water column (Schelske and Stoermer, 1971; Schelske *et al.*, 1983). Other DSi declines are a consequence of the construction of reservoirs, which may alter the morphological and hydrological characteristics of rivers and their watersheds. Reservoir construction can decrease riverine DSi fluxes to the coastal zone through increased retention of dissolved silica in freshwater systems (Humborg *et al.*, 1997; Jickells, 1998).

Until recently, there was not considered to be a risk of Si becoming a limiting nutrient for diatom production in the Baltic Sea. However, declines in DSi concentrations and DSi:DIN ratios have been found in the Baltic waters (Sandén *et al.,* 1991; Rahm *et al.,* 1996). These changes have been attributed to ongoing eutrophication in the Baltic Sea. Further, this has raised questions about the potential for Si limitation and concerns about its possible ecological consequences.

Effects of agricultural and other human activities (in particular regulation of rivers) in watersheds in the Baltic region have intensified since the 1950s, as they have in most industrial regions, resulting in increased pressure on the freshwater and marine ecosystems. The role of the river regulation and the eutrophication in the decrease of DSi levels in the Baltic Sea, and the role of DSi decrease in both occurred and anticipated changes in the phytoplankton species composition and dominance have motivated a closer look at the Si cycling in the Baltic Sea.

1.1 Objective of this study

The main objective of the research presented in this thesis was to contribute to a better understanding of changes in Si biogeochemical cycling in the Baltic Sea during the 20th century, including temporal and spatial changes in DSi concentrations.

Within this framework, the following specific tasks were defined:

- To evaluate the temporal changes in DSi concentrations and the DSi:DIN, DSi:DIP and DIN:DIP nutrient ratios, and analyse these changes with respect to the ongoing eutrophication and changes in riverine loads in the Baltic Sea (Papers I and II).

- To determine if Si is becoming a limiting nutrient in the Baltic Sea (Paper II).

- To estimate the basin-wise DSi fluxes and quantify the respective internal sinks/sources in order to develop and examine a recent spatially differentiated DSi budget, and to develop a retrospective DSi budget (Papers IV and III).

- To develop a time-dependent water budget based on inverse salinity modelling in combination with evaluation of solution methods aiming to handle problems associated with performance of traditional budget models (Paper V).

1.2 Thesis outline

Section 2 provides a description of silica cycling in the world ocean. The Baltic Sea as a study area is described in Section 3. The materials and methods used for the data analyses and the

modelling approaches are outlined in Section 4. Section 5 summarizes the results and describes their implications. Finally, the conclusions are presented in Section 6.

This thesis is based on five papers. Paper I focuses on an analysis of the DSi trends in the Baltic Sea between 1970 and 2001. The temporal variation in DSi levels is discussed in relation to both ongoing eutrophication and changes in riverine loads. Paper II continues the study of DSi in the Baltic Sea with a specific emphasis on the temporal and spatial variations of DSi:DIN and DSi:DIP nutrient ratios, and the occurrence of low DSi concentrations in the Baltic Sea. The DSi budgets are in the focus of Papers III and IV. Paper IV presents the spatially differentiated water and DSi budget models for the period 1980 to 2000 followed by estimates obtained with it of the water flows and DSi fluxes between basins, and the magnitude of the internal sinks. In Paper III, data on the DSi concentrations in the water column, estimates of riverine DSi loads and accumulation rates of BSi in sediments are used to evaluate the state of the biogeochemical Si cycle in the Baltic Sea during the 20th century, in particular, to obtain a retrospective estimate of the DSi levels at the beginning of the 20th century. Finally Paper V continues the budget modelling, focusing on attempts to improve the performance of the time-dependent inverse salinity model.

2. Silica cycling in the world ocean

Apart from oxygen, silicon (^{14}Si) is the most abundant element (~28 %, w/w) in the Earth's crust, more than 50% of which is composed of amorphous and crystalline silica, silicate or aluminosilicate minerals (Ahmetov, 1981). Silicon is also one of the major constituents of seawater, where it is present in both dissolved and particulate forms. The overall mean concentration of silicic acid in the world ocean is ~ 84 μM (Sarmiento and Gruber, 2006). In the surface waters of the oceans, the concentration of dissolved silica is generally low, but in some parts of the North Pacific Ocean and the Southern Ocean, surface winter DSi concentrations can be between 45 and 100 μM, respectively (Tréguer *et al*., 1995; Sarmiento and Gruber, 2006). The deep waters are generally enriched with silicic acid, with concentrations up to 180 μM. Both the surface and deep oceans are undersaturated with respect to biogenic silica. Inputs of silica are approximately balanced by the burial of biogenic silica (Fig. 2.1). The residence time of DSi in the ocean is ~ 16 000 years and the cycling time of DSi in the surface ocean (euphotic zone) is ~ 400 years. Hence, silica entering oceanic waters will participate in biogenic uptake and dissolution processes ca. 40 times, on average, before being buried permanently.

2.1 DSi sources
Most Si is bound in silicate minerals and is therefore unavailable for biological uptake. Silicic acid is supplied to the oceans through three pathways (Fig. 2.1):
- riverine transport of weathered products of silicate and aluminosilicate minerals,
- atmospheric deposition (Eolian transport),
- hydrothermal weathering (mainly through high temperature weathering of the oceanic crusts).
Riverine transport is the most important Si pathway to the oceans. Rivers in temperate regions contribute approximately 20% of the total riverine Si, and this figure increases to 74% in tropical regions (Tréguer *et al*., 1995). Rates of weathering are dependent on bedrock types, climatic conditions, precipitation, vegetation type and abundance, presence of both inorganic and organic acids and the time that the water solution spends in contact with rock minerals. Although the riverine flux of suspended matter by far exceeds the flux of dissolved silica, the low rate of dissolution makes it negligible on the time scales considered in this thesis (several

decades to a century). The contribution of eolian transport is also likely to be negligible over these temporal scales. Although this pathway carries substantial quantities of silica to the oceans, only 5-10% will dissolve in seawater (Tréguer *et al.,* 1995).
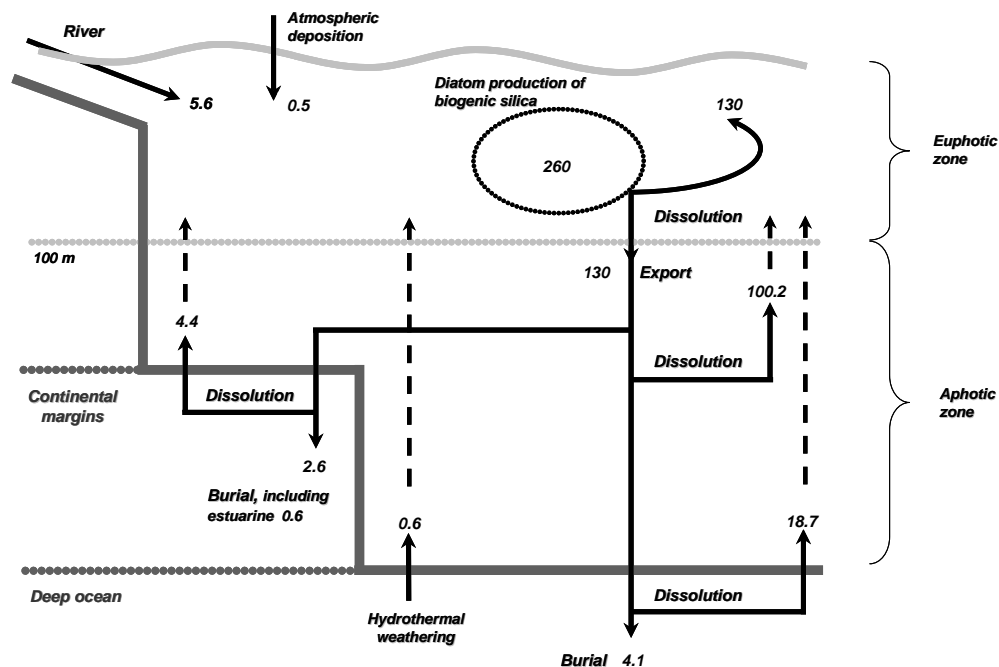
Figure 2.1 Schematic presentation of the ocean silica budget based on Tréguer *et al.* (1995), Nelson *et al.* (1995), DeMaster (2002) and Sarmiento and Gruber (2006). Si fluxes and BSi production in Tmol Si yr^{-1}.

2.2 Diatom production of BSi

Silicon is an essential nutrient for sponges, radiolarians, silicoflagellates, and diatoms that constitute the group of planktonic marine and freshwater biota, all of which use dissolved silicic acid ($Si(OH)_4$, often referred to as DSi) as the building material. Diatoms are considered to have played a primary role in the biogeochemical cycling of silicon since recent geological history (Spencer, 1983; Racki and Corday, 2000). These algae take up dissolved silicic acid to create their cell walls, called frustules, which are composed of amorphous silica

($SiO_2 \cdot nH_2O$, named biogenic silica or opal, BSi). Diatom frustules are the major source of biogenic silica in the ocean.

Diatoms are considered to benefit from environments that are nutrient-rich (as they generally have large cells with a low surface area to volume ratio) and turbulent (being essentially non-motile). These algae often dominate in environments that offer such conditions, *e.g.* during spring blooms, in coastal upwelling regions and in river plumes. In temperate and boreal coastal zones, diatoms are usually among the first algae to grow in spring and usually form a spring bloom. They are adapted to low temperature and low light intensity conditions, and benefit from the intensive mixing and abundance of nutrients that occur after winter.

Diatoms are capable of both rapid consumption of the available nutrients and rapid cell growth (Sarmiento and Gruber, 2006). There is no single theory explaining the success of diatoms compared to other phytoplankton, although their siliceous frustules are likely to contribute to their success. Diatom blooms are usually terminated as a result of nutrient exhaustion. After dying, the algae sink out of the euphotic zone. Diatoms grazed by copepods form part of the food chain subsequently available for pelagic fish. The diatom production (individual cells or aggregates) also fuels the benthic fauna that, in turn, may serve as food for demersal fish and other benthic species. The production of faecal pellets as a result of grazing and the formation of aggregates accelerate the sedimentation process and contribute to the export of organic matter out of the euphotic zone.

2.3 DSi sinks

The burial of biogenic silica in sediments is the ultimate sink for Si in the oceans. Approximately one fourth of the biogenic silica reaching sediments, or ~ 3% of the gross diatom production, accumulates permanently (Fig. 2.1). According to De Master (2002), 60% of the BSi is buried in the deep ocean and the remaining 40% on the continental margins. A substantial part of the biogenic opal dissolves in the upper part of the water column; the remainder continues to dissolve while settling through the water column and after reaching the seabed. Model calculations by Nelson *et al.* (1995) indicate that approximately 50% of the BSi dissolves in the upper 100 m. Various factors, including salinity, temperature, surface area of the diatom cell wall and the concentration of aluminium, can influence the rate of dissolution of biogenic opal (Van Cappellen *et al.,* 2002). While higher temperature and a

larger surface area facilitate dissolution, the presence of aluminium ions decreases dissolution (Ragueneau *et al.*, 2000; Dixit *et al.,* 2001).

2.4 Changes in Si biogeochemical cycling

As the effects of eutrophication in water bodies and human intervention in watersheds are becoming more visible, attention has been drawn to the effects of human activities on silicon cycling, and to the consequences of silicon deficiency in freshwater and marine ecosystems. For example, Tréguer *et al.* (1995) took into account eutrophication and damming effects on riverine Si input, when reviewing the literature on Si cycling and re-estimating the oceanic Si budget.

Hydrological changes in watersheds**,** such as changes in flows caused by dam and reservoir construction, along with eutrophication, influence the total amounts of nutrients and the ratios of these nutrients delivered to coastal zones or other recipient water bodies (Justić *et al.*, 1995b; Humborg *et al.*, 1997; Jickells, 1998). The decrease in Si is attributed to the fact that anthropogenic nutrient inputs may compensate for the retention of N and P in perturbed watersheds, but not for Si due to its primarily natural origin.

Influential limnological studies by Schelske and Stoermer (1971) and Schelske *et al.* (1983) conducted in the North American Laurentian Great Lakes led to the hypothesis that high external loads of P (due to human waste and fertiliser use) trigger increased diatom production and, thus, higher Si accumulation in sediments, resulting in Si depletion in the water column. These authors also claimed that such depletion of Si may cause a shift in the dominance of diatoms to non-siliceous algal groups. This hypothesis was further discussed by Officer and Ryther (1980), who presented a number of arguments in support of the role of Si in changing the oceanic, coastal and freshwater phytoplankton communities from diatom- to flagellate-dominated ones. Si depletion in the water column is attributed to the enhanced sedimentation of diatoms and the slow recycling of sequestered Si compared to N and P, as documented by several authors including Smayda (1990), Conley *et al.* (1993), Nelson and Dortch (1996) and Gilpin *et al.* (2004).

2.5 Nutrient limitation

The concept of nutrient limitation is important when considering the influence of nutrient availability on both individual species and the entire phytoplankton community. In accordance with von Liebig's 'Law of the minimum' (Liebig, 1840), the nutrient that is least abundant in the environment will determine the limits of growth. Nitrogen and phosphorus are generally regarded as the least-abundant nutrients. However, iron and silicon have recently received increased attention as limiting factors in the aquatic environment. Signs of Si limitation have been intensively studied, with particular emphasis on the DSi uptake characteristics of diatoms in coastal waters and in the open ocean (*e.g.* Nelson and Tréguer, 1992; Brzezinski and Nelson, 1996; Nelson and Dortch, 1996; Leynaert *et al.*, 2001).

Comparisons of the stoichiometric ratios of nutrients required for balanced phytoplankton growth with ratios in ambient substrates (in this case - concentrations in the water masses) are often used to anticipate nutrient limitation. This approach helps identification of the nutrient that is potentially limiting (Dugdale *et al*., 1995). When nutrient levels are balanced, the atomic Si:N:P ratio, reflecting the average composition of marine diatoms, is ~ 16:16:1 (Redfield *et al.,* 1963; Harrison *et al.*, 1977; Brzezinski, 1985). Deviations from this ratio (DSi:DIP < 16 or DSi:DIN<1) suggest Si is a potentially limiting nutrient for the diatom population.

Another approach that can be used to identify nutrient limitation is to consider the influence of nutrient concentrations on rates of phytoplankton's growth, based on the Monod equation (Monod, 1949). This approach is based on the hypothesis that low nutrient concentrations may limit algal growth and/or uptake of the corresponding nutrient. Diatom half-saturation constants vary depending on the species and environmental conditions. For example, according to a review by Officer and Ryther (1980), reported half-saturation constants for uptake / growth range from 0.5 to 5.0 µM Si. Claquin *et al.* (2006) reported a range of 0.1 to 14.5 µM Si, depending on the species and geographic location, with an overall mean of 2.6 µM Si. Egge and Aksnes (1992) showed that diatom generally dominated, irrespective of the season if the DSi concentration exceeded a threshold of ~ 2 µM Si. A finding assumed to be due to diatoms having a higher maximum growth rate (at non-limiting DSi levels) than other planktonic groups. Sarthou *et al.* (2005), compiled available data on diatom growth parameters in the ocean, and reported half-saturation constants in the range 0.2 to 22 µM, with

an average of 3.9 μM. In a recent study of DSi uptake by spring diatoms from the Baltic Sea reported by Spilling *et al.* (2010), the most common diatom species were found to be relatively lightly silicified, with half-saturation uptake constants of < 2 μM Si. However, diatom growth stopped when the DSi concentrations were between 1.7 and 5.6 μM. This suggests that some diatom species may still grow under nutrient replete conditions, while others are in distress with regard to the Si availability.

Diatoms may also adapt to low DSi concentrations by producing less silicified frustules or changing the cell morphology so that less or no siliceous spines are developed (Ragueneau *et al.*, 2000 and references therein). In several regions, a switch from N or P to Si limitation has been investigated especially with regard to changes in nutrient supplies to the coastal zones and ongoing coastal eutrophication, *e.g.* Conley and Malone (1992), Justić *et al.* (1995b) and Humborg *et al.* (1997). Many ecosystems perturbed by elevated N and P loads in a combination with unchanged or reduced Si loads may undergo or have already experienced a shift from diatom to non-diatom dominated communities. Another effect is alterations in the diatom community composition, which is manifested in favoring species with relatively low DSi requirements (Rousseau *et al.,* 2002).

3. Study area – the Baltic Sea

The Baltic Sea is located in Northern Europe between 54º to 66º N and 9º30' to 31º E (Fig. 3.1). This brackish, non-tidal, semi-enclosed sea is commonly separated into several basins: the Gulf of Bothnia (the Bothnian Bay and Bothnian Sea), the Gulf of Finland, the Baltic Proper, the Gulf of Riga, the Belt Sea and Kattegat. The largest central region of the Baltic Sea, the Baltic Proper, is further divided into the Northern Central, Western Gotland, Eastern Gotland, Bornholm and Arkona basins. The catchment area is four times the size of the sea surface area, or ~$1.7 \cdot 10^6$ km^2 (HELCOM, 2003) and accommodates ~85 million inhabitants. This area spans a large climate gradient, from sub-arctic conditions with high precipitation in the north, to relatively mild winters and warm summers with limited precipitation in the south. The Gulf of Bothnia is typically ice-covered in winter, but the Baltic Proper usually remains ice-free. In general, the catchment of the Gulf of Bothnia is sparsely populated and water courses have been less affected by eutrophication than the cultivated watersheds in the south-east and south-west Baltic region (Humborg *et al.*, 2008).

The northernmost Bothnian Bay and Sea are connected via the Northern Quark by two narrow and shallow channels (Stigebrandt, 2001). The Southern Quark, which links the Bothnian Sea and the Åland Sea, is wider and deeper than its northern counterpart. The Åland Sea and Archipelago Sea connect the Northern Baltic Proper with the Bothnian Sea. The Åland Sea is a deep, but rather narrow region, while the Archipelago Sea is a shallow area with a large number of islands (Marmefelt and Omstedt, 1993). The Gulf of Finland is a direct extension of the Baltic Proper as no shallow sills separate these basins, while the Gulf of Riga is a semi-enclosed basin separated from the Baltic Proper by narrow and shallow straits. The Belt Sea region and the Kattegat are transition areas between the Baltic Proper and the North Sea (Skagerrak). The Darss and Drogden Sills are entrances that directly border the Baltic Proper (Elken and Matthäus, 2008).
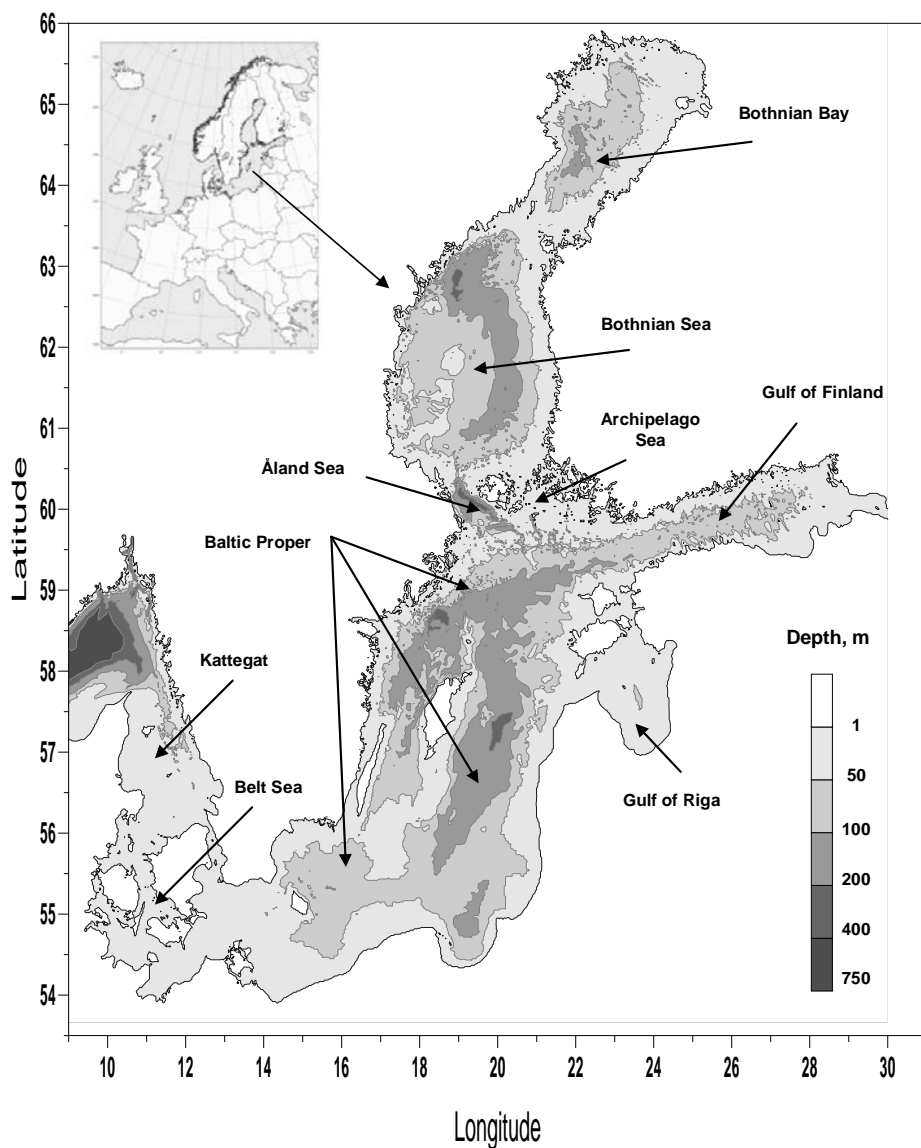
Figure 3.1 Bathymetric map of the Baltic Sea and its basins.

3.1 Hydrographic characteristics

The entrance sills act as barriers that restrict water exchange between the brackish Baltic Sea and the saline North Sea, resulting in long water residence times in the Baltic Sea (*e.g.* 25 to 35 yrs according to Matthäus and Schinke (1999); 15 yrs according to Savchuk (2005)). The

restricted saline water exchange with the North Sea and the large freshwater supply (from riverine runoff and net precipitation) results in horizontal and vertical salinity gradients in the water masses. Horizontally, the Baltic Sea is characterised by a significant spatial gradient in surface salinities, ranging from 15 to 25 practical salinity units (PSU) in the southern-western parts down to 2 to 3 PSU in the northernmost areas (Fig. 3.2). The vertical salinity stratification is weak in the Gulf of Bothnia, where there is almost complete biannual turnover down to 60 m. The vertical salinity distribution is rather uniform in the water column off the Gulf of Riga. The Gulf of Finland is characterised by strong vertical and horizontal salinity gradients. The Baltic Proper, comprising the central and southern sea regions, has a permanent halocline between 40 m in the Arkona basin and 60 to 80 m in the Eastern Gotland basin. This leads to a permanent three-layer density profile: a well-mixed surface layer; a halocline with a steep increase in salinity; and a stratified deep layer extending to the bottom. In the Kattegat, the horizontal and vertical salinity gradients are strong and the halocline is located at ~15 m. There is also a seasonal thermocline that develops in all basins during the summer at ~ 20 to 30 m. Both the permanent halocline and the seasonal thermocline dampen the turbulent diapycnal mixing and 'isolate' the deep water masses from the upper part of the water column.

The large-scale horizontal circulation of the basins is characterised by a counter-clockwise rotation (Elken and Matthäus, 2008). The circulation is governed by the inflow of dense, oxygen-rich, saline water from the Kattegat (Stigebrandt, 1987). This intrusion must be of a certain salinity and volume to ventilate the deeper parts of the Baltic Proper and to strengthen the stratification. These events are infrequent and have occurred only a few times in the recent decades, in 1993, 1997 and 2003 (Matthäus, 2006). During these events the saline water spills over the shallow entrance sills into the Arkona and Bornholm Basins and renews the deep water of the Eastern Gotland Basin (Elken and Matthäus, 2008). Afterwards the saline water moves into the Western Gotland Basin and the Gulf of Finland (*ibid.*). On its way to the deep parts of basins the inflowing dense water masses are diluted by the entrainment of the overlying water that is less saline (Stigebrandt, 1987). In periods between the major inflows, waters with less density renew the intermediate water masses in the Baltic Proper just below the halocline (Stigebrandt, 2001). Further propagation of deep water in a northward direction is hindered by the shallow sills of the Åland and Archipelago Seas, therefore the Bothnian Sea is renewed mainly by surface water from the Northern Baltic Proper (Marmefelt and Omstedt, 1993; Carlsson, 1997).
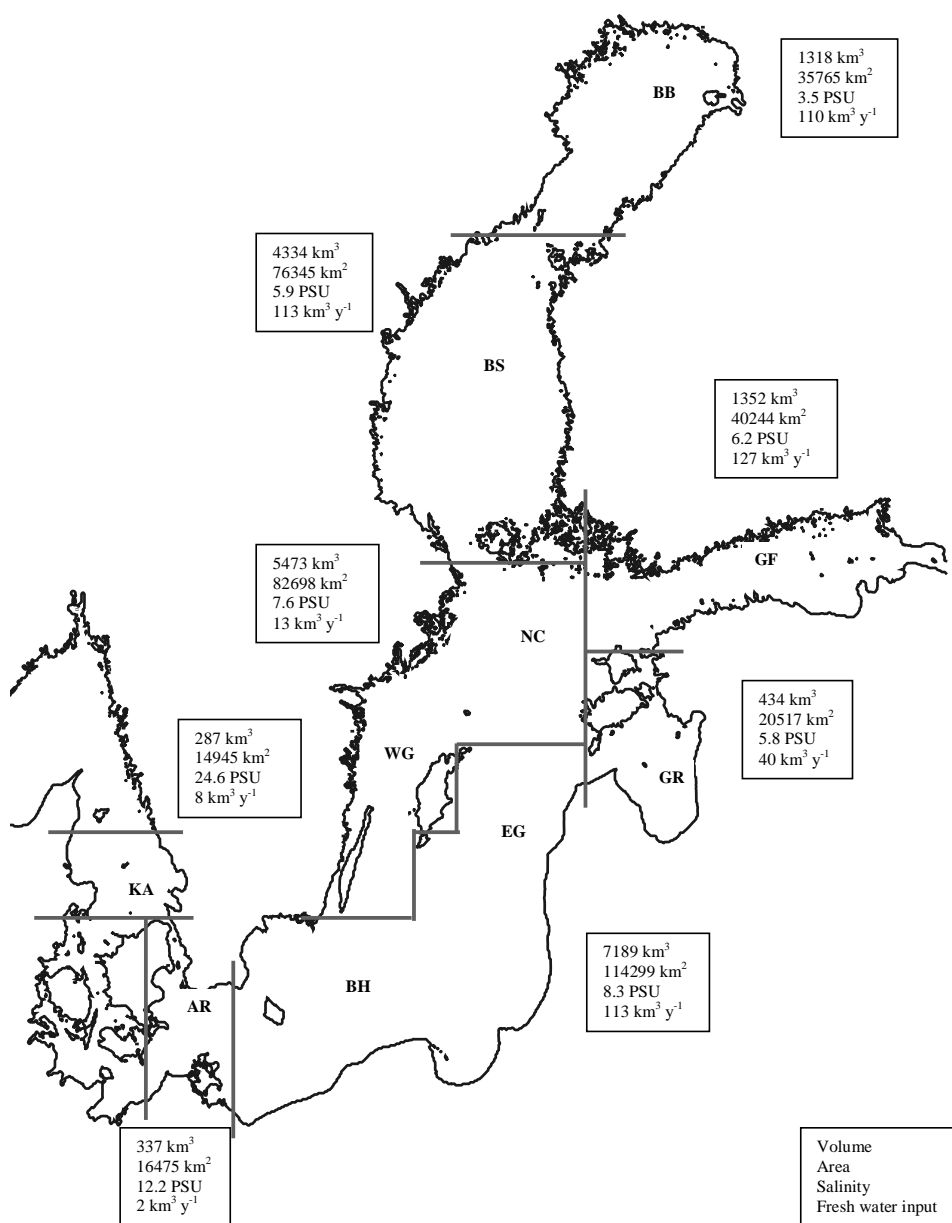
Figure 3.2 The major basins of the Baltic Sea, their volume, surface area, average volume-weighted salinity and fresh water input. The basin delineation and the period of time for salinity and freshwater input (1980 – 2000) correspond to those chosen for the budget modelling in Paper IV. Basins: BB – Bothnian Bay, BS – Bothnian Sea, GF – Gulf of Finland, NC – Northern Central, WG – Western Gotland, EG – Eastern Gotland, BH – Bornholm, GR – Gulf of Riga, AR – Arkona, KA – Kattegat.

3.2 Hydrological characteristics

As mentioned above, climatic conditions vary substantially over the Baltic Sea region. The annual mean air temperature in the northern part is -2 to 0ºC, while in southern regions the annual mean temperature is ~ 9ºC (for a review see Heino *et al.,* 2008). According to data for 1931 to 1960, the lowest mean monthly temperatures occurred in January and February, and the highest in July and August (Bergström *et al*., 2001). Precipitation shows a clear annual cycle with the highest monthly precipitation in July and August and the lowest during February to April. Mean annual precipitation over the entire Baltic Sea basin amounts to approximately 750 mm yr^{-1} (Elken and Matthäus, 2008). The 1970s was considered a comparatively dry period, while the 1980s and particularly the 1990s were wet (Fig. 5 in Paper I). Precipitation and evaporation are climatic factors affecting runoff. Seasonally, runoff is highest in April and May. According to Bergström and Carlsson (1994), who examined flows in the period 1950 to 1990, the average river inflow was ~ 446 km^3 yr^{-1}. There was considerable inter-annual variation and no statistical trends were revealed in annual runoff data, although an overall increasing tendency was found between 1901 and 2002 (Lindström and Bergström, 2004). The fresh water input (net precipitation plus riverine runoff) estimated for the time period 1980 to 2000 are presented in Fig. 3.2.

3.3 Eutrophication

Several distinguishing characteristics (restricted water exchange with the ocean, vertical stratification, brackish water, low biodiversity, a large catchment area and high runoff) make the Baltic Sea a vulnerable ecosystem. During the 20th century the Baltic Sea was subjected to massive anthropogenic pressure. Nitrogen and phosphorus loads changed radically due to increases in agricultural and industrial production, and in the number of people living within the catchment area. Larsson *et al*. (1985) reported four-fold and eight-fold increases in nitrogen and phosphorus loads, respectively, from the beginning of the 20th century to the time of their study, most of which occurred after the 1950s. Spatially, there is a north-south gradient in nutrient loads, with up to four times higher inputs in the southern part of the Baltic Sea, which can be attributed to the distributions of the human population, agricultural activities, major rivers and point sources (Sweitzer *et al.,* 1996; Savchuk *et al.,* 2008). The increased anthropogenic nutrient loads have led to nutrient enrichment in the Baltic Sea (Sandén *et al.* 1991; Sandén and Rahm, 1993; Kuparinen and Tuominen, 2001), with

consequent increases in phytoplankton production followed by decreased water transparency, oxygen depletion in the bottom waters, the spread of anoxic sediments, increased frequency of harmful algal blooms, and alterations in fish populations. Substantial efforts have been made to reduce the nitrogen and phosphorus inputs from land-based activities into the Baltic Sea using various remedial actions. The HELCOM's goal to reduce discharges by 50% has been achieved for phosphorus, but not for nitrogen (HELCOM, 2003).

In general, Stålnacke *et al.* (1999) concluded that the total annual riverine loads of N and P were almost constant between 1970 and 1993, despite changes in agricultural praxis, wastewater treatment and atmospheric deposition. Similarly, lack of trends was also observed in the 1990s (HELCOM, 2002). Despite the significant efforts to cut emissions from various nutrient sources, the high nutrient load is still one of the major concerns with respect to ongoing eutrophication and its consequences for both the flora and fauna of the Baltic Sea (Rönnberg, 2001). In fact, P that is stored in the sediments can be mobilised under hypoxic conditions, releasing the equivalent of many years of P input from the land directly to the water mass (Conley *et al.*, 2002) and making any remedial action ineffective.

3.4 Si characteristics

The nutrient concentrations in the surface layers of the Baltic Sea follow a characteristic pattern related to seasonal changes in the weather, nutrient loads and primary production (Andersson *et al.*, 1992; Wulff *et al.*, 1994; Hagström *et al.*, 2001). Hence, there is considerable temporal variation within single years with the highest nutrient concentrations occurring during winter and the lowest during summer. These characteristic patterns are more pronounced in the southern parts of the Baltic Sea than in the northern regions. Winter concentrations of DSi and annual DSi riverine loads are presented in Table 3.1. There is obvious heterogeneity in the DSi concentrations in the water column of the Baltic Sea, concentrations being highest in the northernmost basins and lowest in the southern-eastern Baltic Proper and western Baltic (Table 3.1). Also, the Baltic Sea is a non-homogeneous water body with regard to water runoff and silica loads (Fig. 3.2 and Table 3.1). DSi concentrations in the rivers discharging into the Baltic Sea have been described and analysed by Humborg *et al.* (2008). The rivers with the highest DSi levels enter the Gulf of Bothnia with median concentrations of ~ 100 μM, while the lowest DSi concentrations are found in

two of the ten major rivers draining the Baltic Sea catchment, the Neva (8 μM) and Göta Älv (~17 μM), which discharge into the Gulf of Finland and the Kattegat, respectively. Only a few significant negative trends have been reported for riverine DSi loads during 1970-1990 (Rahm *et al.*, 1996). Humborg *et al.* (2008) concluded that annual riverine DSi loads to the Baltic Sea declined by 30 to 40% during the 20th century and are now ~ 420 ktons less than before damming and eutrophication.

Table 3.1 Basin-wide averages (1980-2000) of DSi concentrations[1] and DSi loads[2] in the Baltic Sea.

Basin	Bothnian Bay	Bothnian Sea	Northern Central and Western Gotland		Eastern Gotland and Bornholm		Gulf of Finland	Gulf of Riga	Arkona	Kattegat
			above halocline	halocline and below	above halocline	halocline and below				
DSi, (μmol l^{-1})	27.7	17.5	14.3	32.0	13.4	35.1	14.8	11.6	12.4	9.3
DSi riverine loads, (ktons yr^{-1})	234	202	10	---	220	---	91	65	---	14

[1] The estimates of DSi concentrations are based on data retrieved from Baltic Environmental Database (Sokolov *et al.*, 1997).
[2] The estimates of loads are based on data from Laznik *et al.* (1999), Stålnacke P. (*pers. comm.*), Wulff *et al.* (2001) and SLU database (http://info1.ma.slu.se/ma/www_ma.acgi$Project?ID=StationsList&P=FLODMYNN).

4. Materials and methods

The research presented in this thesis is based on some of the data collected in the frame of several monitoring programs carried out in the Baltic Sea region. The retrieved and compiled arrays of data were further analysed by statistical methods and used to develop both water and Si budget models described below.

4.1 Data materials

The hydrographic and hydrochemical data covered the period from 1970 to 2001 and were retrieved from the Baltic Environmental Database (Sokolov *et al*., 1997). Measurement frequencies showed that the sampling was particularly intense around some monitoring stations in pelagic regions (Paper IV). In addition, sampling was more frequent in the southern and western regions, because they remain ice-free, than in the northern areas. Using measurement quality codes, which were linked to the data, records containing information of insufficient quality or duplicated data were eliminated.

Monthly riverine runoff data, covering the entire Baltic Sea, required for the budget modelling, were retrieved from the BALTEX (http://www.smhi.se/sgn0102/bhdc/index.htm) and SLU databases (http://info1.ma.slu.se), along with other published sources. These data are summarised according to basins borders. The precipitation and evaporation estimates provided by Omstedt and Rutgersson (2000) and Omstedt and Nyberg (1996) were recalculated to correspond to the basin delineations used in the budget studies presented in Papers IV and V. DSi riverine data were based on published information sources, public databases and personal communications (for more details see Paper IV). In the trend analyses (Papers I and II) and the water budget study (Paper V), data corresponding to the entire year were utilised, while only winter measurements were used in the Si budget calculations (Paper IV) to avoid substantial variation in concentrations related to the DSi sequestration during the productive season.

Hourly water level data (Paper V) were provided by the Swedish Meteorological and Hydrological Institute (SMHI). The data from stations along the Swedish coast of the Gulf of

Bothnia (Furuögrund, Ratan, Spikarna, Forsmark) and in the northern part of the Baltic Proper (Stockholm) were aggregated on a monthly basis.

4.2 Data smoothing

To deal with the large and likely unphysical variation in the calculated water flow between basins (Paper V), the salinity and riverine inflow time series have been subjected to smoothing by means of moving averages. This technique is frequently used for analyses of hydrological, meteorological and hydrochemical time series (*e.g.* Inosako *et al.*, 2006). In this study, the equal weight was given to all observations included in the moving average formula.

4.3 Statistical methods

The non-parametric Kruskal-Wallis one-way analysis of variance was used for identifying statistically significant differences in winter nutrient concentrations among monitoring stations selected for the trend analysis (Paper I). In addition, the post hoc range tests and pair-wise multiple comparisons were applied to determine where (between which monitoring stations) differences were found. Further, the non-parametric monotonic seasonal Mann-Kendall test elaborated by Hirsch *et al.* (1982) and Hirsch and Slack (1984) was used for trend detection (Papers I and II). The slopes of the trends were determined using the Kendall seasonal estimator (Hirsch *et al.*, 1982). The DSi, DIN and DIP time series were characterised by seasonality related to primary production. Therefore, to deal with the corresponding impact on nutrient concentrations, the trends were determined for each season and then aggregated to obtain annual trends (Papers I and II). These methods have been used previously to estimate nitrogen, phosphorus and silica trends in the Baltic Sea (see Sandén *et al.*, 1991; Sandén and Rahm, 1993).

Regression analysis was used to acquire missing data points in the salinity and DSi time series, which was especially important for the data series collected in the northernmost basins, where sampling was infrequent during winter (Papers IV and V). Also, interpolation and long-term averages were used for this purpose. Thereafter, the basin-wide salinity and DSi concentrations were calculated as volume-weighted estimates for each year, month, and depth layer.

4.4 Budget modelling

The ultimate purpose of most of budgets calculated for water bodies is to deepen the insight into the behaviour of chemical elements or anthropogenic compounds. Focus is often on the water flows and biogenic element fluxes between basins, and internal sinks/sources in the system (*e.g.* Papers III and IV). In Paper V, the efforts are concentrated on a time-dependent water budget, constructed using water flow calculations based on classical Knudsen's theorem (Knudsen, 1899), where salinity is used as a conservative tracer. The inverse model is formulated as a system of linear algebraic equations based on mass and volume continuity. Each basin is described by two equations: one for water flow and one for salt mass flux. When both basin volumes and salinity stocks are considered to be time-dependent, the water and salinity balance equations for each basin can be expressed as:

$$\frac{dV_i}{dt} = \sum_{j:(j,i)\,\in\,Exch} Q_{ji} - \sum_{j:(i,j)\,\in\,Exch} Q_{ij} + q_i^R + q_i^{P-E}$$

$$\frac{d(V_i\,S_i)}{dt} = \sum_{j:(j,i)\,\in\,Exch} (S_j\,Q_{ji}) - S_i \sum_{j:(i,j)\,\in\,Exch} Q_{ij}$$

(1)

where V_i is the volume of basin i, Q_{ij} is the flow from basin i to basin j, S_i represents the mean salinity in the basin i, q_i^R is the freshwater discharge from the land to basin i and q_i^{P-E} is the supply of water due to net precipitation in the basin i. *Exch* is a set of indexes (i,j) corresponding to all possible flows Q_{ij} between basins.

A forward difference scheme was applied due to the simplicity of its realisation (Paper V). Hence, the derivatives in the left-hand side of equations (1) are approximated by finite differences according to:

$$\frac{dV_i}{dt} = A_i \frac{dh_i}{dt}$$

$$\frac{d(V_i S_i)}{dt} = V_i \frac{dS_i}{dt} + S_i \frac{dV_i}{dt} = V_i \frac{dS_i}{dt} + S_i A_i \frac{dh_i}{dt}$$

$$(2)$$

$$\frac{dh_i}{dt} \approx \frac{h_i^{k+1} - h_i^k}{\Delta t}$$

$$\frac{dS_i}{dt} \approx \frac{S_i^{k+1} - S_i^k}{\Delta t}$$

where A_i and h_i are the surface area and water level in the basin i, respectively; Δt is the time step (one month in Paper V) and k is the number of steps from the start.

At steady-state, both volumes and salinity stocks are considered to be constant in each basin for the considered time period, thus the solutions are not time-dependent. The corresponding water and salt balances for each basin can be written as a system of linear algebraic equations (Papers III and IV):

$$\sum_{j:(j,i)\,\in\,Exch} Q_{ji} - \sum_{j:(i,j)\,\in\,Exch} Q_{ij} + q_i^R + q_i^{P-E} = 0$$

$$(3)$$

$$\sum_{j:(j,i)\,\in\,Exch} (S_j\,Q_{ji}) - S_i \sum_{j:(i,j)\,\in\,Exch} Q_{ij} = 0$$

The direction of flow is explicitly included in the model formulation. In the systems of equations (1) and (3), any flows out of and into a basin are denoted by '$-Q_{ij}$', respectively, '$+Q_{ji}$'. To be physically meaningful the solutions of both the time-dependent and steady-state models should contain only non-negative values of Q, otherwise the modelled flow will transport water with salinity equal to the salinity in the receiving basin, which is not physically possible.

In the studies reported in Papers III and IV the quantified water flows were further used in the development of a DSi budget to estimate historical DSi concentrations in three main sea

regions (Paper III), and examine spatial patterns of DSi cycling in the Baltic Sea more closely (Paper IV). In general form, the equation for each basin i is written as:

$$\sum_{j:(j,i)\,\in\,Exch}(C_j\,Q_{j\,i}) - C_i \sum_{j:(i,j)\,\in\,Exch} Q_{i\,j} + q_i^{DSi} + I_i = 0 \qquad (4)$$

where C_i represents the mean DSi concentration, q_i^{DSi} is the riverine DSi load, and I_i is the difference term, characterising internal DSi sinks/sources.

Simplified model structures are presented in Fig. 4.1a and 4.1b for water flows and material fluxes, respectively.
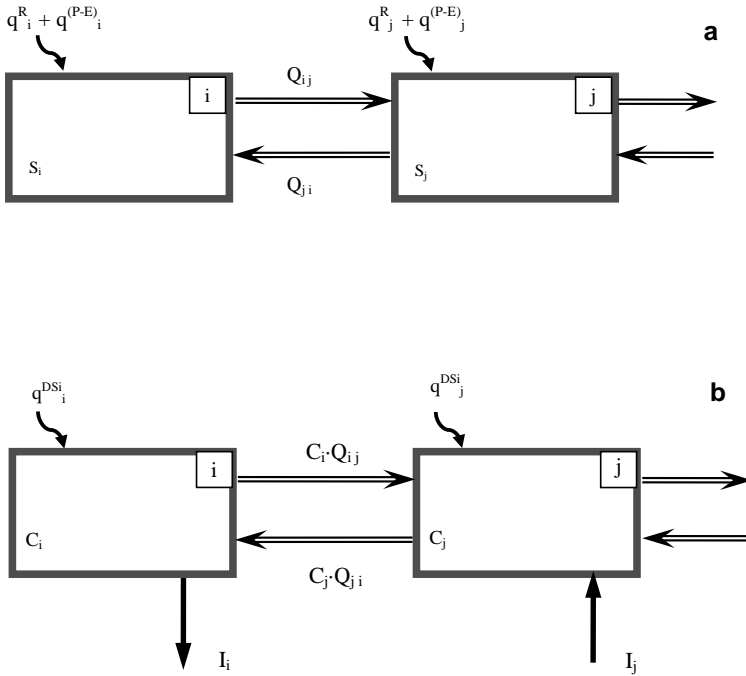
Figure 4.1 Schematic representation of water flows (**a**) and non-conservative material (e.g. biogenic elements) fluxes (**b**) in one-layer model structure. The straight arrows between boxes (without shading) represent water flows (**a**) and material fluxes (**b**). The curved arrows directed into the boxes (black shading) represent fresh water inputs (**a**) and material inputs (e.g. riverine loads) (**b**). The straight arrows directed in and out of the boxes (black shading) represent internal material sources and sinks (**b**), respectively.

4.5 Optimisation

Inverse salinity modelling has proved to be a robust and convenient method for analysing empirical data (*e.g.* Gordon *et al.*, 1996; Smith, *et al.*, 2005). However, some problems can be encountered, specifically solutions that have very high water flow values and a lack of solutions with all non-negative water flows. These problems seem to be more frequent when time-dependent models are used and likely emanate from uncertainties in the input data (*e.g.* salinity stocks) and model structure.
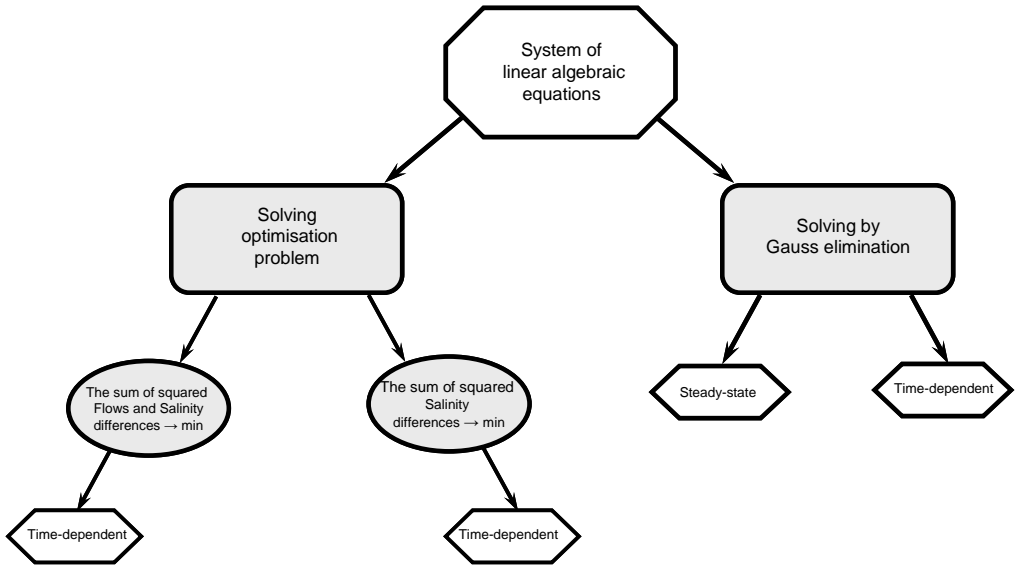
Figure 4.2 Flow chart depicting the modelling process with regard to the applied solution methods.

The time-dependent and steady state implementations correspond to the system of equations (1) and (3), respectively. The obtained systems of linear algebraic equations were solved by MatLab$^{©}$ operator, called *left division*, applying Gauss elimination with row pivoting (Pärt-Enander and Sjöberg, 2001). Furthermore, the sets of solutions obtained were filtered according to the constraints imposed on sign $Q_{ij} \geq 0, \ \forall \ (i, j) \in Exch$ and the magnitude of the water transport out of a basin $\sum_{j:(i,j) \in Exch} Q_{ij} \leq V_i$ at each time step.

The task of solving the system of equations (1) with above-mentioned constraints was also re-formulated as an optimisation problem (quadratic programming with linear constraints) as suggested by Sakov and Parslow (2004). Two modifications of the objective function were implemented. The first modification was to obtain the smallest possible, but physically meaningful, water flows between adjacent basins at the smallest possible differences between the observed and modelled salinities. In the second modification, only differences between the observed and modelled salinities were minimised. Optimisation was carried out in an AMPL environment by the MINOS package employing a reduced gradient approach (Fourer *et al.,* 1997). The use of constraints guaranteed non-negative water flows and restrictions on the volume of water leaving a basin at any time step.

The employed solution methods were initially tested on an artificial data array generated to evaluate their performance (see Paper V). A flow chart depicting the modelling process for obtaining a time-dependent water budget for the Gulf of Bothnia (Paper V) is shown in Fig. 4.2. Two structures were studied: 3 box (Fig. 4.3a) and 4 box (Fig. 4.3b) models.
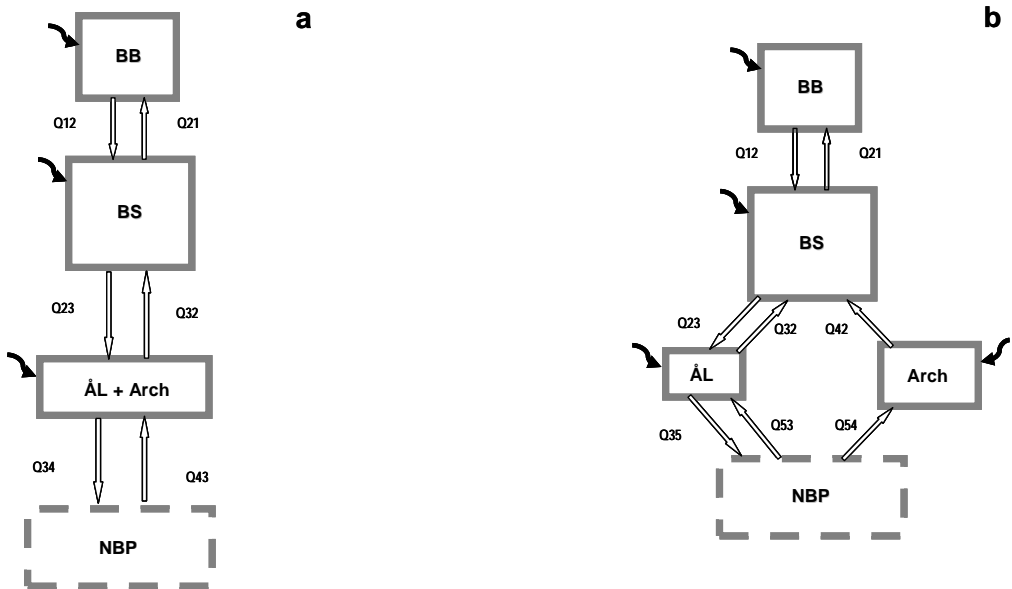
Figure 4.3 Model structures, 3 boxes (**a**) and 4 boxes (**b**), designed for calculating the time-dependent water budget of the Gulf of Bothnia. **BB** – Bothnian Bay, **BS** – Bothnian Sea, **ÅL** –Åland Sea, **Arch**-Archipelago Sea, **NBP** – Northern Baltic Proper. The straight arrows between boxes (without shading) represent water flows. The curved arrows directed into the boxes (black shading) represent fresh water inputs.

4.5.1 Evaluation of the method and model performance

The method and model performance were evaluated using the *mean square error* (MSE) between the generated and calculated water flows as follows:

$$MSE = \frac{\sum\limits_{(i,j)\in Exch} \sum\limits_{k=1}^{K} (Q^k_{gen\ ij} - Q^k_{ij})^2}{K\ N_{Exch}} \qquad (5)$$

where $Q^k_{gen\ ij}$ and Q^k_{ij} are the generated, respectively, calculated water flows in the basin i at time step k; K is the number of time steps; and N_{Exch} is the number of flows between basins.

5. Results and discussion

This thesis highlights the importance of DSi in the Baltic Sea and reports significant declines in DSi concentrations over time, indications of silica limitation and its effects on diatom production.

5.1 Temporal changes in DSi concentrations

There have been long-term declines in DSi concentrations in many aquatic ecosystems around the world due to anthropogenic activities, resulting in altered nutrient fluxes to coastal/marine ecosystems (Conley, 2000; Cloern, 2001; Dortch *et al.*, 2001; Turner *et al.*, 2003). These ecosystems represent a wide spectrum of past and present DSi levels (Table 5.1). The largest annual decreases and percentage changes in DSi have been registered in Lake Michigan, followed by the Black Sea and the northern Gulf of Mexico. For example, in the Black Sea DSi declined by 66 to 85% from the mid-1960s to mid-1980s (Yunev *et al.,* 2007). In the Baltic Sea, as shown in Paper I, from 1970 to 2001 there were significant downward DSi trends (ranging from -0.05 to -1.2 µmol Si l^{-1} yr^{-1}) at most depth intervals, except in the northernmost Bothnian Bay (Fig. 4a in Paper I). After the 1990s, a few positive trends are found (Table 2 in Paper I). Examination of DSi trends for respective monitoring stations revealed some general tendencies for negative trends to be stronger in the deeper waters

The DSi trends were most pronounced during the first two decades (1970 -1990), annual rates of decline being 15 - 41% higher than for the entire period (1970-2001). This is in accordance with negative trends in the upper layers of the Gulf of Bothnia as well as the northern and western Baltic Proper found by Sandén *et al.* (1991) for the period 1968 to 1986. The slight discrepancy between the results presented in Paper I and those obtained by Sandén *et al.* (1991), who reported fewer declines, can be explained by differences in the amount of data for investigated hydrographic stations available for the analyses in the two studies.

The DSi levels at the beginning of the 20th century were similar to those in the 1950s and approximately double current levels (Paper III). This decline reflects the significant change**s** in land use and retention over the last 50 years. The modifications in the Si cycling can be viewed as consequences of a two-fold impact - a decrease in riverine loads to the Baltic Sea (due to river regulation and eutrophication of river basins and lakes), and increases in diatom blooms and subsequent sedimentation caused by the eutrophication (Paper III).

Table 5.1 Examples of the DSi trends in freshwater and marine ecosystems.

Area	DSi, [μM]	Trend, [μM yr^{-1}]	Change, [% yr^{-1}]	Time period	Reference
Lake Michigan	38 to 3 (summer min)	- 2.3	-11.4	1955 – 1970	Conley *et al.* (1993) and references therein
	85 to 25 (winter max)	- 4.0	-7.3		
Lake Michigan (the city of Chicago)	80 to 100, in 1926	-1.6	-3.4	1926 – 1970	Officer and Ryther, (1980) and references therein
	17, in 1955				
	2.5, southern basin in 1970				
	4.3, northern basin				
Black Sea					Yunev *et al.* (2007)
1. Dnepr, S. Bug and Dnestr Rivers	26.4 to 9.0	-0.74	-4.2	1963 – 1986	
2. Danube River	41.3 to 6.0	-1.38	-5.8	mid-1960s to 1985 – 1993	
3. Bulgarian coastal zone	38.0 to 5.9	-1.51	-6.9	mid-1960s to 1984 – 1995	
Northern Gulf of Mexico	8.97 to 5.34	-0.12 – -0.15	-1.9	1960[1] to 1985 – 1991	Justić *et al.* (1995a)

Table 5.1 (continued).

Baltic Sea	Annual mean, depth 0 – 20 m	Annual trends	1968 – 1986	Sandén et al. (1991)
1. BB[2]	19.6	- 0.82	-4.2	
2. BS[3]	16.8 and 14.25	- 0.76 and - 0.57	-4.5 and -4.0	
3. BP[4]	12.3 – 12.65	- 0.40 – -0.45	-3.1 – -3.6	
Baltic Sea	Winter mean, depth 0 – 20m	Winter trends	1970 – 2001	Paper I
1. BS[5]	15.6	-0.14 (p $\leq$ 0.1)[6]	-0.9 and -1.1	
2. BP	12.6 – 17.3	-0.13 – -0.34	-1.6 – -2.0	
3. GF (mouth of the Gulf)	11.8	-0.30	-2.6	
Baltic Sea	Annual mean, depth 0 – 20 m	Annual trends	1970 – 2001	Paper I
1. BS	12.2 and 12.0	-0.27 and - 0.34	-2.2 and -2.8	
2. BP	9.6 – 12.6	-0.12 – -0.26	-1.0 – -2.6	
3. GF (mouth of the Gulf)	10.2	-0.18	-1.8	

[1] Reconstructed data.
[2] DSi concentrations and DSi trends are for monitoring stations in the southern Bothnian Bay.
[3] DSi concentrations and DSi trends are for monitoring stations in the northern Bothnian Sea and at the monitoring station SR5.
[4] Monitoring stations in the Northern Central and Western Gotland basins.
[5] DSi concentration and DSi trend are for the monitoring station US5B.
[6] At US5B monitoring station, trends are not significant at p $\leq$ 0.05.

5.1.1 Decrease in DSi concentrations – effects of eutrophication and reduced DSi loads

Decreasing DSi trends are generally coupled with eutrophication within watersheds and within the water body itself, and with hydrological regulations that have reduced the DSi load (Paper I; Humborg *et al.*, 2008; Paper III). Eutrophication within water bodies causes DSi depletion in the water column and raises accumulation rates in sediments. This is also found in the Baltic Sea, and the negative trends of DSi follow the increasing trends of inorganic nitrogen and phosphorus (Paper I). However, the nitrogen and phosphorus inputs seem to have stabilised and even declined during the 1980s, while the DSi load remained relatively constant. This may also have contributed to the stabilisation or reversal of the DSi trends since the early 1990s.

Construction of water reservoirs for water resource regulation usually changes the hydrological regime and increases the water residence time. Dam construction may transform rivers into lakes, creating conditions that are favourable for phytoplankton growth. In case of diatoms, these conditions promote the sedimentation and trapping of diatom frustules in sediments. Hydrological alterations that influence DSi loads have been reported, for example, for the Aswan Dam (Van Bennekom and Salomons, 1980), the Black Sea (Humborg *et al.* 1997) and Finnish and Swedish rivers discharging into the Gulf of Bothnia (Conley *et al.*, 2000; Humborg *et al.*, 2000). Humborg *et al.* (2008) suggested that the riverine DSi loads to the Baltic Sea declined by 30 to 40% during the last century. This decrease is attributed not only to eutrophication and retention of nutrients in lakes and reservoirs, but also to changes in the hydrological regime of the river basins, which have reduced riverine water interactions with the surrounding soil/bedrock minerals.

5.1.2 Role of vertical stability of the water column in stabilising DSi concentrations

Two other factors likely to affect the DSi concentrations in the water column are salt water intrusion and the strength of the halocline. The vertical distribution of DSi in the water column largely follows the salinity distribution. The 1980s and 1990s were characterised by high precipitation (Paper I) and runoff, which reduced salinity in both surface and deep waters (Stigebrandt and Gustafsson, 2007). Coupled with the windy winters in the early 1990s, these conditions weakened the stability of the halocline and increased diffusive fluxes. In 1993, a major inflow of saline water from the North Sea, followed by a number of less significant intrusions in 1994, contributed to a strengthening of the halocline. When the deep water is

replaced during major inflows, older water masses are forced upwards (*ibid.*). These water masses may contain large stocks of silica. To summarise, a less stable halocline and deep water replacement due to the major inflow in 1993/1994 were probably responsible for the observed increase in DSi concentrations (Paper I).

5.2 Inference of Si limitation

5.2.1 Low DSi concentrations in the Baltic Sea

Spatial and temporal DSi limitations are considered in Paper II. Based on the data presented by Egge and Aksnes (1992) and global average estimates, the levels of 2 μM and 4 μM were used in the study reported in Paper II to distinguish sea areas where diatoms may be limited by low levels of DSi. In the Gulf of Bothnia, DSi concentrations remained at a high level (≥ 25 μM in Bothnian Bay and ≥ 10 μM in the Bothnian Sea) throughout the year during the study period, with no signs of DSi limitation. In the Baltic Proper, the occurrence of low DSi concentrations varied during the study period. In total, less than 25% of the recorded DSi concentrations were lower than 2 μM. In the Gulf of Riga the proportion of recorded DSi levels that were ≤ 4 μM decreased from almost 100% in the mid-1980s to less than 10% by the end of 1990s, while the frequency of DSi levels ≤ 2 μM increased until 1996. In the Gulf of Finland the frequency of low DSi concentrations varied, but was generally higher during 1991-1997, peaking at 70% (2 μM < DSi ≤ 4 μM). Examination of the seasonal patterns showed that low DSi concentrations were rare during winter, due to low biological activity, but present more frequently during spring and summer .

Based on the concept of growth limitation by low concentrations, DSi limitation may be anticipated in the Gulf of Riga and Gulf of Finland, while it is less likely in the Baltic Proper. This is consistent with indications of DSi limitation found in diatom morphology reported by Olli *et al.* (2008), because deformed diatom valves were found in the Gulf of Riga, but not in the Gulf of Finland, the Baltic Proper or the Kattegat. Evidence of Si-limited diatom growth in the Gulf of Riga has also been reported by Yurkovskis *et al.* (1999) and Yurkovskis (2004).

5.2.2 Limitation patterns and trends based on nutrient ratios

Changes in Si:N:P ratios that have been observed in many coastal areas have been regarded as ecosystem responses to alterations in the ratios of riverine nutrient loads and to eutrophication of coastal waters. For example, low Si:N ratios, indicative of potential nutrient limitation of diatom growth, have been recorded in the Gulf of Mexico which receives discharge from the Mississippi river (Dortch and Whitledge, 1992). Smayda (1990) presented evidence that decreases in Si:N and Si:P ratios were associated with more frequent and extensive harmful algal blooms in coastal waters worldwide (Baltic Sea, Kattegat, Skagerrak, Dutch Wadden Sea, North Sea and Black Sea). Turner *et al.* (1998) examined the impact of changes in nutrient ratios (decrease in the DSi:DIN ratio from 3:1 to less than 1:1) on the structure of a coastal food web supported by diatoms in the Mississippi continental shelf. These authors concluded that the abundance of copepods decreased while the proportion of flagellates increased. Such ratio fluctuations may also influence the diatom-zooplankton-fish food web (Turner *et al.,* 2003).

In the Baltic Sea, both nitrogen and phosphorus are considered to be limiting nutrients, but for different basins and seasons. The primary production in pelagic regions is mainly N-limited (HELCOM, 2002), but the limitation patterns may differ in proximity to freshwater sources (Pitkänen and Tamminen, 1995). A good supply of phosphorus (due to decades of sediment loading) is assumed to be the main reason for the huge cyanobacteria blooms that occur in the Baltic Proper (Lignell *et al.*, 2003; Nausch *et al.*, 2004). Winter DIN:DIP ratios during the period 1970 to 2001 ranged from 8:1 to 13:1 in the open Baltic Proper and from 2 to 18:1 in the Gulf of Finland (Paper II). These low ratios suggest that spring blooms following initial diatom blooms were likely to have been N-limited. In summer, the patterns can change from potential nitrogen limitation to phosphorus limitation due to the nitrogen fixation by cyanobacteria (HELCOM, 2002; Hansson and Håkansson, 2007). The Kattegat-Belt Sea area is potentially N-limited in its open parts and P-limited in the bights and estuaries (Ærtebjerg *et al.,* 1998). Also, the Bothnian Bay is considered to be P-limited (Andersson *et al.*, 1996; Tamminen and Andersen, 2007; Paper II). In the Bothnian Sea the N:P ratio varies depending on season and is typically in the range (6 - 23):1. Areas close to the Swedish coast are N-limited, while those in the vicinity of the Finnish coast are P-limited (Rönnberg, 2001; Lehtoranta *et al.*, 2008). In the Gulf of Riga, DIN:DIP ratios (>24:1) are indicative of potential phosphorus limitation for phytoplankton production during late spring and the entire summer, while during the rest of the year the ratios are (8-15):1 (Paper II). In addition,

together with the decreasing DSi concentrations, DSi:DIP ratios are indicative of silica limitation in early spring and autumn (Paper II).

The seasonal and annual nutrient ratio trends were evaluated for the period 1970 to 2001 (Paper II). In the Baltic Proper most of the trends were detected in winter, and the DSi:DIN ratio annual trends ranged from -0.08 to -0.17 $\mu M\ yr^{-1}$ (Table 5.2). For the DSi:DIP ratios, the trend slopes ranged from - 0.48 to -1.03 $\mu M\ yr^{-1}$ (Table 5.2), with the largest number of trends found during winter. The trends were relatively similar throughout the Baltic Proper, while no significant temporal trends were found in the two Gulfs.

Table 5.2 Annual and winter season (January – March) ratio trends (1970 – 2001).
The numbers represent the statistically significant slopes *($\alpha = 0.05$)*;
n.s denotes that no significant trends could be detected.

Trends / Basin	DSi:DIN		DSi:DIP		DIN:DIP	
	Annual	*Winter*	*Annual*	*Winter*	*Annual*	*Winter*
Baltic Proper						
north – western	**-0.08 − -0.17**	**-0.12 − -0.93**	**-0.48 − -1.03**	**-0.52 − -0.74**	**0.05 and 0.11**	**0.08 − 0.15**
south – eastern	**-0.08**	**-0.10 and -0.16**	**-0.69 and -0.75**	**-0.58 and -0.83**	*n.s.*	*up to* **0.08**
Gulf of Finland	**-0.10**	**-0.06**	*n.s.*	*n.s.*	*n.s.*	*n.s.*
Gulf of Riga	**0.07**	*n.s.*	*n.s.*	*n.s.*	**-2.64**	*n.s.*
Bothnian Sea						
northern	**-0.18**	**-0.11**	**-4.30**	*n.s.*	*n.s.*	*n.s.*
southern	**-0.27**	*n.s.*	**-6.45**	*n.s.*	*n.s.*	*n.s.*
Bothnian Bay	*n.s.*	*n.s.*	*n.s.*	*n.s.*	**2.40**	*n.s.*

In the Bothnian Sea, there were large declines in both the DSi:DIN and DSi:DIP ratios during spring. For the DIN:DIP ratios, the trends showed substantial variation between basins (Table 5.2). Furthermore, stations in the Baltic Proper demonstrated positive trends during winter and negative trends during both spring and autumn. To conclude, the DSi:DIN and DSi:DIP ratios remain well above the balanced nutrient composition for diatoms in all basins, except the Gulf of Riga. However, the negative ratio trends found at several locations during winter indicate that the following productive period may not have been favourable for diatoms.

5.3 Si budget

Generally, DSi has a shorter residence time than its hydraulic counterpart, implicating the importance of internal processes related to the non-conservative behaviour of silicon. The residence time of DSi in the world ocean is approximately 16000 years (Sarmiento and Gruber, 2006). In the Baltic Sea (calculated at the outer border of the Arkona basin), it is approximately 20 years for water and 11 years for DSi (Paper IV). The basin-wise DSi residence times range from less than 2 months to more than 3 years (Table 3 in Paper IV). The large differences between basins are attributed to basin-specific characteristics, such as the presence of sills restricting water exchange, the intensity of water flow, hydrochemical and ecological properties (such as the amount of phytoplankton production), riverine loads and the magnitude of the internal Si sinks/sources.

5.3.1 DSi sinks

In the oceanic Si budget created by Tréguer *et al.* (1995), the silica removal rate in estuaries was set to ~10% of the DSi riverine flux. However, considerable amounts of Si are often removed in water bodies representing proximal zones of the coastal ocean (including large bays, the open water part of estuaries, deltas, inland seas, and salt marshes). Examples of such areas are the Rhine river estuary and Chesapeake Bay, where Si removal rates are 50% (van Bennekom *et al.,* 1974) and more than 40% (Conley and Malone, 1992), respectively. In contrast, the net estuarine silica removal in the Amazon shelf is only 4% (DeMaster, 2002 and references therein). In a recently developed model of the global Si cycle by Laruelle *et al.* (2009) a removal of 20% was applied.

For the Baltic Sea, the DSi removal during the study period, 1980-2000, was ~70% (or ~1.5 g Si m^{-2} yr^{-1} calculated as the silica sink divided by surface area of the water body) of the total DSi riverine load (Paper IV). The higher removal rate in the Baltic Sea compared to other areas is attributed to its semi-enclosed character and eutrophic conditions. Within the Baltic Sea, the semi-enclosed basins also act as efficient Si traps, with removal rates of 2.0, 4.9 and 2.8 g Si m^{-2} yr^{-1} in the Gulf of Bothnia, the Gulf of Finland and the Gulf of Riga, respectively. In contrast, much lower removal rates have been reported for open areas; for example, Northern Central/Western Gotland basin (1.2 g Si m^{-2} yr^{-1}), Eastern Gotland/Bornholm basin (0.2 g Si m^{-2} yr^{-1}) and Kattegat (0.6 g Si m^{-2} yr^{-1}). The Arkona is a small and shallow basin,

which has insignificant internal DSi sources, intensive and highly variable through-flow not favouring a high deposition rate.
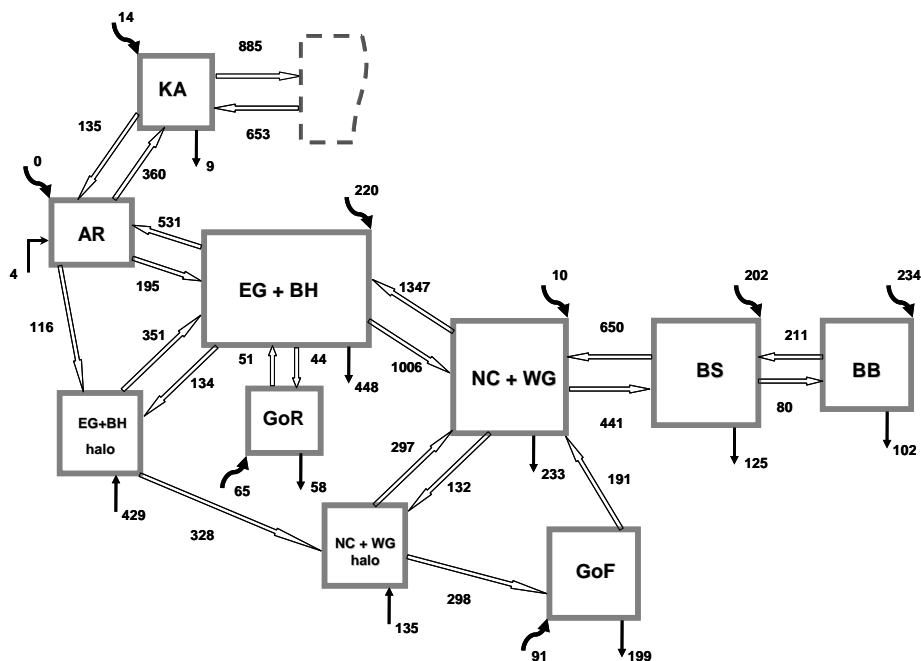

Figure 5.1 The annual budget of dissolved silica averaged for the period 1980-2000. All numbers are in kt Si yr^{-1}. The straight arrows between boxes (without shading) represent silica fluxes. The curved arrows directed into the boxes (black shading) represent riverine silica loads. The straight arrows directed in and out of the boxes (black shading) represent silica sources and sinks, respectively.

The surface waters of the Baltic Proper comprise a substantial Si sink, largely compensated by high Si "sources" in deep water (Fig. 5.1). The DSi "sources" in the boxes below the halocline of the Baltic Proper (Paper IV) is assumed to be due to the export of BSi from the deep boxes and biogeochemical processes. Large anoxic/hypoxic areas are present in the Eastern Gotland basin. Berelson *et al.* (1987) and Belias *et al.* (2007) suggested that silica fluxes from sediments might be larger at times of low oxygen conditions. This is supported by Bauerfeind and Bodungen (2006), who postulated that anoxic conditions may account for the dissolution rates of biogenic silica being higher in the Baltic Sea (the Eastern Gotland basin)

than in the North Atlantic. A similar effect of anoxia on the DSi content in bottom waters of the Kiel Bight was reported by Bodungen (1986). Also, Spilling and Lindström (2008) observed an increased DSi flux out of sediment under anoxic conditions in an experimental study.

Other factors known to influence the dissolution rates of BSi are salinity, temperature and pH (Hurd, 1983; Spencer, 1983; Van Cappellen and Qiu, 1997). Therefore, the conditions in the central and southern Baltic Proper, where water is both warmer (Fonselius and Valderrama, 2003) and more saline than in the northern parts, are potentially favourable for BSi dissolution. In addition, bacterial activity may facilitate the dissolution process by increasing pH on a micro-environmental scale (Spencer, 1983) and accelerating removal of the organic layer covering the diatom shells (Bidle *et al.,* 2003).

The total Si sink in the Baltic Sea, excluding the Kattegat, amounted to approximately 600 kton Si yr^{-1} from 1980 to 2000 (Paper IV). Estimates of Si accumulation based on sediment core data are approximately 1070 kton Si yr^{-1} (Paper III). To obtain a retrospective estimate of DSi levels at the beginning of 20th century, a Si budget was reconstructed (Paper III). The contemporary Si retention was ~ 70% (Paper IV), corresponding to a three-fold increase compared to the beginning of the 20th century (Paper III).

5.3.2 Diatom export production

In a study of diatom production under Si- and N-limitation, Harrison *et al.* (1977) found that the elemental composition of diatom cells depended on the type of limitation and algal species considered. Under nitrogen limitation the Si:C diatom ratios were similar to, or higher than, those obtained for non-limited cells, while diatoms grown under Si-limited conditions exhibited significantly lower Si:C ratios. The amount of carbon taken up by diatoms can be estimated from the amount of silica sinking out of surface waters by applying a Si:C ratio of 0.13 (Brzezinski, 1985). This provides estimates of diatom export production of 9 g C m^{-2} yr^{-1} for the Northern Central/Western Gotland basin and 13 g C m^{-2} yr^{-1} for the Eastern Gotland/Bornholm basin. The upper boxes of these basins encompass the upper 60 m of the water column. Therefore, the estimated export production will be influenced by the amount of silica dissolved below the euphotic zone and the amount released from sediments in shallow areas. An overall estimate of the net export production in the Baltic Proper presented by Pers and Rahm (2000) was in the range of 26 to 60 g C m^{-2} yr^{-1}. These estimates not only include

diatom primary production, but also the production by other phytoplankton. It implies that the diatom export production for the entire Baltic Proper accounts for ~ 19 to 44% of the net production that is exported (Paper IV). These values are within the range reported for the world ocean, where diatoms are responsible for 20 to 90% of organic matter export (Sarmiento and Gruber, 2006). According to Heiskanen and Tallberg (1999), the share of the total net primary production lost in the pelagic system due to sedimentation ranges between 30 and 48%. Lignell *et al.* (1993) found that approximately 70% of the primary production sinks out of the euphotic zone. This higher estimate is for the vernal production which is dominated by large and rapidly sinking algal cells, while the estimates presented in Paper IV correspond to the annual primary production involving phytoplankton other than diatoms to a greater degree than during spring**.**

5.3.3 Changes in phytoplankton communities in the Baltic Sea: dinoflagellates vs. diatoms

Both diatoms and dinoflagellates dominate the spring plankton bloom in the Baltic Sea (Cederwall *et al.*, 1992; Blomqvist and Heiskanen, 2001) and shifts in phytoplankton communities have been observed in long-term data sets (HELCOM, 2006). In recent decades several studies have reported that dinoflagellates have become more abundant in spring in various parts of the Baltic Sea (Rahm *et al.*, 1996; Kuparinen and Tuominen, 2001; Wasmund and Uhlig, 2003).

For the time period 1979 to 1998 the phytoplankton biomass has increased in spring in the central and western Baltic Proper (HELCOM, 2002). This increase is mainly related to the biomass of dinoflagellates, and is attributed to changes in climatic conditions and stratification patterns (Heiskanen, 1998; Wasmund *et al.*, 1998; Spilling, 2007; Toming and Jaanus, 2007). In the northern Baltic Proper the total mean biomass has decreased by 50%, mostly due to the reduction in the diatom biomass (HELCOM, 2002). In the Gulf of Riga, the proportion of diatoms decreased between 1994 - 1998 compared with 1980 - 1993, due to silicate deficiency in spring, while that of dinoflagellates have increased (HELCOM, 2002). It is likely that diatoms became less important contributors to primary production over this period. Previous studies (*e.g.* Wasmund *et al.*, 1998; Wasmund and Uhlig, 2003) have reported a decline in the diatom abundance and biomass in the eastern and southern Baltic Proper, while dinoflagellates have generally prospered.

5.4. Optimised budget modelling

Different methods, including solving the system of linear algebraic equations by Gauss elimination and optimisation techniques, were used to develop the time-dependent box model based on inverse modelling. These methods were tested and evaluated using an artificial data set, and then applied to the data from the Gulf of Bothnia. The Gauss elimination and optimisation by minimising salinity differences performed well, regardless of the model structure (3 or 4 boxes). When both water flows and salinity differences were minimised, there was a significant improvement in the agreement between generated and modelled flows at high values of the weight coefficient at salinity differences (Paper V).

When applied to the time-dependent model in the Gulf of Bothnia, only the optimisation technique proved able to handle a 'typical' inverse modelling problem; the lack of physically meaningful solutions (which can be attributed to the uncertainties resulting from data deficiencies, especially in the salinity time series of the Archipelago Sea).

5.4.1 Water exchange of the Gulf of Bothnia

As shown by results from water exchange models for the Gulf of Bothnia compiled in Table 5.3, the flows presented in Paper V are within the range of flows reported in previous studies, which vary depending on the modelling method applied and time period considered. Modelling results obtained by the applied solution methods (4 box model) are presented in Table 5.4. For the Bothnian Bay, the calculated inflow and outflow were in the ranges of 162 to 172 km^3 yr^{-1} and 282 to 291 km^3 yr^{-1}, respectively. The main route to and from the Bothnian Sea is via the Åland Sea, for which estimates given in Paper V (outflow of 1612 to 2182 km^3 yr^{-1} and inflow of 1330 to 1902 km^3 yr^{-1}). Most of this outflow is further transported into the Baltic Proper (1324 to 1362 km^3 yr^{-1}). The inflow from the Baltic Proper is mainly via the Åland Sea (1042 to 1081 km^3 yr^{-1}) and only a minor inflow occurs via the Archipelago Sea (ca. 40 km^3 yr^{-1}). This is then transported to the Bothnian Sea (ca. 50 km^3 yr^{-1}).

Table 5.3 Compilation of the results of the water exchange modelling for the Gulf of Bothnia obtained in the different studies and for different time periods.

1. Paper IV, the study period is 1980 – 2001; the Åland and Archipelago Seas are included in the Bothnian Sea basin. **2**. Wulff and Stigebrandt (1989); 1977-1981. **3**. Wulff et al. (1994); 1991; Åland and Archipelago Seas are included in the Bothnian Sea basin; flows are from figures presented in this article. **4**. Carlsson (1998); 1979-1987; only the Åland Sea is considered. **5**. Savchuk (2005); 1991-1999. **6**. Omstedt and Axell (2003); 1980-1998; the Åland and Archipelago Seas are included in the Bothnian Sea basin. **7**. Wulff et al. (2001); 1971-1990; with transition zones between the adjacent basins. **8**. Algesten et al. (2006); 1971-1990; salinity stocks as in Wulff et al. (2001), but without transition zones. **9**. Myrberg and Andrejev (2006); the water exchange between the Gulf of Bothnia and the Baltic Proper using a 3-D numerical model.

Basin [6]	Present study [1]	Present study [2]	1	2	3 [3]	4 [4]	5	6	7	8	9 [5]
BB → BS	282	282	272	280	280	373	290	524	319	424	
BS → BB	163	162	162	176	176	273	173	404	209	255	
BS → BP	1369	1362	1324	1400	1400	694	1237	2201	1223	990	3648
BP → BS	1124	1118 (1080+38)	1101	1191	1191	501	1009	1955	1000	770	3480

Flows, km³ yr⁻¹

[1] Water flows correspond to the time-depended model formulated and solved by minimising differences between modelled and observed salinities; smoothed data; 3 box structure.

[2] The solution method is the same as in [1]; smoothed data; 4 box structure.

[3] Water flows in figures are in km³ month⁻¹.

[4] Flows through the Northern Quark and the Åland Sea.

[5] The magnitude of flows depends on the method of summarising.

[6] The Åland and Archipelago Seas are included in the Bothnian Sea basin.

Table 5.4 Comparison of results of the applied solution methods (4 box model) - water flows[1] presented as annual averages.

System of linear algebraic equations:	Flows, km^3 yr^{-1}							
	BB→BS Q$_{12}$	BS→BB Q$_{21}$	BS→ÅL Q$_{23}$	ÅL→BS Q$_{32}$	Arch→BS Q$_{42}$	ÅL→NBP Q$_{35}$	NBP→ÅL Q$_{53}$	NBP→Arch Q$_{54}$
Solving by Gauss elimination	*Unsmoothed data*							
Steady-state	215	130	1958	1732	48	1178	950	40
Time-dependent	301	175	1844	1475	102	1295	921	88
Optimisation of water flows and salinity differences	*Unsmoothed data*							
W$_S$=1	125	5	271	11	25	276	14	17
W$_S$=10 000 000	291	172	1612	1330	47	1333	1048	39
Optimisation of water flows and salinity differences	*Smoothed data*							
W$_S$ = 1	123	4	268	10	23	273	13	16
W$_S$ = 10 000 000	287	167	1613	1332	45	1324	1042	38
Optimisation of salinity differences	*Unsmoothed data*							
	287	167	2101	1819	47	1366	1081	39
Optimisation of salinity differences	*Smoothed data*							
	282	162	2182	1902	45	1362	1080	38

[1] At each time step (except the first one), the optimisation process is started with optimised salinities obtained at previous time step.

Application of the optimisation approach to the Gulf of Bothnia model resulted in water flows with considerable variation. Smoothing of the salinity and riverine input data improved the model performance with regard to the variation (Table 5.5), something seen in the previous study by Wulff *et al.* (1994). This procedure may, however, introduce difficulties related to the evaluation of the optimal level of smoothing. Hence, the level of smoothing was kept to a minimum. With regard to the flow magnitude and flow distribution the results demonstrate similar patterns for the smoothed and unsmoothed input data (Table 5.4). The variation in the unsmoothed salinity time series is relatively low compared to the variation found in the unsmoothed river data. It is therefore reasonable to assume that the smoothing of the river data contributed to the decreased variation in the results to a larger extent.

Table 5.5 Comparison of results of the applied solution methods (4 box model) - coefficients of variation of monthly water flows[1] .

System of linear algebraic equations:	Coefficient of variation, %							
	BB → BS Q12	BS → BB Q21	BS → ÅL Q23	ÅL → BS Q32	Arch → BS Q42	ÅL → NBP Q35	NBP → ÅL Q53	NBP → Arch Q54
Solving by Gauss elimination	*Unsmoothed data*							
Steady-state	30	30	27	28	79	27	28	81
Time-dependent	53	70	54	59	85	53	57	100
Optimisation of water flows and salinity differences	*Unsmoothed data*							
$W_S = 1$	76	351	84	280	119	86	270	234
$W_S = 10\,000\,000$	110	178	37	46	197	39	39	234
Optimisation of water flows and salinity differences	*Smoothed data*							
$W_S = 1$	69	372	82	296	120	84	283	242
$W_S = 10\,000\,000$	53	73	21	28	92	29	21	88
Optimisation of salinity differences	*Unsmoothed data*							
	112	184	58	67	198	55	64	235
Optimisation of salinity differences	*Smoothed data*							
	55	74	51	56	92	50	53	88

[1] At each time step (except the first one), the optimisation process is started with optimised salinities obtained at previous time step.

5.4.2 Model characteristics

Andrejev *et al.* (2004) criticised box modelling on the basis that it does not provide sufficient information about water renewal and exchange compared to 3-D models. This critique is justified in many ways. Process-orientated models with high spatial and temporal resolution can provide outputs that cannot be produced by box models (Müller and von Storch, 2004). Inverse box modelling in marine systems usually employs conservative state variables, such as the total amount of salinity within basins and the corresponding net freshwater discharge, to estimate the transport between adjacent basins. Furthermore, spatially distributed variable fields are difficult to manage without a significant increase in the number of boxes. This requires precise salinity data that are rarely available for this type of modelling. On the other hand, 3-D models also have shortcomings as the key processes, such as deep water mixing, are still not fully understood. They require intensive calculations and extensive data arrays. In addition, the results obtained by 3-D hydrodynamic models are not infrequently aggregated in order to fit them to lower resolution biogeochemical models (e.g. Lacroix *et al.*, 2004; Lancelot *et al.*, 2005). This offsets the advantages of 3-D models with high spatial resolution and provides a good reason to try to improve box models. It is also important to ensure that any selected model is appropriate for addressing the questions posed, and in this respect it should be noted that the applicability of 3-D and box models may differ depending on the spatial and temporal resolution required. For these reasons, the budget estimates and the inverse box modelling are still important tools when attempting to understand various coastal ecosystems and oceanic processes (*e.g.* Crossland *et al.*, 2005; Wunsch, 1996).

6. Conclusions

The results presented and discussed in this thesis provide new information on spatial and temporal changes in DSi concentrations and nutrient ratios in the Baltic Sea. The analyses of DSi fluxes and internal DSi sinks/sources revealed basin-wise patterns with regard to silica cycling. The Gulfs of Finland and Riga, together with the northernmost basins, the Bothnian Bay and Bothnian Sea, are distinguished from other areas in the Baltic Sea by having substantially higher rates of silica removal. The Arkona basin and Kattegat act mainly as regions of rapid through-flow. The Baltic Proper has low silica accumulation rates, despite high total primary production. This may be attributed to the impact of its relatively high salinity, relatively mild climate and anoxic conditions in deep water.

Declining DSi trends were found between 1970 and 2001, which are mainly attributable to the ongoing eutrophication within the Baltic Sea since no major changes in the riverine DSi load occurred during this period. This is supported by increases in the trends of inorganic nitrogen and phosphorus. These trends also have implications for the nutrient ratios, DSi:DIN and DSi:DIP, which are important indicators of the state of an ecosystem. The DSi levels stabilised during the last decade of the 20th century, but the DSi "situation" can not be considered unproblematic as eutrophication continues in this vulnerable water body.

The occurrence of DSi concentrations close to levels considered as potentially limiting has been revealed for some regions. While DSi concentrations are still high in the Bothnian Bay and Bothnian Sea, they have fallen close to or below critical levels in other areas. Several basins, such as the Gulfs of Riga and Finland and even the Baltic Proper, may be at risk of developing Si limitation if the decrease in DSi concentrations persists. This may, in turn, influence the entire ecosystem since Si depletion may inhibit the growth of diatoms, re-shape the phytoplankton community and modify species dominance in favour of non-siliceous phytoplankton. These alterations in food chains may lead to reductions in the abundance of valuable commercial fish populations that feed on diatom-grazing zooplankton.

From a longer perspective, the decrease in DSi is related to both eutrophication and anthropogenic perturbations in the catchment. In fact, the retrospective DSi budget indicates that the DSi concentrations before major hydrological alterations and eutrophication were approximately twice the present concentrations.

Finally, a time-dependent water budget of the Gulf of Bothnia, based on inverse modelling, was developed to estimate monthly water flows between 1990 and 2000. Employed solution techniques were initially tested and evaluated on an artificial data array to facilitate the comparisons. The results obtained show that the optimisation technique was capable of overcoming difficulties often encountered when dealing with time-dependent inverse salinity models, such as negative or too high water flows between adjacent basins.

The results of this study contribute to a greater understanding of the changes in Si cycling during the 20th century. The results show that the Baltic Sea has changed from a water body with sufficient DSi levels to support diatom production, to one that may experience Si limitation. This Si depletion is a warning sign that ongoing anthropogenic activities may have profoundly damaging effects, not only within the Baltic Sea region, but also in other areas where human influence on aquatic environments is altering Si concentrations.

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