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The Carbon Dioxide System
in the Baltic Sea Surface Waters

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Abstract

The concentration of carbon dioxide (CO_2) in the atmosphere is steadily increasing because of human activities such as fossil fuel burning. To understand how this is affecting the planet, several pieces of knowledge of the CO_2 system have to be investigated. One piece is how the coastal seas, which are used by people and influenced by industrialization, are functioning. In this thesis, the CO_2 system in the Baltic Sea surface water has been investigated using observations from the last century to the present. The Baltic Sea is characterized of a restricted water exchange with the open ocean and a large inflow of river water.

The CO_2 system, including parameters such as pH and partial pressure of CO_2 (pCO_2), has large seasonal and inter-annual variability in the Baltic Sea. These parameters are affected by several processes, such as air–sea gas exchange, physical mixing, and biological processes. Inorganic carbon is assimilated in the primary production and pCO_2 declines to ~150 µatm in summer. In winter, pCO_2 levels increase because of prevailing mineralization and mixing processes. The wind-mixed surface layer deepens to the halocline (~60 m) and brings CO_2-enriched water to the surface. Winter pCO_2 may be as high as 600 µatm in the surface water. The CO_2 system is also exposed to short-term variations caused by the daily biological cycle and physical events such as upwelling. A cruise was made in the central Baltic Sea to make synoptic measurements of oceanographic, chemical, and meteorological parameters with high temporal resolution. Large short-term variations were found in pCO_2 and oxygen (O_2), which were highly correlated. The diurnal variation of pCO_2 was up to 40 µatm.

The CO_2 system in the Baltic Sea changed as the industrialization increased around 1950, which was demonstrated using a coupled physical-biogeochemical model of the CO_2 system. Industrialization involved an increased nutrient load with eutrophication as a result. With more nutrients, primary production increased and amplified the seasonal cycle. Model results indicate that the Baltic Sea was clearly a source of atmospheric CO_2 before 1950, and with eutrophication CO_2 emissions decreased. The increased nutrient load may have counteracted the pH drop that otherwise would have been caused by the overall increase in atmospheric CO_2. Observations from the period 1993-2009, indicate that the central Baltic Sea was a net source of atmospheric CO_2 while Kattegat was a net sink.

Total alkalinity (A_T) is higher in the south-eastern Baltic Sea than in the northern parts, these differences are attributed to river runoff and geology in the drainage area. River runoff entering the south-eastern Baltic Sea drains regions rich in limestone, which have been exposed to long-term weathering. Weathering of limestone contributes to an increased A_T. The analyze of historical data indicated that during the last century, A_T increased in the river water entering the Gulf of Finland while decreasing in rivers entering the Gulf of Bothnia.

Key words: Baltic Sea, carbon dioxide, pCO_2, total alkalinity, pH, air-sea gas exchange, inter-annual, seasonal.

Preface

This thesis consists of a summary (Part I) and the following appended papers (Part II), which are referred to by their roman numerals.

Paper I:
Sofia Hjalmarsson, Karin Wesslander, Leif G. Anderson, Anders Omstedt, Matti Perttilä, Ludger Mintrop, 2008. Distribution, long-term development and mass balance calculation of total alkalinity in the Baltic Sea. *Continental Shelf Research*, 28, 593-601.

Paper II:
Karin Wesslander, Anders Omstedt, Bernd Schneider, 2010. Inter-annual and seasonal variations of the air–sea CO_2 balance in the southern Baltic Sea and the Kattegat. *Continental Shelf Research*, 30, 1511-1521

Paper III:
Karin Wesslander, Per Hall, Sofia Hjalmarsson, Dominique Lefevre, Anders Omstedt, Anna Rutgersson, Erik Sahlée, Anders Tengberg, 2011, Observed carbon dioxide and oxygen dynamics in a Baltic Sea coastal region. *Journal of Marine Systems*, 86, 1-9.

Paper IV:
Anders Omstedt, Erik Gustafsson, Karin Wesslander, 2009. Modelling the uptake and release of carbon dioxide in the Baltic Sea surface water. *Continental Shelf Research*, 29, 870-885.

Paper I was initiated by Anderson and Omstedt and the paper is a result of many interdisciplinary discussions. Wesslander was responsible for the box model calculations.

In paper II, Wesslander made most of the analysis, wrote most of the paper and handled the revisions.

Paper III was initiated by Wesslander and Omstedt. Wesslander planned much of the expedition and made analysis of nutrients on board. Interpretations of data were made jointly of all authors and Wesslander wrote the final paper and handled the revisions.

In paper IV, Wesslander was contributing with the first stage of the biogeochemical model and also with the verification data on CO_2 parameters. Omstedt and Gustafsson finalised the paper while Wesslander was on maternity leave.

Contents

Part I

Summary

1 Introduction

Since the beginning of the industrial era, the atmospheric level of carbon dioxide (CO_2) has steadily increased because of human activities such as fossil fuel burning (IPCC, 2007). When atmospheric CO_2 enters the ocean, it dissolves into a weak acid and changes the equilibrium between the dissolved inorganic carbon species, the total CO_2 (C_T). The oceanic acid balance becomes perturbed, which results in the lowering of the pH - a process termed ocean acidification (e.g., Doney et al., 2009). The average ocean surface water has already dropped 0.1 pH units, which is attributable to an anthropogenic increase in CO_2 levels (Caldeira and Wickett, 2003). Because of its solubility and chemical reactivity, CO_2 is effectively taken up by the ocean. In fact, the oceanic carbon inventory is 60 times larger than the atmospheric inventory, indicating that the ocean plays an important role in controlling atmospheric CO_2 levels.

As a consequence of changing CO_2 levels, the atmosphere and ocean are in imbalance with each other. To compensate for this and strive to achieve balance, a constant air–sea gas exchange is going on. The CO_2 balance between the atmosphere and the ocean is driven mainly by the CO_2 partial pressures (pCO_2) in the atmosphere and the ocean. Superimposed on the anthropogenic increase in atmospheric pCO_2, is the variation due to seasonality in terrestrial vegetation. This is relatively small when compared with the seasonal variation in the oceanic pCO_2, which is controlled by changes in C_T, pH, total alkalinity (A_T), temperature, and salinity. Variations of these properties are caused by interacting biological, physical, and chemical processes, such as primary production/respiration, mixing, and the formation/dissolution of calcium carbonate ($CaCO_3$). The last process is important, for example, for A_T, which is defined as the excess of bases (e.g., carbonate ions, CO_3^{2-}) over acids (e.g., hydrogen ions, H^+). A_T may be regarded as a key parameter of the CO_2 system, since it is a measure of the ability of the water to neutralize acids. This means that seawater with high A_T can better resist pH changes caused by perturbed atmospheric CO_2, as it has a higher buffer capacity. In, for example, weathering of limestone, CO_3^{2-} is produced and increases A_T and the buffer capacity. Weathering processes, however, are relatively slow and can be compared with similar timescales as for the residence time of the water. One may say that the background value of A_T sets the scene for the CO_2 system.

Estimates of global oceanic CO_2 uptake indicate that about one third of the anthropogenic CO_2 emitted to the atmosphere has been taken up by the oceans (Sabine et al., 2004). The globally most important regions for atmospheric CO_2 uptake are the temperate zones in both hemispheres, and the North Atlantic, which is the major region for deep water formation, while the equatorial zones are the most important CO_2 source areas (e.g., Takahashi et al., 2009). These global studies have yielded little information concerning the sea area close to land, the marginal sea. Although the marginal sea covers only a small part, 7%, of the oceanic area, it produces 20% of the total oceanic organic matter (Gattuso et al., 1998). As much as 30% of the ocean CO_2 uptake may originate from the continental shelves (Chen and Borges, 2009), which make these areas important when considering the marine carbon cycle. The marginal seas are complex systems that differ from the global oceans; they are exposed to river input, intense biological processes, upwelling, tides, and exchange with sediments. This implies that their biogeochemical and physical environments are specific to particular regions. The biogeochemical scene is set by, for example, inputs of nutrients and carbon from land and

rivers, while the physical environment determines characteristics such as water exchange and stratification.

Studies of coastal seas in Europe have found large variability in the CO_2 system. Stratified shelf regions, such as the northern North Sea, have been found to be significant CO_2 sinks (Bozec et al., 2005; Prowe et al., 2009; Thomas et al., 2004). Organic material, produced in the surface water during the productive season, sinks through the stratification and is mineralized in the subsurface water. The CO_2-enriched deeper water is finally exported to the adjacent deep ocean, in this case the North Atlantic. This process, which exports carbon from the continental shelves, has been termed the continental shelf pump (Tsunogai et al., 1999). Other coastal sea regions may instead function as CO_2 sources. This is the case with the southern North Sea, which is shallow and mixed year round, production and remineralization taking place in the same water column (Bozec et al., 2005; Prowe et al., 2009; Thomas et al., 2004). Estuaries have also turned out to be CO_2 sources due to inputs of terrestrial organic carbon (Borges, 2005; Borges et al., 2005, 2006). In addition, there is a tendency for latitudinal variation, coastal seas at high and temperate latitudes being sinks for atmospheric CO_2, while regions at low latitudes are CO_2 sources (Borges et al., 2005).

The marine environment is exposed to global changes, and the responses of the CO_2 system are not yet fully understood. According to a sensitivity study conducted by Riebesell et al. (2009), pCO_2 will be most strongly affected by changes in carbon withdrawal through biological production and by changes in sea surface temperature, if CO_2 levels continue to rise. This will mainly have implications for the seasonality of the oceanic uptake/release of atmospheric CO_2. Another sensitivity study (Omstedt et al., 2010) demonstrated that the northern parts of the Baltic Sea are more sensitive to rising CO_2 levels because of considerably lower A_T than that of the southern Baltic.

The constituent of this thesis focus on the CO_2 system in the Baltic Sea, a Nordic marginal brackish sea that is semi–enclosed with a limited water exchange. Many of its properties, such as salinity and A_T, have large gradients from south to north. The Baltic Sea is constantly under the influence of natural variations and of the 85 million people who live in the Baltic Sea drainage basin, with eutrophication, over fishing, and pollution being the consequences. Large amounts of nutrients, such as phosphate and nitrate (e.g., HELCOM, 2009; Savchuk and Wulff, 2009), as well as A_T (e.g., Dyrssen, 1993; Hjalmarsson et al., 2008; Beldowski et al., 2010), and total organic carbon (TOC) (e.g., Pettersson et al., 1997; Humborg et al., 2010; Skoog et al., 2011), are discharged via the river waters. Nutrients and CO_2 are stored and transformed in the deep water, which is often depleted in oxygen because of the restricted water exchange.

This thesis is based on Papers I–IV. Paper I examines the distribution of A_T in the Baltic Sea, using a box model to model the A_T in the river water discharging into the Baltic Sea. Paper II, based on observations, deals with the air–sea gas exchange of CO_2 in the Baltic Sea; seasonal to inter-annual variations and annual flux estimates are discussed. A coastal field experiment is presented in Paper III, in which CO_2 and oxygen (O_2) are studied on short-term time scales, while Paper IV models the uptake and release of CO_2 in Baltic Sea surface water.

2 Description of the Baltic Sea

The Baltic Sea, which can be considered a large estuary, is one of the world's largest bodies of brackish water with a total area of 377,500 km^2 and a volume of 21,200 km^3 (inside the entrance).[1] Its drainage area is 1.7 million km^2 and is home to 85 million people. The connection with the open sea is narrow, and extends through the Belt Sea and Öresund with maximum sill depths of only 18 and 8 m, respectively (Figure 2.1). Kattegat, located just outside this entrance area and with a mean depth of 20 m, borders on Skagerak, which connects to the North Sea. The Baltic Sea system can be divided into several sub-basins, namely, the Baltic Proper (including the Arkona and Bornholm basins), Gulf of Riga, Gulf of Finland, Bothnian Sea, and Bothnian Bay, linked by straits, sills, and channels. Bothnian Sea and Bothnian Bay are also called the Gulf of Bothnia. The average depth of the Baltic Sea is 55 m and the maximum depth of 460 m is found at the Landsort Deep, northwest of the island of Gotland.
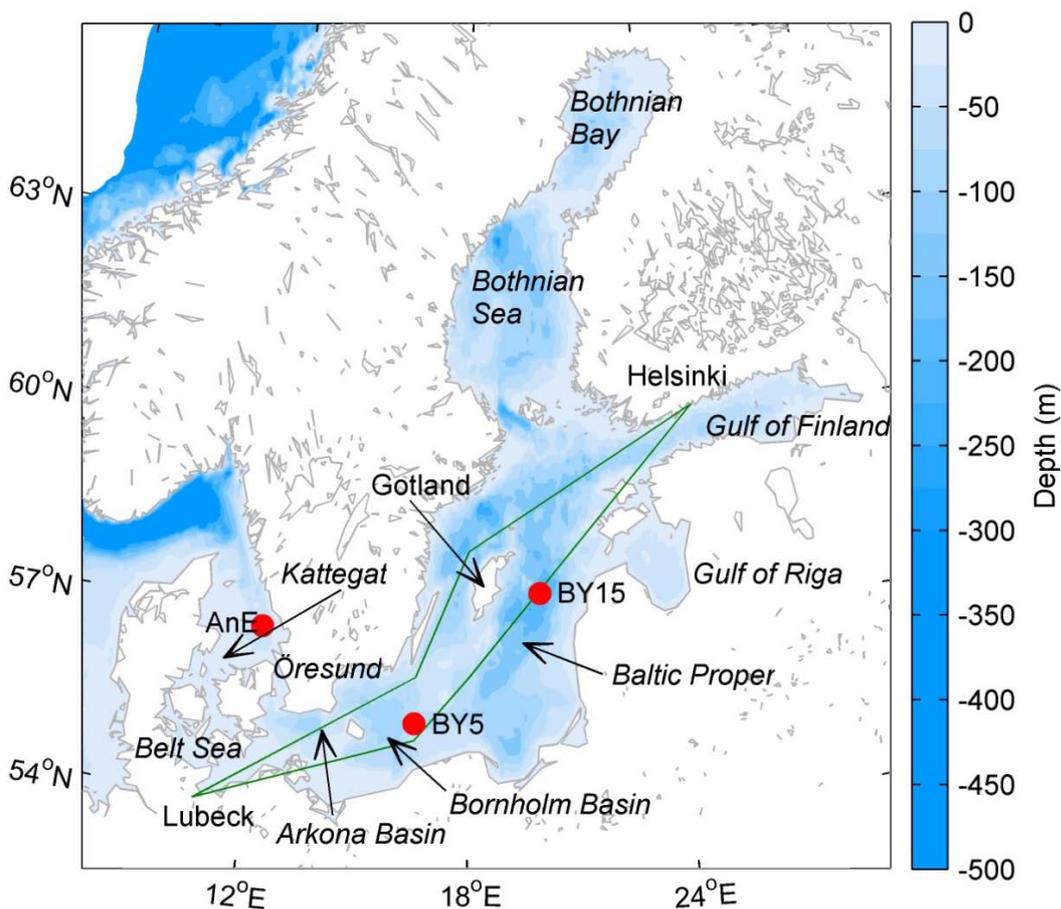
Figure 2.1: *The Baltic Sea with shades of blue indicating the depth distribution. Major basins and sea regions are named in italics. AnE, BY5, and BY15 are monitoring stations that yielded data used in this thesis. The green line indicates the route of the cargo ship Finnpartner.*

Information about the area and volume of the Baltic Sea is available at:

[1] http://www.ne.se

2.1 Oceanography: circulation and water exchange

Freshwater from river runoff and net precipitation (defined as precipitation minus evaporation) drives the large-scale estuarine circulation in the Baltic Sea. Although subject to large seasonal and inter-annual variations, the long-term mean river runoff entering the Baltic Sea amounts to 14,000 m^3 s^{-1} (Bergström and Carlsson, 1994) and the net precipitation is 1500 m^3 s^{-1} (Rutgersson et al., 2002). Most of the river input enters the Baltic Sea through the gulfs of Finland, Riga, and Bothnia, which is reflected in their sea surface salinity (Figure 2.2). In the gulfs of Bothnia and Finland, the sea surface salinity is as low as 2, while in the central Baltic Sea it increases to 7; in the transition area, i.e., Öresund and Belt Sea, the horizontal salinity gradient is steep and increases towards oceanic values.
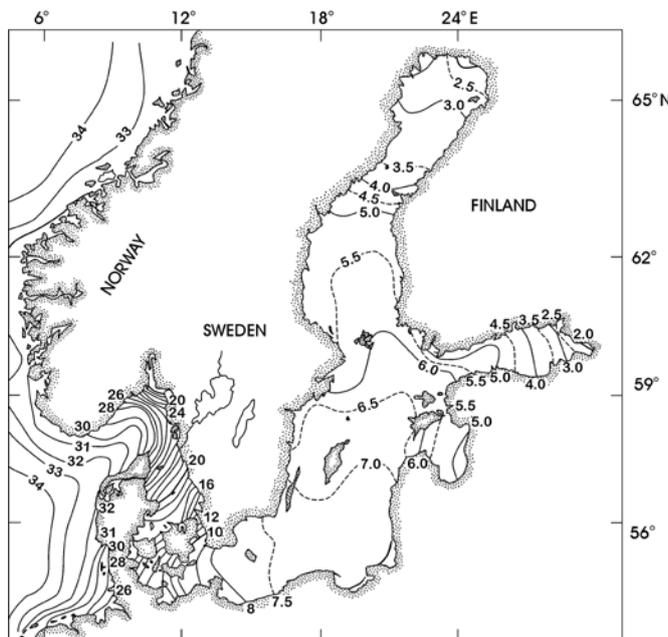
Figure 2.2: *The distribution of sea surface salinity in the Baltic Sea. Redrawn from Rodhe (1998) and available in Hjalmarsson et al. (2008); see Paper I.*

On its way through the Baltic Sea, the freshwater mix with Baltic Sea water and creates a brackish sea surface layer that is larger in volume than the added freshwater and that leaves the system at the entrance area. This brackish outflow, which has a salinity of ~8 (Stigebrandt, 2001), is compensated for by a saline inflow that is restricted because of the narrow sea entrance. This estuarine circulation creates two water masses that are not easily mixed and that are separated from each other by a permanent halocline at ~60 m depth.

There are both baroclinic and barotropic inflows to the Baltic Sea. Baroclinic inflows are driven by density gradients, especially caused by salinity differences across the Belt Sea and Öresund. The barotropic inflows, which are driven by the difference in sea level between Kattegat and the southern Baltic Sea, are responsible for the main water exchange of the deepwater. Sea level differences are highly variable, which is reflected in the frequency and volume of the barotropic inflows. These inflows come as pulses of water with various salinities, temperatures, and volumes, which determines how far and deep into the Baltic Sea the inflowing water reaches. Minor inflows are relatively frequent and contribute to the ventilation of the upper water masses, but are not sufficient for deep water renewal. The deep water ventilation in the Baltic Sea is completely reliant on heavy and massive inflows termed Major Baltic Inflows (MBI) (e.g., Schinke and Matthäus, 1998; Fischer and Matthäus, 1996; Matthäus and Franck, 1992). The frequency and intensity of MBIs have decreased since the mid 1970s, and since then there have only been two strong inflows, in 1993 and 2003. Between two major inflows as these, the deepwater become stagnant and depleted in oxygen, which results in anoxic condition often occurring at depths below 150 m (Figure 2.3c). As oxygen is used in mineralization processes, nutrients and C_T are released and the deepwater becomes enriched in these properties.

Figure 2.3a-c shows time series for salinity, temperature, and oxygen from monitoring station BY15 in the Eastern Gotland Sea. The permanent halocline is seen in Figure 2.3a, and we also clearly see how it is fluctuating with depth. Major deepwater inflows, such as the MBIs in 1993 and 2003, are characterized of rapidly increasing salinity and oxygen levels in the deepwater (Figures 2.3a and c). The surface layer is heated in summer, when a stable thermocline is established at ~20 m (Figure 2.3b). Each summer, river water becomes trapped in this thermal stratification and spreads over large parts of the Baltic Sea. Eilola and Stigebrandt (1998) call this "juvenile freshwater", which can be used as a natural tracer for pollutants, for example.Below the seasonal thermocline, the colder intermediate winter water is found.
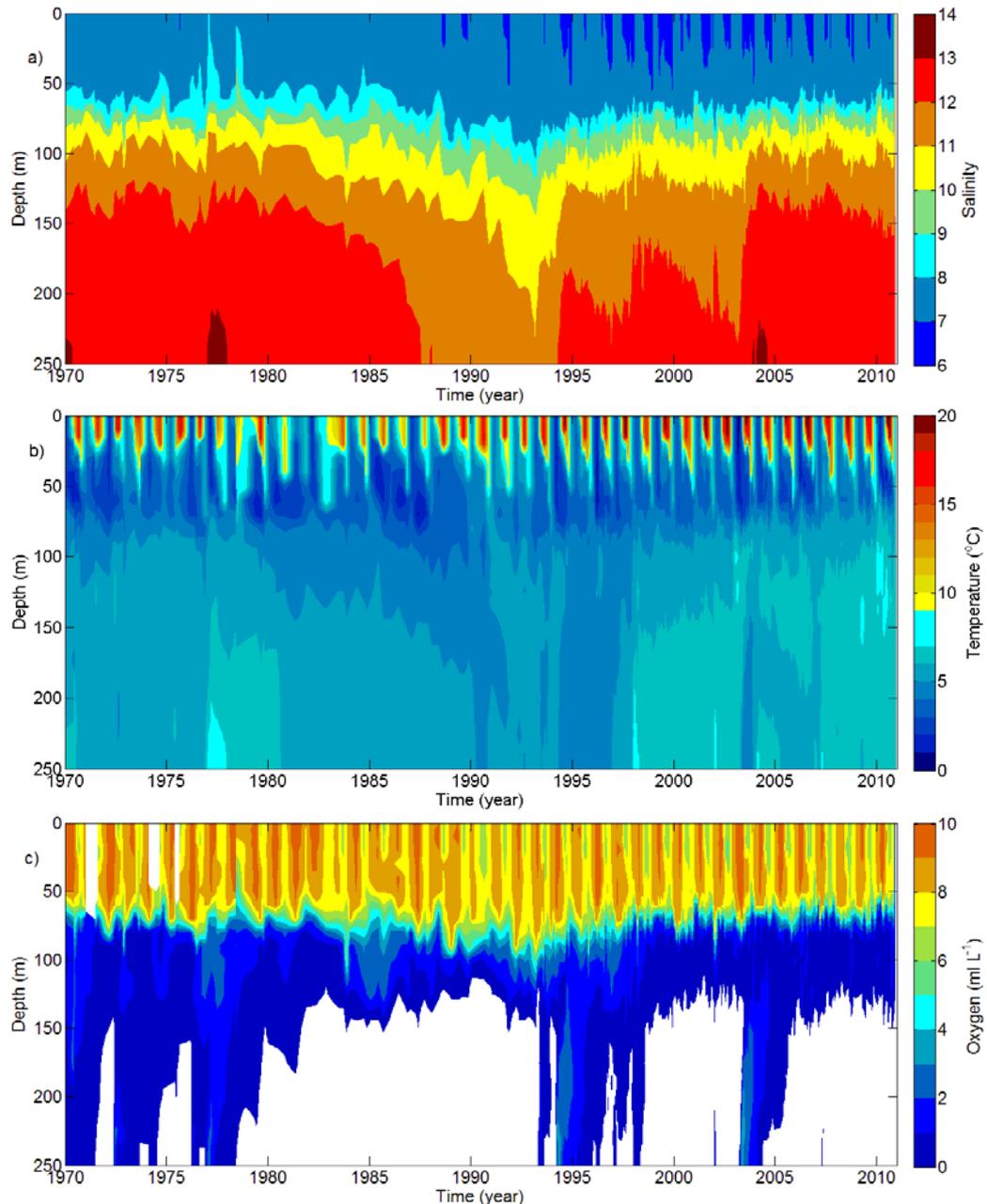
Figure 2.3: *Observations of a) salinity, b) temperature, and c) oxygen concentration at monitoring station BY15 in the Eastern Gotland Sea. Oxygen concentrations below zero are indicated by the colour white (Note: The colour white in the surface layer indicates no data). Data source: Swedish meteorological and hydrological institute.*

7

Upwelling events occur frequently in narrow coastal belts in the Baltic Sea and bring water from the intermediate layer up to the surface (e.g., Lehman and Myrberg, 2008). This result in a rapid drop in sea surface temperature and also brings phosphate to the surface layer (Lass et al., 2010). An upwelling event can vary from days to weeks in duration, and is dependent on the time-scale of the process causing the event.

Only one third of the inflowing dense water to the Baltic Sea originates from Kattegat deepwater and is considered to take part in the renewal of the Baltic Sea water (Stigebrandt and Gustafsson, 2003). The other two thirds of the inflow are recirculated Baltic Sea surface water, which does not contribute to the renewal. Descriptions of the baroclinic inflow have indicated that the mean salinity in the incoming water is ~17.5, with mean inflow of 15,000 m^3 s^{-1} (e.g., Stigebrandt, 2001; Stigebrandt and Gustafsson, 2003). With this in mind, and adding the freshwater contribution, the residence time of Baltic Sea water is about 30 years.

3 Inorganic Carbon Chemistry

In seawater, carbon is present in four inorganic forms; aqueous CO_2 (CO_{2aq}), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). Aqueous CO_2 is formed when the gaseous form of CO_2 (CO_{2g}) becomes hydrated, CO_{2aq}, and then reacts with water to form carbonic acid. The forms of inorganic carbon in seawater exist in a state of equilibrium:

$$CO_{2g} + H_2O \leftrightarrow CO_{2aq} + H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+ \qquad (3.1)$$
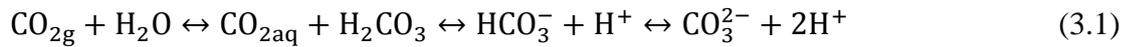
where H^+ is the concentration of hydrogen ions, which is a measure of the acidity, pH: $pH = -\log[H^+]$. Note that equation (3.1) indicates equilibrium and not reaction pathways. Since it is difficult to distinguish analytically between CO_{2aq} and H_2CO_3, it is common to combine these two species into one, here, the notation CO_2 will be used. The sum of the inorganic carbon species is referred to as dissolved inorganic carbon, or total carbon (C_T):

$$C_T = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \qquad (3.2)$$

where brackets denotes total concentrations. In seawater, the typical distribution is $[CO_2]$: $[HCO_3^-]$: $[CO_3^{2-}]$ ~0.5% : ~86.5% : ~13% (Zeebe and Wolf-Gladrow, 2001), respectively, and the equilibrium relationships are given by:

$$K_0 = \frac{[CO_2]}{pCO_2} \qquad (3.3a)$$

$$K_1 = \frac{[HCO_3^-][H^+]}{[CO_2]} \qquad (3.3b)$$

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \qquad (3.3c)$$

where pCO_2 is the partial pressure of CO_2 and K_0, K_1, and K_2 are equilibrium constants, K_0 being the solubility constant and K_1 and K_2 the first and second dissociation constants of carbonic acid. The equilibrium constants depend on temperature, salinity, and pressure.

When atmospheric CO_2 comes in contact with seawater, it dissolves and reacts chemically. This is unlike other gases, such as oxygen, which dissolve in water without reacting with it. Most of the atmospheric CO_2 entering the ocean reacts with carbonates to create bicarbonate:

$$CO_2 + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^- \tag{3.4}$$
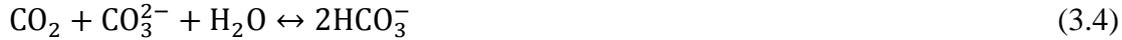
while the rest remains as CO_2 (e.g., Sarmiento and Gruber, 2006). A small part of the resulting HCO_3^- dissociates further into CO_3^{2-} and H^+ and reduces pH. Hence, the pH reduction is reduced since the carbonate ions, which are already present in seawater, take care of the CO_2 and act as a buffer. With the increasing CO_2 emissions the world is experiencing today, more CO_2 will dissolve into the ocean with a subsequent reduction in the amount of carbonate buffer. Consequently, more H^+ will be free and contribute to a decreased pH. According to equation (3.1), the CO_2 entering the ocean, or escaping it, must be equilibrated with the entire C_T pool, which is a fairly slow process when considering the surface mixed layer to be equilibrated. A 50-m-deep oceanic surface mixed layer takes about 8 months to reach chemical equilibrium after a perturbation in the atmospheric or oceanic CO_2 concentration (e.g., Zeebe and Wolf-Gladrow, 2001).

The next essential quantity for describing the carbonate system is total alkalinity (A_T), which, including only the major contributions, is explained as the excess of bases (proton acceptors) over acids (proton donors):

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$
$$\mp \text{minor components} \tag{3.5}$$

where $[B(OH)_4^-]$ is the concentration of borate and $[OH^-]$ is the concentration of hydroxide ions. Minor components include the contributions of ammonium (NH_3) and hydrogen sulphide (HS^-), which are important under the anoxic conditions often experienced in Baltic Sea deepwater.

The concentration of CO_3^{2-} enters the definition of A_T (equation 3.5) by a factor of two, and A_T can be considered as a measure of the buffer capacity. High A_T indicates a high buffer capacity and a great ability to neutralize additions of acid, such as CO_2, with a small change in pH. Furthermore, A_T is a conservative property: it does not change with temperature or pressure, and is used as a tracer in identifying water masses (e.g., Fransson et al., 2001; Hjalmarsson et al., 2008).

4 Processes controlling the CO_2 system

The marine CO_2 system is controlled by several processes, such as biological production and mineralization of organic matter, river inflow, and air–sea gas exchange. It is also affected by vertical mixing and water exchange with surrounding seas, which may import/export carbon in various forms in the studied region (Figure 4.1). Deepwater is often enriched in C_T and A_T, and, for example, during up-welling events, this water will change the surface properties. The further description of the factors controlling the marine CO_2 system will be divided according to the biological and physical factors.
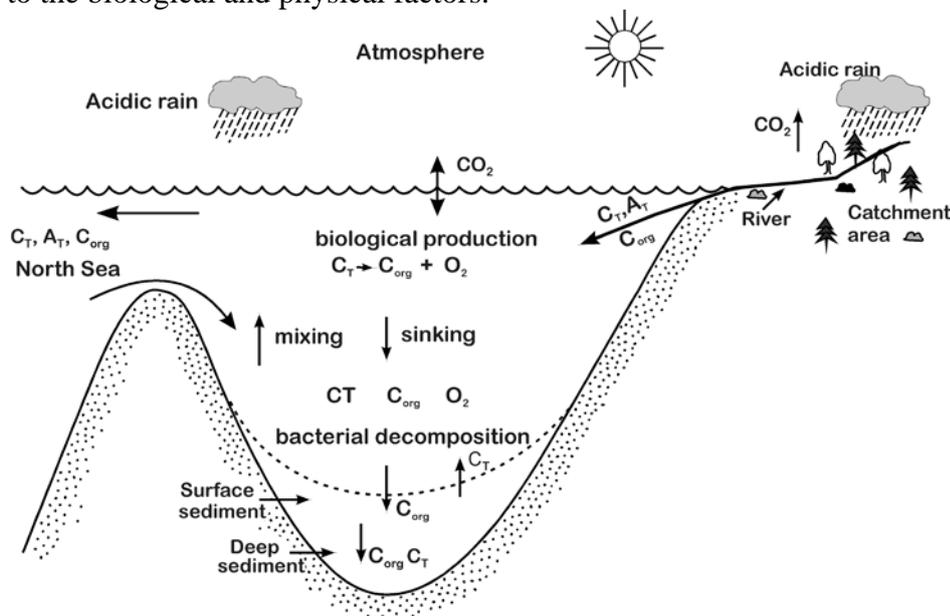
Figure 4.1: *Schematic of the carbon dioxide (CO_2) system in the Baltic Sea, and the connection with the North Sea. Main processes are shown, such as biological production, mineralization, and air–sea gas exchange. C_T – total inorganic carbon, A_T – total alkalinity, and C_{org} – total organic carbon. From Omstedt et al. (2009): see Paper IV.*

4.1 Biological processes

One of the major factors controlling the marine CO_2 system is the biological uptake of CO_2 via the production of organic matter in surface waters. When there is enough light and nutrients, and when the mixed layer is shallower than the euphotic zone, primary production begins. The latter criterion has to be fulfilled, since otherwise the plankton will spend too much time in the dark zone and cannot grow enough to increase the biomass. In photosynthesis, C_T together with nutrients, such as nitrate (NO_3^-) and phosphate (PO_4^{3-}), are used to form organic matter (or particulate organic carbon, POC):

$$106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4 \leftrightarrow \underbrace{(CH_2O)_{106}(NH_3)_{16}H_3PO_4}_{\text{organic matter}} + 138O_2 \qquad (4.1)$$
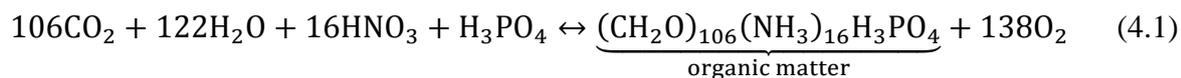
The stoichiometric ratios of carbon: nitrogen: phosphorous: oxygen ($C:N:P:O_2$) are under scientific discussion, but the ratios in equation (4.1), 106:16:1:-138, are the Redfield ratios (Redfield et al., 1963), which are often referred to in the literature. The formation of organic matter influences also A_T, since the assimilation of nitrate increases A_T, though this effect is of minor importance. The surface water contains plenty of C_T, which is hence not a limiting

factor for biological production; instead, the availability of nutrients is the limiting factor. As the organic matter sinks and eventually dies, it is degraded and mineralized, equation (4.1) is reversed, and CO_2 together with nutrients are released as O_2 is consumed. Carbon is transported from the surface to deeper layers, in a transport process often termed the biological pump. In the open ocean, the biological pump can transport carbon deep into the ocean depths, while this process is less effective in shallow coastal seas. Organic matter is mainly mineralized in deeper layers, though also in the surface water, where the so-called renewed nutrients can immediately be reused in primary production.

In the surface water, marine organisms, such as coccolithophores and foraminifera, form calcium carbonate ($CaCO_3$) to build up their shells and skeletons: $Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O$. In this process, A_T decreases and, when the organisms later on sink and die, their calcareous shells dissolve in the deep water or in the sediments, and A_T is increased. Globally, the formation and dissolution of $CaCO_3$ is an important process in the marine carbon cycle since, for example, it transports A_T to the deepwater. It has, however, been demonstrated that the organisms governing this process are not abundant in the Baltic Sea, which has been explained by the undersaturation in $CaCO_3$ in winter (Tyrrell et al., 2008). The formation and dissolution of $CaCO_3$ caused by calcifying organisms can therefore be neglected in the Baltic Sea. However, the dissolution of $CaCO_3$ caused by weathering processes in the drainage area is still important, as it influences A_T in the river water (see section 5.2, Distribution of A_T and C_T).

4.2 Physical processes

The air–sea gas exchange of CO_2 (FCO_2, expressed in mol m^{-2} s^{-1}) is a physical process driven by the gradient of the partial pressure of CO_2 between water and air according to equation (4.2):

$$FCO_2 = kK_0(pCO_2^{water} - pCO_2^{air})$$ (4.2)

where k is the gas transfer velocity (m s^{-1}) and K_0 is the solubility constant (mol m^{-3} atm^{-1}). Several processes influence k, such as surface films, bubble entrainment, rain, and boundary layer stability, but the dominant effect is caused by the wind speed (u), which is the reason that parameterizations of k are often related to wind speed (see e.g. the review in Wanninkhof et al., 2009). There are several expressions for k, the effect of wind speed being assigned various strengths (e.g., Liss and Merlivat, 1986; Nightingale et al., 2000; Wanninkhof, 1992; Wanninkhof and McGillis, 1999; Weiss et al., 2007). Depending on which expression is used, various results are achieved. When calculating FCO_2 in the Baltic Sea, using k according to Wanninkhof (1992) yields twice as large a flux as does using the Liss and Merlivat (1986) value (Paper II). The value of k according to Nightingale et al. (2000) yields a flux intermediate between these two (e.g., Sarmiento and Gruber, 2006). However, the expression of k according to Wanninkhof (1992) is a commonly used parameterization that facilitates comparisons with other studies (equation 4.3):

$$k = 0.31u^2 \sqrt{\frac{660}{S_c}}$$ (4.3)

where 660 is the Schmidt number (S_c) of CO_2 in seawater at 20°C. The Schmidt number is dimensionless and depends on temperature. It is defined as the kinematic viscosity of water

divided by the diffusion coefficient of the gas and is here calculated according to Wanninkhof (1992).

The solubility constant of CO_2 is dependent on temperature, in the sense that solubility decreases as temperature increases. For the global distribution of pCO_2, this results in equatorial surface water having a higher pCO_2 than does polar surface water, since less CO_2 can be dissolved in warmer seawater, which also has a smaller potential to absorb atmospheric CO_2 (e.g., Takahashi et al., 2009). In contrast, colder water has a larger potential for atmospheric CO_2 uptake, which becomes especially important in regions for deepwater formation where cold water takes up CO_2 and sinks due to increased density. In similar analogy to the biological pump, this transport process is called the solubility pump. The temperature effect is also evident in seasonal temperature variations, which in the Baltic Sea range between ~0°C in winter and ~20°C in summer. Temperature also affects pressure, so pCO_2 in warmer water is higher due to the decreased pressure.

The equilibrium constants are sensitive to salinity, though less than to temperature, increasing salinity leading to decreasing pCO_2. This might affect the Baltic Sea surface distribution because of the large horizontal salinity variations. The seasonal changes in salinity, however, are small compared with those in temperature, so the salinity effect on the equilibrium constants is of minor importance, at least for seasonal variations.

Furthermore, air–sea gas exchange affects the concentration of C_T, since pCO_2 changes, but it is important to note that A_T will not change through this process. Under oceanic conditions, variation of A_T is mainly determined by salinity. In other words, A_T in the ocean varies with evaporation and precipitation, becoming either more diluted or more concentrated. Since the range of oceanic salinity is small, the same is the case with A_T. In coastal regions such as the Baltic Sea, however, A_T is largely affected by freshwater supply from rivers, and by the geology in the drainage basin.

5 The CO$_2$ system in the Baltic Sea

In this chapter, the CO_2 system in the Baltic Sea will be described, referring mainly to Papers I–IV but also to the work of others.

5.1 Data and methods

Data

There is a long tradition of seawater measurements in the Baltic Sea (see e.g., Fonselius and Valderrama, 2003). Parameters such as salinity, temperature, oxygen, nutrients, pH, and A_T have routinely been measured by the national monitoring programmes since the beginning of the twentieth century. C_T and pCO_2 have not been routinely measured or monitored, though there have been occasional expeditions (e.g., Algesten et al., 2004, 2006; Beldowski et al., 2010; Kuss et al., 2006; Schneider et al., 2003; Thomas and Schneider, 1999; Wesslander et al., 2011). Most earlier studies of the CO_2 system in the Baltic Sea were conducted in the Baltic Proper, especially in the Eastern Gotland Sea, and knowledge of the northern Baltic is fairly poor. However, observations from the Eastern Gotland Sea are often representative of the whole Baltic Proper, which makes studies of this area important. In recent years, there has been increased interest in using ferry boxes to make direct measurements of pCO_2 on cargo ships in the Baltic Sea (e.g., Kuss et al., 2006; Schneider et al., 2006). Such a measurement

strategy has many advantages: a cargo ship follows a fixed route at a high frequency (measured in just days), allowing data to be collected cost effectively. As the technique is improving, we hope to see this strategy used more often in the Baltic Sea.

The seawater data used in this thesis have been extracted from the Swedish oceanographic data centre, which is maintained by SMHI, and from BED.[2, 3] However, pH measurements are only reliable since 1993 (SMHI, personal communication), so the study presented in Paper II starts in that year. Paper I uses A_T data from numerous sources (for references, see Table 1, Paper I). In Paper II, stations with the best temporal resolution were chosen, which resulted in monthly data from the monitoring stations BY15 in the Eastern Gotland Sea, BY5 in the Bornholm Sea, and Anholt East (AnE) in Kattegat (see Figure 2.1). Kattegat is located right at the entrance area, has oceanic characteristics, and its CO_2 system differs from that of the Baltic Sea. In addition, ferry box data from the cargo ship Finnpartner were used; the Finnpartner route extends from Lübeck in Germany to Helsinki in Finland. Furthermore, data used in Paper III were from outside Östergarnsholm, a small island east of Gotland, and collected by the authors in 2006.

Methods
If two of the four measurable parameters (i.e., C_T, A_T, pH, and pCO_2) are known, the other two can be calculated together with temperature and salinity. Since only pH and A_T are included in the monitoring programs, these have been used to calculate pCO_2 in this thesis. The calculations were made using the CO2SYS program (Pierrot et al., 2006). Several studies have examined the equilibrium constants K_1 and K_2, which need to be chosen carefully, since they must be valid for various conditions. In Paper II, the constants in Mehrbach et al. (1973) as refitted by Dickson and Millero (1987, 1989) were used for Kattegat, and in the low saline Baltic Sea, the Millero et al. (2006) values were used.

When the air–sea gas exchange is calculated in this thesis, equation (4.2) is used with various parameterizations of *k*: Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999) and Weiss et al. (2007). This was done to illustrate how the result depends on the choice of parameterization. In this thesis, the air–sea gas exchange is positive when going from the sea surface to the atmosphere; in other words, positive values indicate that the sea is a source of, or is releasing, atmospheric CO_2. Negative air–sea gas exchange values indicate uptake, i.e. that the sea is acting as a sink of atmospheric CO_2.

This thesis applies two modelling approaches, which will be further described and discussed in section 5.6, Modelling approaches.

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[2] SMHI: Swedish meteorological and hydrological institute, http://smhi.se.
[3] BED: Baltic environmental database, Stockholm university, http://nest.su.se/bed.

5.2 Distribution of A_T and C_T

As previously described, the Baltic Sea is an estuarine system with freshwater contributions from many rivers draining the region resulting in a decreasing salinity gradient from south to north (see Figure 2.2). This gradient feature is also reflected in surface A_T (Figure 5.1a), since A_T is closely related to salinity because HCO_3^- and CO_3^{2-} are major components of seawater. Paper I investigated the distribution of A_T in the Baltic Sea using measurements of surface A_T over the twentieth century. The A_T decreases from ~1800-2000 µmol L^{-1} in the entrance area towards the low saline gulfs in the eastern and northern parts, where most of the freshwater is discharged. However, despite almost the same low salinity, the A_T in the Gulf of Finland is still higher (~1200 µmol L^{-1}) than in Bothnian Bay (~800 µmol L^{-1}), which indicates that something more than salinity alone determines the A_T in this region.
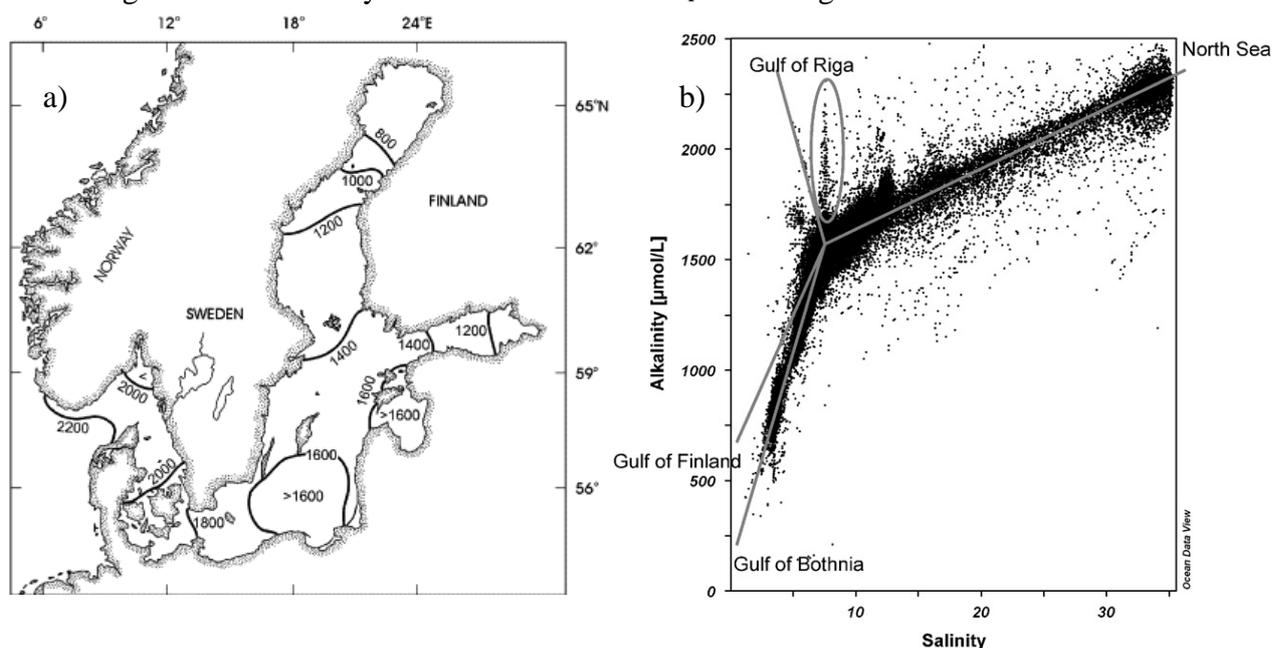
Figure 5.1: *a) Mean surface water total alkalinity in the Baltic Sea (µmol L^{-1}). b) Total alkalinity versus salinity for all the Baltic Sea data. Straight lines are guidelines, indicating the mixing regimes. From Hjalmarsson et al. (2008); see Paper I.*

In an A_T/S diagram of Baltic Sea data, water masses of different origins can be defined (Figure 5.1b). The linear relationships in the figure indicate mixing lines for the gulfs of Bothnia, Finland, and Riga. By extrapolating the lines to zero salinity, it is possible to estimate the A_T in the river water entering each gulf, i.e., ~150 µmol L^{-1} in the Gulf of Bothnia, ~600 µmol L^{-1} in the Gulf of Finland, and ~3000 µmol L^{-1} in the Gulf of Riga. Where the mixing lines join, we find the A_T/S values typical of the central Baltic Sea surface water (~1600 µmol L^{-1} / ~7), which is a mixing zone for all of these water masses. The fourth line in the figure is the mixing line for the zone between the central Baltic Sea and the transition area towards the North Sea. The freshwater end member for this line gives us the mean A_T in the river waters entering the Baltic Sea, ~1400-1500 µmol L^{-1}. Hence, the rivers discharge water with different A_T concentrations; why is this so? Well, the large amounts of river water discharged into the Baltic Sea drain areas of different geological profiles. In the northern parts, the bedrock is dominated by granite, while carbonate rocks, such as limestone, dominate the southern parts. During limestone weathering, bicarbonate is released into the river water and increases the A_T according to $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$. This is probably the main reason for the high A_T in gulfs of Finland and Riga, despite the same low salinity as in the Gulf of Bothnia. The above weathering process consumes CO_2 that

14

originates either from the atmosphere or more likely from the river water. An investigation of the Swedish Baltic watershed (Humborg et al., 2010) found extremely high CO_2 supersaturation in the river mouth, as high as about 1300 µatm on average. The high pCO_2 values in the river water were attributed to the mineralization of organic matter.

Long-term trends in the river water A_T (in Paper I) indicated a decrease in the Gulf of Bothnia and an increase in the Gulf of Finland. Similar results have previously been found by Dyrssen (1993), who made a similar study but using much fewer data. It has been suggested that trends such as these at least partly depend on acid rain (e.g., Dyrssen, 1993; Hjalmarsson et al., 2008). When acid rain falls over water with low A_T and that hence is badly buffered, the A_T will decrease even further, since HCO_3^- will be used when neutralizing the acid. In contrast, acid rain falling over an area of limestone may instead increase A_T through weathering processes. Furthermore, the low A_T in the Gulf of Bothnia means that this region is more sensitive to pH changes, which has been demonstrated in a sensitivity study by Omstedt et al. (2010). However, we still need comprehensive attribution studies to describe in greater detail the processes determining A_T in the Baltic Sea and its inflowing river water.
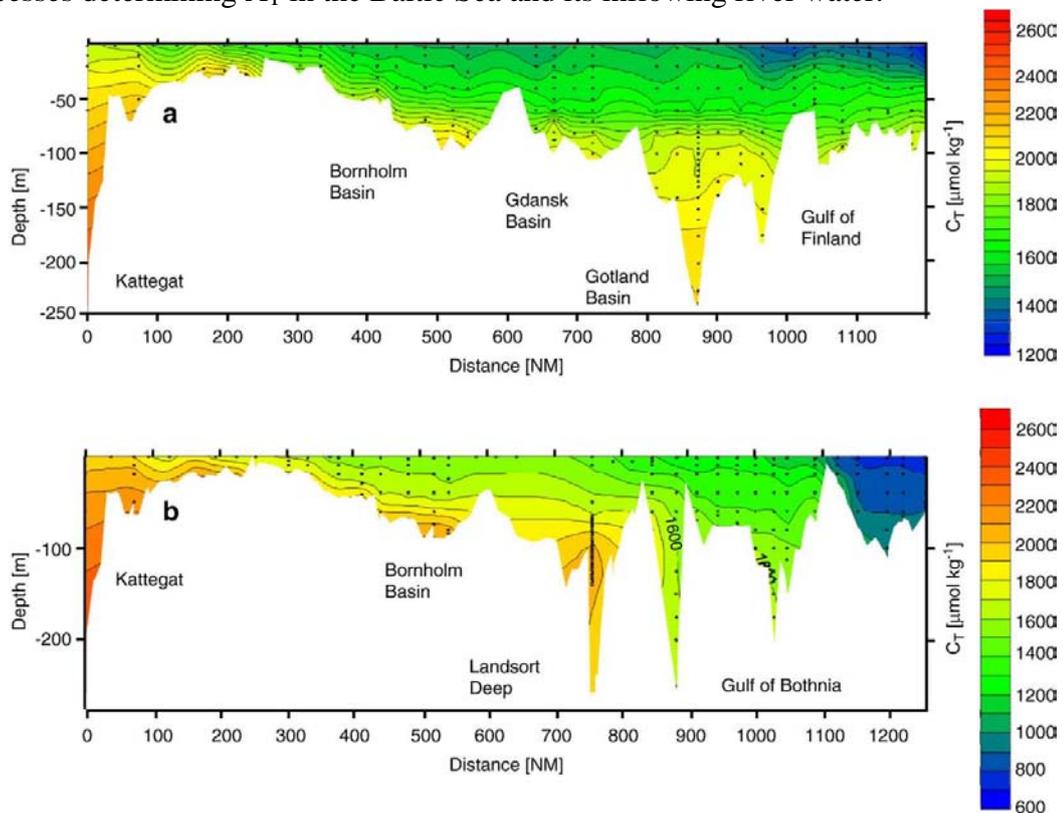
Figure 5.2: *Depth distribution of total CO_2 (C_T) along an eastern (a) and a western (b) track in the Baltic Sea in summer 2008.[4]*

The horizontal distribution of A_T and salinity described above are also seen in the surface distribution of C_T (Figure 5.2). A recent investigation by Beldowski et al. (2010) made extensive measurements of the concentration of C_T. From a C_T/S plot, the authors concluded that the background C_T in the surface water is controlled mainly by A_T; it is also evident that A_T has a close relation to C_T in the Baltic Sea. The water column in the Baltic Sea is permanently stratified and the surface water has little contact with deeper layers.

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[4] Reprinted from Journal of Marine Systems, 81, Beldowski, J., Löffler, A., Schneider, B., Joensuu, Distribution and biogeochemical control of total CO_2 and total alkalinity in the Baltic Sea, 252-259, 2010, with permission from Elsevier.

Nevertheless, vertical mixing and upwelling events contribute to the exchange between layered water masses. According to Schneider et al. (2000), a net flux of carbon occurs through the halocline towards the surface. The depth distribution of C_T depicted in Figure 5.2 gives increasing C_T with depth. This increase depends on the mineralization of organic matter and, since the Baltic Sea deepwater is often stagnant, C_T also accumulates. By measuring C_T in the deepwater during a stagnation period, it is possible to determine the mineralization rate. This was done by Schneider et al. (2002), who demonstrated that only 15% of the organic matter produced in the surface water of the Eastern Gotland Sea was mineralized at the sediment surface, whereas 85% was more rapidly mineralized at depths above 140 m.

5.3 Seasonality

The CO_2 system in the Baltic Sea displays a pronounced seasonality. This is described in Paper II, in which pCO_2 was calculated from time series (1993–2009) of A_T and pH together with salinity and temperature. Figure 5.3a shows surface pCO_2 and pH for an average year at station BY15 in the Eastern Gotland Sea, along with the monthly standard deviation. The seasonality in pCO_2 is characterized by large amplitude, ranging from high values in winter (~500 µatm) to low values in summer (~150 µatm). The corresponding difference between winter and summer pH is ~0.5 units.
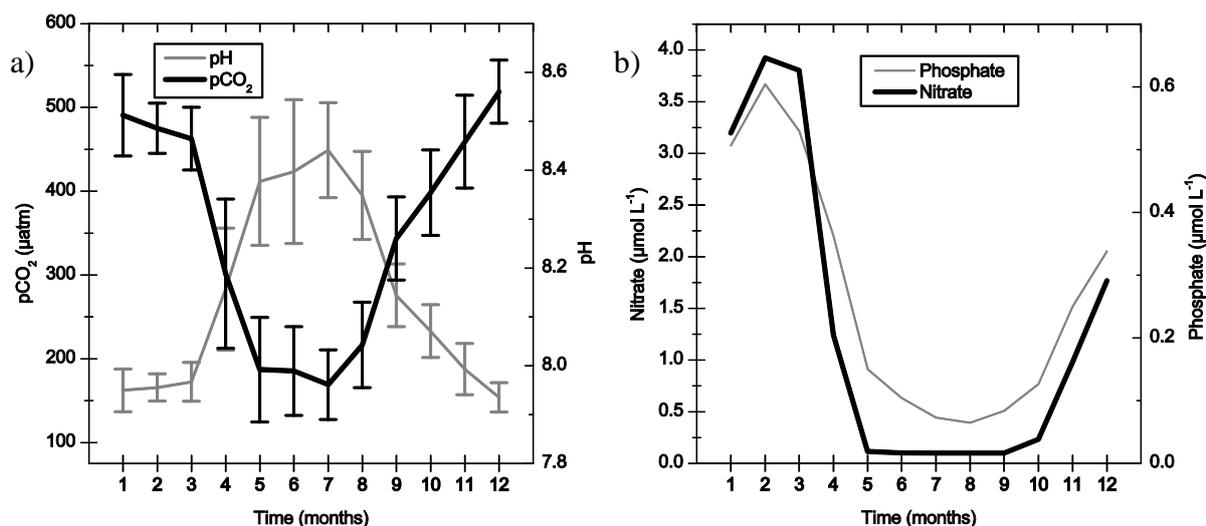
Figure 5.3: *a) The pCO_2 (black) and pH (thin grey) and b) concentrations of nitrate (black) and phosphate (thin grey) in the surface water at BY15 in the Baltic Sea in an average year. pH is converted to total scale from NBS scale as follows: $pH^{tot}=pH^{NBS}$-0.13 (Lewis and Wallace, 1998). Error bars indicate standard deviations.*

Seasonal variations are controlled by biological and physical processes. In March, the surface pCO_2 drops rapidly and remarkably, coinciding with a similar drop in phosphate and nitrate (Figure 5.3b). These changes are evidence of the start of intensive primary production. As CO_2 is consumed in the water, C_T and pCO_2 decreases and pH increases. In the spring bloom, the first nutrient to be used up is nitrate, which happens in May, when the decrease/increase in pCO_2/pH levels out. Later in summer, a second bloom is dominated by cyanobacteria, which are favoured by the warm, calm summer weather. Since cyanobacteria can fix nitrogen in gaseous form, they are favoured by the low nitrate levels in the water and limited by phosphate. In the pCO_2 data, this second bloom is seen as a second minimum in July. The decrease in summer pCO_2, however, is counteracted by the temperature effect that at the same time increases pCO_2. Therefore, some of the summer pCO_2 drop may be "hidden" behind the

temperature effect. A thorough investigation of the production season in the Baltic Sea was conducted by Schneider et al. (2009), who used pCO_2 measurements to identify the different production periods. The seasonality in pCO_2 was nicely demonstrated using measurements from a ferry box system (Figure 5.4). In addition to the late summer bloom, Schneider et al. found a production period connected to the late spring bloom, which they called "cold fixation", since it was dominated by cyanobacteria thriving in colder water.

Figure 5.4: *Measurements of pCO_2 (μatm) made using a ferry box system on a cargo ship passing between Lübeck and Helsinki.*[5]
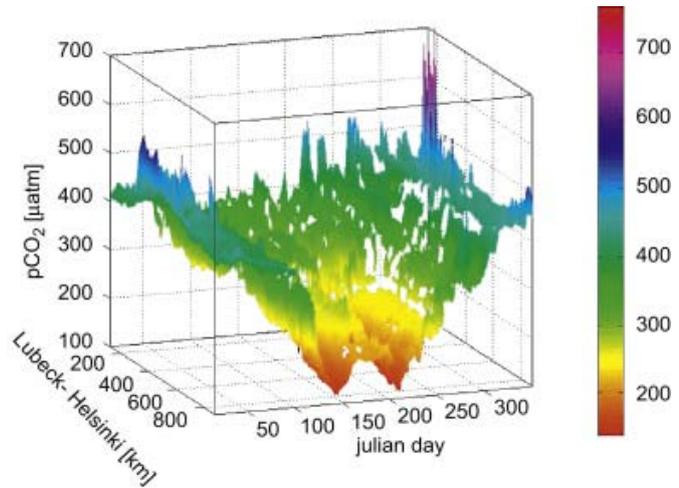
In autumn, the productive season finally comes to its end and the pCO_2 drops to ~150 μatm. This happens when nutrients are depleted, and the mixed layer deepens because of enhanced wind mixing. Mineralization processes now dominate production. As the thermocline breaks down, the mixed layer reaches down to the halocline, where the water contains higher concentrations of C_T and nutrients. The pCO_2 and concentrations of C_T and nutrients start to rise in the surface layer due to vertical mixing. The surface pCO_2 is high throughout winter, which indicates that mixing processes are constantly feeding the surface layer with CO_2.

The annual cycle of pCO_2 in the Baltic Sea has previously been described, for example, by Borges et al. (2006), Rutgersson et al. (2008), and Thomas and Schneider (1999). However, Paper II contributes additional information, since time series of pCO_2 are analysed for the first time. Time series reveal the inter-annual variability caused by the interaction of the variability of all the biological and physical processes (Figure 5.5).
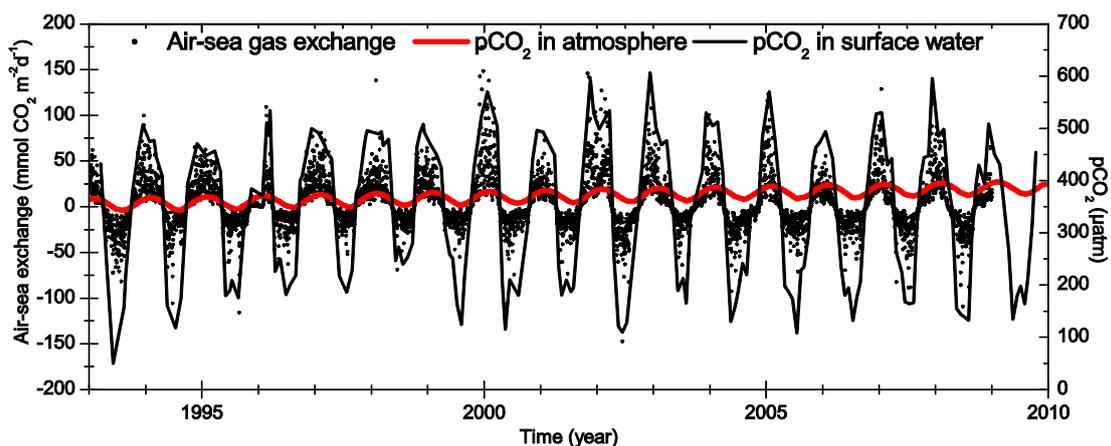
Figure 5.5: *The pCO_2 in the surface water (black line) and the daily air–sea gas exchange of CO_2 (black dots) at BY15 in the East Gotland Sea in the Baltic Sea. Calculations are made using the gas transfer velocity according to Wanninkhof (1992). Red line is the pCO_2 in the atmosphere. For further discussion see Wesslander et al. (2010), Paper II.*

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[5] Reprinted from Continental Shelf Research, 29, Schneider, B., Kaitala, S., Raateoja, M., Sadkowiak, B., A nitrogen fixation estimate for the Baltic Sea based on continuous pCO_2 measurements on a cargo ship and total nitrogen data, 1535–1540, 2009, with permission from Elsevier.

The strongest inter-annual variability of pCO_2 is in summer, which reflects the variability of the primary production.

In addition to the processes described above, the annual cycle of the CO_2 system is influenced by the air–sea gas exchange of CO_2 according to equation (4.2). In Paper II, the uptake/release of CO_2 is calculated and the seasonality is evident (Figures 5.5 and 5.6). The seawater is supersaturated in pCO_2 from October to March, which results in the release of CO_2 to the atmosphere in autumn/winter. From April to September, when the biological production reduces pCO_2, the seawater becomes undersaturated and instead takes up atmospheric CO_2. Hence, the biological drawdown of CO_2 is partially compensated for by the uptake of atmospheric CO_2. Seasonal variations in atmospheric pCO_2 over the Baltic Sea were estimated to ± 10 µatm and the annual increase to 1.9 µatm year^{-1} (Figure 5.5).
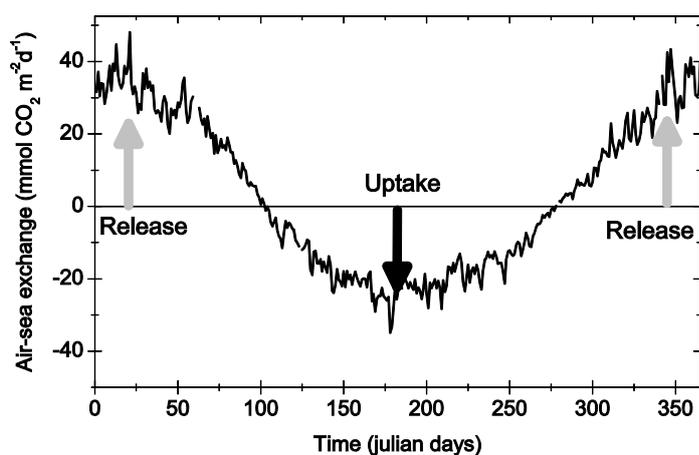
Figure 5.6: *The average daily flux of CO_2 at BY15 in the East Gotland Sea in the Baltic Sea. Grey arrows indicate the direction of the CO_2 flux in winter/autumn and the black arrow in spring/summer. Calculations are made using the gas transfer velocity according to Wanninkhof (1992).*

5.4 Short–term variability

Superimposed on the seasonality are short-term variations, such as daily biological cycles and upwelling events. In Paper III, we investigated the short-term variability of pCO_2 and O_2 using highly resolved direct measurements of pCO_2 (one hour) and O_2 (1-5 minutes). The result was a high correlation (correlation coefficient=0.8) between the two parameters (Figure 5.7). When pCO_2 drops, O_2 rises, and vice versa. An interesting aspect of these measurements was the magnitude of the short-term variation. Occasionally, the diurnal variation of pCO_2 was as much as 40 µatm and could be quite rapid. These changes were attributed to a combination of production/mineralization processes, advection, and air–sea gas exchange. This clearly illustrates the intensity of pCO_2- and O_2 changes and the processes governing them. An example of an upwelling event is clearly illustrated in Figure 5.4, where extreme high pCO_2 values of ~700 µatm are shown.
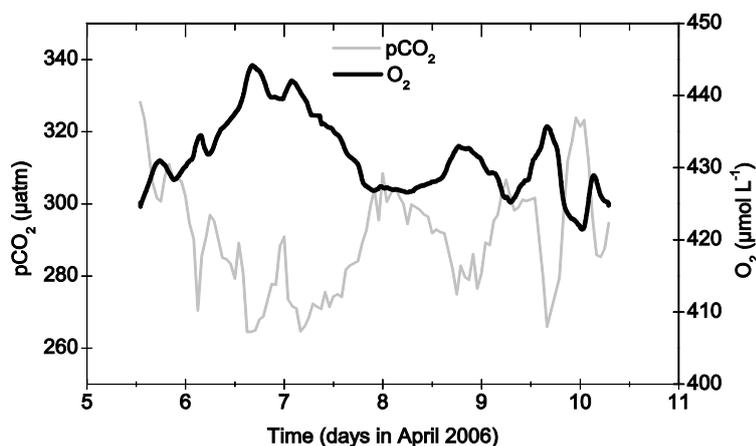
Figure 5.7: *Concentration of oxygen, O_2 (black) and pCO_2 (thin grey) in the surface water at Östergarnsholm in the Baltic Sea. Redrawn from Wesslander et al. (2011); see Paper III*

5.5 Is the Baltic Sea a sink or source of atmospheric CO₂?

The global ocean is considered to be a net sink of atmospheric CO_2 (Sabine et al., 2004), whereas coastal seas display great variability in the CO_2 system (e.g., Borges et al., 2006; Chen and Borges, 2009; Gypens et al., 2011). The Baltic Sea is a coastal system that receives large amounts of organic matter from its many rivers, which may contribute to a heterotrophic state. In a heterotrophic system, mineralization processes exceed production processes. In contrast, the large summer reduction in pCO_2 instead demonstrates an autotrophic system, where production processes dominate. So, what is the net effect of these extremes?

From the daily air–sea fluxes of CO_2 (shown in Figure 5.5), the net annual flux was calculated in Paper II and the result for BY15 in the East Gotland Sea is seen in Figure 5.8. Despite large variation between years, the net effect is clearly a net release of CO_2 to the atmosphere. Similar results were found at BY5 in the Bornholm Sea. The largest inter-annual variability of the air–sea gas exchange is in winter, because of the highly variable wind conditions. Wind speed is also higher in winter than in summer, producing a more efficient air–sea exchange. Together with the high winter pCO_2 and organic matter contribution from rivers, this can explain the CO_2 source function of the Baltic Proper. The Baltic Sea exports C_T to the North Sea, according to, for example, Hjalmarsson et al. (2010), which indicates that the excess CO_2 released to the atmosphere comes from the rivers.
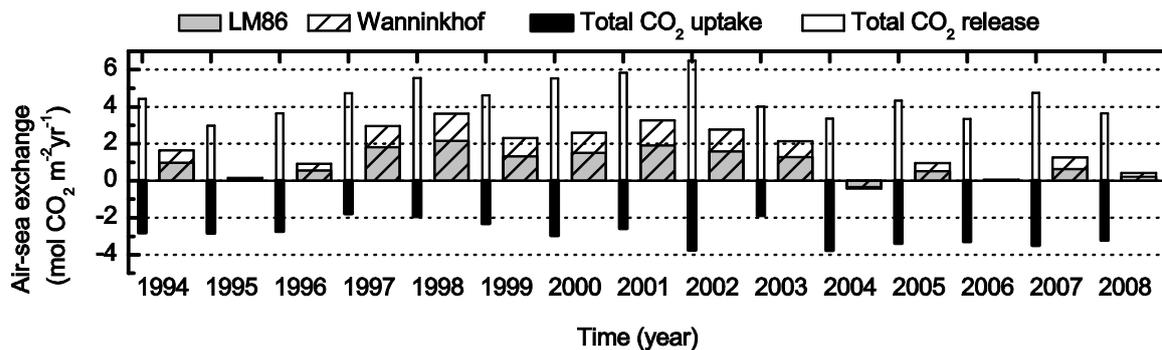
Figure 5.8: *Annual net air–sea gas exchange of CO₂, at BY15 in the Baltic Sea. Calculations are made using the gas transfer velocity according to Liss and Merlivat (1986) (grey), and Wanninkhof (1992) (dashed lines). The annual net air–sea gas exchange is divided into annual net CO₂ uptake (black) and release (white). Redrawn from Wesslander et al. (2010); see Paper II.*

However, the results presented here do not agree with earlier findings of, for example, Kuss et al. (2006) and Thomas and Schneider (1999), who demonstrated that the same region was a net sink of CO_2. These earlier studies are both based on direct pCO_2 measurements, which strengthen their results, but they are also based on only one year of measurements. There seem to be several answers to the question posed in the heading of this section. Maybe the most correct answer is that the Baltic Sea alternates between being a sink and a source. The work by Chen and Borges (2009) indicate that estuaries are CO_2 sources while continental shelves are sinks. They also state that some continental shelves are reported to be CO_2 sources, although these are fewer in number. The model study presented in Paper IV suggests that, before industrialization, the Baltic Sea was a much larger CO_2 source than it is today.

So far, we possess little information on either inter–annual or seasonal variability in the northern Baltic Sea. However, Algesten et al. (2004) concluded that the Gulf of Bothnia was a CO_2 source in 2002.

The air–sea exchange of CO_2 was also estimated in Kattegat (Paper II), which is at the entrance to the Baltic Sea, more oceanic in character, and not that influenced by river water. It turned out that Kattegat was a CO_2 sink, since its pCO_2 level was fairly low in winter. Compared to the Baltic Sea, Kattegat is a shallow, dynamic, and well-mixed region, and its surface water is not fed with CO_2-enriched deepwater in winter as is the case in the Baltic.

The above results indicate that calculations of air–sea gas exchange are sensitive and a matter of uncertainty, which is a problem when addressing the sink/source issue. The uncertainty depends partly on the parameterization of the gas transfer velocity, *k*, and Rutgersson et al. (2008) found large differences between measured and calculated gas exchange. The annual net fluxes shown in Figure 5.8 also indicate that the Wanninkhof (1992) parameterization gave twice as large a flux as did the Liss and Merlivat (1986) parameterization. To improve the parameterization of *k*, more experimental studies would be needed. Furthermore, when pCO_2 is calculated, uncertainties in the measured parameters and in the choice of equilibrium constants need to be considered. For more accurate calculations of the air–sea gas exchange, direct pCO_2 measurements should be used.

5.6 Model approach

A mathematical model of a system is a useful tool for testing one's understanding of processes. When a model delivers results that can be verified by measured data in an acceptable way, the model may also be used for adjacent regions where measurements are less frequent.

This thesis develops two types of models for different purposes. In Paper I, a box model was used for the water budget in the Baltic Sea. In Paper IV, a process-oriented coupled basin model was used for the CO_2 system in the Baltic Sea.

Box model
Box models are the starting point for most modelling activities, and are based on the conservation principals of water volume, salinity, and other properties. If information of total alkalinity in the river water (A_{TR}) is missing, this can instead be calculated from empirical relations between salinity and alkalinity in the seawater. In Paper I, a two-layer box model was introduced to compare these empirical relations with the conservation principals for A_T. By dividing the Baltic Sea into sub-basins, using conservation of salinity and volume, based on Knudsen's relationships (Knudsen, 1900), and conservation of A_T, the inflow (Q_{in}) and outflow (Q_{out}) between basins and the A_{TR} was calculated. Assuming steady state, the conservation equation of volume, salinity and A_T, reads, respectively:

$$Q_{out} = Q_{in} + Q_f \tag{5.1}$$

here, the freshwater flow (Q_f) consist of freshwater from the river as well as net precipitation.

$$Q_{out}S = Q_{in}S_{in} \tag{5.2}$$

$$Q_{out}A_T = Q_{in}A_{Tin} + Q_fA_{TR} \tag{5.3}$$

The outflow is considered to bring the mean S and A_T from the certain basin to the next while the properties in the inflow are denoted S_{in} and A_{Tin}. When applying this method, the calculated A_{TR} came close to the values from the empirical relation, see Paper I.

Process-oriented model

In Paper IV, a biogeochemical model was developed and coupled to a physical model for the Baltic Sea. The physical model, the PROBE-Baltic numerical model, has been extensively used in several investigations of the Baltic Sea (e.g., Hansson and Omstedt, 2008; Omstedt and Axell, 2003; Omstedt and Hansson, 2006a,b; Omstedt and Nohr, 2004) and can accurately calculate, for example, the Baltic Sea sea temperature, ice, and salinity structures. The biogeochemical model is based on time-dependent, one-dimensional conservation equations for O_2, nutrients, phytoplankton, C_T, and A_T. For an arbitrary variable (ϕ) the conservation equation may be written as:

$$\underbrace{\frac{\partial \phi}{\partial t}}_{\text{Change in time}} + \underbrace{w\frac{\partial}{\partial z}\phi}_{\text{Vertical advection}} = \underbrace{\frac{\partial}{\partial z}\left(\Gamma_\phi \frac{\partial \phi}{\partial z}\right)}_{\text{Turbulent diffusion}} + \underbrace{S_\phi}_{\text{Source/sink}} \qquad (5.4)$$

where t denotes time, w is the vertical velocity, z is the vertical coordinate, Γ_ϕ is the variable dependent turbulent diffusion coefficient, and S_ϕ is related to sources and sinks for each variable. By determine the inflow and outflow together with the horizontal surface area (Area(z)) for the depth z, the vertical velocity can be calculated according to:

$$w(z) = \frac{Q_{in}(z) - Q_{out}(z)}{Area(z)} \qquad (5.5)$$

The boundary condition links diffusion to fluxes across the boundaries and is written as:

$$\frac{\partial}{\partial z}\left(\Gamma_\phi \frac{\partial \phi}{\partial z}\right)^{sur,bot} = F_\phi^{sur,bot} \qquad (5.6)$$

where F represent the fluxes of each variable at the air–sea (sur) and bottom-sea (bot) interface. A thorough description of boundary conditions and source/sink terms is found in, for example, Omstedt and Axell (2003) and in Paper IV.

The model was able to reproduce pCO_2 with good agreement (Figure 5.9) and calculations indicated that the Baltic Sea was mainly a source of atmospheric CO_2 before 1950. Concurrent with the increased industrialization around 1950, the load of nutrients to the Baltic Sea increased. With more nutrients available in the surface water primary production increased, which amplified the seasonality in pCO_2 with mainly lower values in summer. The Baltic Sea started to take up CO_2 to a much larger extent than before 1950. According to calculations of pH during the last 250 years (Paper IV), the pH has decreased about 0.03 units (Figure 5.10b). If, however, the concentration of nutrients had stayed the same as they were before 1950, pH should have dropped about 0.1 units (Figure 5.10a). Hence, eutrophication may have amplified the seasonal cycle, and counteracted the drop in pH that otherwise would have been caused by the general increase of atmospheric CO_2. Similar modelling results were also made by Borges and Gypens (2010), who concluded that eutrophication has a larger impact on the carbon chemistry than ocean acidification.
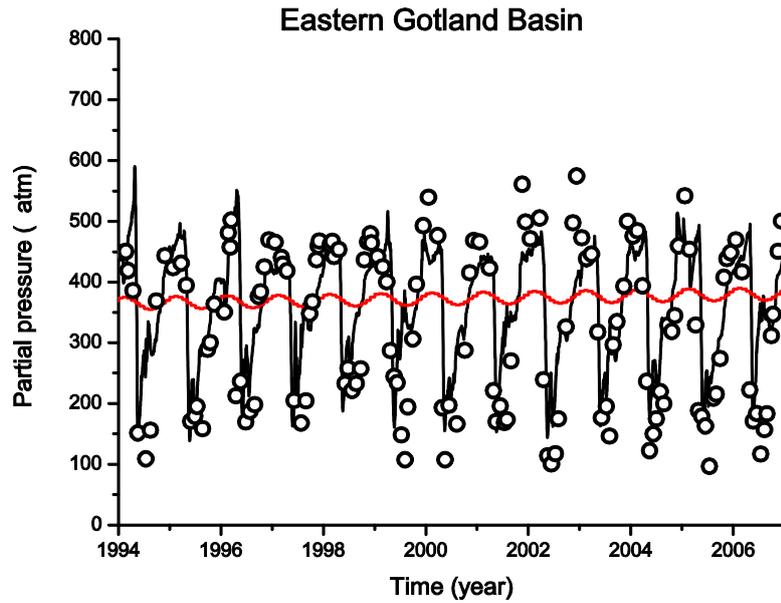
Figure 5.9: *The partial pressure of CO_2 in the surface water in the Eastern Gotland Sea, calculated from observations of pH and total alkalinity (circles) and from the model (line). The red curve illustrates the partial pressure of CO_2 in the atmosphere. From Omstedt et al. (2009); see Paper IV.*
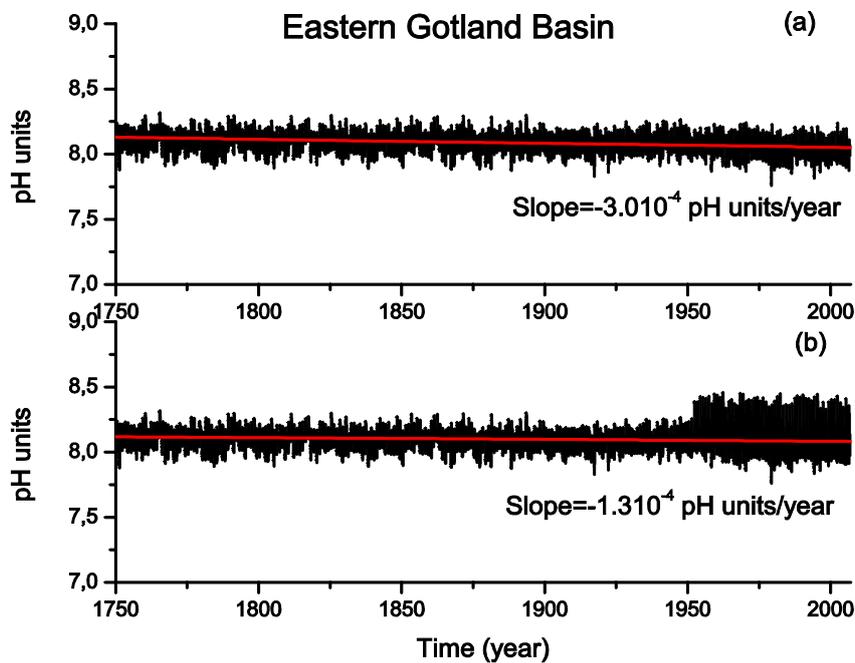
Figure 5.10: *Modelled pH in the surface water of the Eastern Gotland Sea (black lines) and linear trend (red lines). Model assumptions are that anthropogenic CO_2 emissions start in 1750, without a) and with b) eutrophication. The external load of nutrients increased suddenly in 1950 in scenario b). From Omstedt et al. (2009); see Paper IV.*

6 Future outlook

This thesis research succeeded in contributing to our knowledge of the CO_2 system in the Baltic Sea: the regional distribution of A_T has been analysed and mapped, inter-annual and seasonal variations of pCO_2 and air–sea gas exchange have been described, and the first stage of a coupled physical–biogeochemical model has been created. This would not have been achieved without many interesting interdisciplinary meetings and productive discussions. Some questions have been answered while new ones have been raised.

In Paper I, we state that the A_T entering the Baltic Sea via rivers is determined by the drainage area, land use, and geochemical processes such as weathering. It would be of great interest to conduct more research into the river systems, and to investigate how river water chemistry affects the Baltic Sea.

We learned from Paper III that pCO_2 experiences high spatial and temporal variation, which raises questions as to what timescale is best for making measurements on the marine CO_2 system. Currently, the Swedish national monitoring programme measures the A_T and pH once per month in the southern Baltic Sea. In Paper III, we demonstrated that pCO_2 experiences diurnal variation of at least ~40 µatm, so with monthly measurements, one can only imagine what information is being missed. However, resolving diurnal variability may not be an issue for the national monitoring programme, and would not be possible without continuously recording instruments. However, it would definitely be interesting to see more frequent measurements of pH and also direct pCO_2 measurements. The concentration of A_T experiences only small temporal variations in the Baltic Sea, so more frequent A_T measurements is likely unneeded. Furthermore, the use of ferry box systems for direct pCO_2 measurements in the Baltic Sea offers numerous advantages. A cargo ship often takes the same route and can deliver transect information at a high frequency, completing a trip in just days. This type of information would contribute a lot to our knowledge of the CO_2 system and would be interesting to analyse.

Because of poor temporal resolution, data from only three monitoring stations were analysed in Paper II. As more data become available from more locations, it would be interesting to continue this work and see whether the results presented in the paper can be extended to apply to the entire Baltic Sea or whether there are major differences and, if so, why. The studies presented in this thesis have concentrated on the surface waters of the Baltic Sea; it would be very interesting to extend the investigation to the entire water column.

In Paper IV, it is demonstrated that modelling and monitoring needs to come closer. It is not possible to develop models without good data. Neither is it possible to attribute the reasons for any changes without modelling. There is a need for stronger cooperation between the people making decisions about field measurements and the people who develop models.

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